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GROUNDWATER MODELING OF CHROMIUM FROM TANNERY WASTE AND ITS IMPACT ASSESSMENT

A Dissertation

by

Haroon Rashid

In Partial Fulfillment

of the Requirements for the Degree

Doctor of Philosophy (PhD)

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Dedicated To

My Parents and My Wife (Samrah) whose countless prayers, cherished love and strong belief in my capabilities paved the way on which I walked to achieve this important milestone in my life.

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Haroon Rashid / 11-02-2017

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NOTATIONS

AES-ICP	Atomic Emission Spectroscopy – Inductively Coupled Plasma
APHA	American Public Health Association
As	Arsenic
ASTM	American Society of Testing and Materials
ATSDR	Agency for Toxic Substance and Drug Registry
AWWA	American Water Works Association
BCr	Blood chromium
BCS	Basic Chromium Sulphate
BH	bore hole
BOD_5	Biochemical Oxygen demand (5 – days)
CA	Cluster Analysis
$CaCO_3$	Calcium Carbonate
Cd	Cadmium
CEPTP	Common Effluent Pre-Treatment Plant
Cl	Chloride
COD	Chemical Oxygen Demand
Cr	Chromium
Cr(III)	Trivalent Chromium
Cr^{3+}	Trivalent Chromium
Cr(VI)	Hexavalent Chromium
Cr^{6+}	Hexavalent Chromium
Cu	Copper
DG	Din Garrh
DP Road	Debalpur Road
DW	drinking water
EIA	Environmental Impact Assessment
EPD	Environment Protection Department
ft	feet
GIS	Geographical Information Systems
GMS	Groundwater Modeling Software
gpd	gallons per day
GPS	global Positions System
GQI	Groundwater quality index
GW	groundwater
HCl	Hydrochloric Acid
HNO_3	Nitric Acid
HP	Hand pump
i	horizontal hydraulic gradient
IUCN	International Union of Conservation of Nature
K	hydraulic conductivity
kg	kilogram
KIA	Korangi Industrial Area
Km	Kilometer
KTPCP	Kasur Tanneries Pollution Control Project
KTWMA	Kasur Tannery Waste Management Authority
Li	Lithium
LIA	Landhi Industrial Area

m	meter
MAF	Million Acre Feet
MBAS	Methylene Blue Active Substances
mg/kg	milligram per kilogram
mg/L	milligram per liter
MOE	ministry of environment
MW	monitoring well
n	porosity
NEQS	National Environmental Quality Standards
NH3	Ammonia
nmol/L	nanomoles per liter
Ni	Nickel
NO_3^-	Nitrate
NO3-N	nitrate-nitrogen
p	permeability
Pb	Lead
PCA	Principal Component Analysis
PCBs	Polychlorinated Biphenyls
PDE	partial differential equation
PEPC	Pakistan Environment Protection Council
ppm	parts per million
PSGIS	Pakistan Society of Geographic Information Systems
PCRWR	Pakistan Council of Research in Water Resources
PCSIR	Pakistan Council of Scientific and Industrial Research
RS	Remote Sensing
SB	Soil Bore
SDWA	Safe Drinking Water Act
SITE	Sindh Industrial Trading Estate
sq. ft	Feet square
SW	surface water
T	Transmissivity
TCLP	Toxicity Characteristics Leaching Procedure
TDS	Total dissolved Solids
TW	Tube Well
UN	United Nations
UNDP	United Nations Development Program
UNIDO	United Nations Industrial Development Organization
US $	United Stated Dollar (American Dollar)
USEPA	United Sates Environmental Protection Agency
WAPDA	Water and Power Development Authority
WB	World Bank
WEF	Water Environment Federation
WHO	World Health Organization
WTO	World Trade Organization
Zn	Zinc
$\triangle h$	difference in head between the two wells

ABSTRACT

It is the dilemma of the developing countries like Pakistan that on one side industries are playing an important role in establishing a stable economy of the country but on the contrary due to haphazard industrialization and improper planning, untreated hazardous industrial effluent released to the environment poses a serious health risk and also causes immense environmental degradation and pollution. Tannery industry is one of the major revenue generating sectors after textile in Pakistan. There are hundreds of tannery units in operation throughout the country and are contributing to the economy of country. Tannery effluents are ranked as the highest pollutants among all industrial wastes as tanneries are major source of chromium contamination in the environment.

Assessment of contaminated sites having anthropogenic source of contamination from industries is the need of the hour so as to properly investigate and search for mechanism of contamination i.e. how the pollution is spreading out and how much the life in those areas are at risk due to complex environmental scenarios existing at site. In this back ground Kasur tannery area was selected in order to explore the environmental situation regarding industrial pollution mainly caused by major pollutant being released from tanneries i.e. Chromium. The purpose of the study was to thoroughly assess the contaminated site, its adversities, mechanism of contamination and plan to cope with the severe environmental conditions overall at site. Kasur tannery area was thoroughly investigated in order to define the existing environmental condition regarding solid waste management and effluent discharge. Improper and unplanned tannery effluent waste disposal resulted in the formation of huge stagnant ponds adjacent to the tannery area which persisted for long duration consequently becoming a major source of creating mass flux of contaminants into the soil along with flow discharge. In order to investigate the mobility and retention of chromium in soil, detailed field experimentations were conducted. Health survey was also conducted in the localities adjacent to the tannery areas and drains in order to observe the impact of industrial units on health.

Considering the research methodology, initially wide range groundwater samples were analyzed from randomly selected areas. This showed extremely high concentrations of groundwater i.e. within tannery area up to 90 mg/L of total chromium. On the basis of these results detailed investigation on wastewater in carrying drains and soils and groundwater in the surrounding areas was conducted.

Historical background of research site and the level of contamination were of great significance as the detailed study of all the possible scenarios of industrial pollution were aimed to be explored in this regard to trace back the sources and extent of contamination. Data were collected about the initiation of subsurface contamination and the affected areas. Existence of tannery units was evidenced hundred years back. But “chrome tanning” was initiated only in the decade of 1970s after which the tanning industry exponentially flourished. It was not before the year 2000 that there were any measures for the proper collection and disposal of tannery effluent from the tannery units. Malpractice of open disposal of tannery effluent in the adjacent vacant fields was commonly observed, which turned them into stagnant ponds, leading to major source of subsurface contamination and exposed risk to nearby residents.

In the year 2000, wastewater treatment plant was developed to treat the tannery effluent which was carried through two lined drains. Furthermore the treated effluent was carried to final disposal through lined drains and underground sewers. Due to excessive wastewater generation, particularly during peak production season from May to September, most of the time these drains became choked and resulted immense overflow from these drains. It further caused stagnant pond development and became a continuous source of infiltration of contaminants into the soil. Wastewater samples from drains showed extremely higher concentrations of not only total chromium but also other chemical parameters. There were four drains in the research area which were analyzed on seasonal basis to observe the yearly variations of chromium concentrations in these drains. Chromium concentrations in wastewater samples as high as 2,050 mg/L posed a potential risk of soil and groundwater contamination. Due to inefficient treatment plant immense quantities of wastewater left untreated and diverted into other drains for further carriage up to farther distances. In the preliminary investigations surface soil samples were collected from wide spread range in order to observe the impact of wastewater ponds developed due to overflowing in the drains.

Considering high concentrations of total chromium in wastewaters, the downstream side of drains was focused to carry further detailed investigations. In this regard it was found that surface soil samples showed higher concentrations up to 180 mg/kg in the areas adjacent to the drains, which had shown immense overflows near the tannery area. The surface soils from other areas showed no significant results even up to distance of 10 kilometers on downstream side. Furthermore in order to investigate the effect of seepage from the unlined drain and overflow, soil bores were conducted on downstream side. These eight (8) soil bores were sampled at every depth of 1.5 meters up to 30 meters with the purpose to observe chromium concentration variation at every depth and to find out the soil texture beneath the soil. The soil samples were analyzed for leaching capability of soil and total content retention for both total chromium and hexavalent chromium. It was observed that higher the silt and clay proportions, higher the retention of total chromium. However no significant concentrations were found at any depth for both leaching and retention tests. It depicted that infiltration of effluent was not so widespread however it percolated up to considerable depth of soils with higher concentrations up to 91.2 mg/kg for total chromium and 16.1 mg/kg for hexavalent chromium observed at depth of about 17 meters, which is in range of seasonal variation of groundwater table. Groundwater was also monitored periodically by installing eight (8) monitoring wells in the downstream area in order to find out the concentration trend of total chromium in groundwater. The results obtained did not show any significant concentrations in the groundwater with maximum level up to 0.04 mg/L. However seasonal trend of variation in groundwater samples was also observed, which suggested direct infiltration from the cluster source of contaminants nearby.

FEMWATER model was used in order to conduct contaminant transport simulations in the area. Three main scenarios were developed in order to simulate the site for contaminant flow. First scenario was considered with adverse condition with stagnant pond in tannery area in operation with no treatment plant and drains in the area and this scenario was conserved for duration of 20 years from 1980 to 2000 and the second was for no contaminant release into the environment due to properly collected wastewater systems and treatment plant. Furthermore third scenario was based on existing situation, when treatment plant was not working efficiently due to release of excessive tannery effluent from the tannery units. The result of simulation showed very slow movement of contaminant plume indicating that stagnant pond in the tannery area has not affected the downstream side.

In order to investigate the health impact of total chromium in drinking water on the residents in the nearby areas of the tannery units, a detailed health survey was conducted. About 150 house units were surveyed in order to find out the impact of toxic compounds like chromium salts, released from the tannery industries along with other physical and chemical parameters, on human health. It was observed that considerable percentage of residents belonging to all age groups and gender were suffering from dermatitis, stomach related diseases and other skin related issues which were directly linked with the existence of toxic pollutants released from the industries.

Finally based on the findings of the research, recommendations were made to develop a plan to cope with the adverse environmental conditions at Kasur research site. Natural attenuation was proposed to be the most viable option in order to reduce the contaminant levels in the soil and groundwater. Overall trend of contamination was found to be in the form of patches and clusters. No specific trend of contamination could be observed due to nonexistence of a well-defined and properly quantified source of contamination. This problem basically originated from lack of implementation of environmental rules and regulations and following the standard requirements for establishment of an environment friendly industrial site at Kasur tannery area. Along with plan to follow the international environmental policies and laws and it was recommended to root out the main flaws in the industrial solid waste management system and focusing on the immediate need of development of landfill site so as to reduce the tannery waste impact on the environment. This research provided a generalized solution to all such industrial sites with similar pattern of sources of contamination which usually existed in other parts of not only Pakistan but in many other developing countries as well.

CHAPTER 1

INTRODUCTION

1.1 Pros and Cons of Industrialization

Industrialization is the economic process whereby an increasing proportion of income is derived from industrial manufacturing units. Economic aspect of industrialization has special bearing on processing and primary products (Hussain, 2000). This century and the previous, are the centuries of scientific and technological revolutions; completely influencing human life in every respect. The scientific development has altered the lifestyle of individuals and the culture of nations. As the technology advanced it brought more and more innovations in the daily use methods and modified procedures and processes, making so many complex jobs very easy and in the reach of every person. Consequently, this led the whole world into industrial boom, in every run of life and improving the quality of life of humans. The "Industrial Revolution" has brought improvement in quality of human life through mushrooming growth of industries and endless chain of discoveries, innovations, and inventions. The industries have grown seven times since the early 1940s yet today's human being is not contented with the present pace of development and relentlessly struggling to harness the Nature and the natural resources for his well-being and prosperity.

Since the 18th Century, wealth in the developed countries has paralleled industrial growth, and developed countries continue to produce the lion's share of manufactured goods indeed, about 74 percent of the world's industrial output takes place in the developed world. Today, many developing countries are experiencing an Industrial Revolution of their own, capturing an ever-increasing share of industrial growth. The pace of this newest cycle particularly in Asia far exceeds that of developed countries. In China, for instance, industrial growth between 1990 and 1995 reached 18.1 percent a year; East Asia and the Pacific and South Asia experienced growth rates of approximately 15 percent and 6.4 percent a year, respectively. By comparison, North America's industrial output grew by only about 2.6 percent a year during the same period.

It is the dilemma of the developing countries that where on one side the rapid industrialization has paved their way for better economic stability and prosperity of that country, on the other, it has deteriorated the environment to an alarming extent. Improper industrialization, rather haphazard industrialization has caused so many environmental problems which the developing countries are facing the most. The positive economic and social results of industrial growth have been accompanied by serious environmental degradation, however, as well as growing threats to health from occupational hazards. To some extent, these problems are analogous to those of early industrial Europe. In the 19th Century, the shift from a rural, agrarian society to an urban, industrial society initially involved widespread social and economic disruption, unemployment, homelessness, pollution, and increased exposure to health hazards both at work and at home. Many of these same problems characterize cities in the developing world today.

The earlier Industrial Revolution spanned nearly 200 years; recently, countries like Thailand and Indonesia have been undergoing similar changes in just a couple of decades. As part of this growth, industrial wastes are growing in quantity and becoming more varied, more toxic, and more difficult to dispose of or degrade. Densities in cities where much of the industrial production is located far surpass those in developed countries, so the number of people exposed to pollutants is potentially much greater.

Furthermore, a substantial share of industrial growth in developing countries revolves around the transformation of raw materials into industrial products such as steel, paper, and chemicals. A wide range of pollutants is associated with these industries. In contrast, much of economic growth in developed countries is now in the service sector (e.g., education, entertainment, defense, and finance) and communication sector (e.g., computers, cellular phones, and electronics), which is inherently less polluting.

This rapid industrial growth has made water pollution, air pollution, and hazardous wastes pressing environmental problems in many areas of the developing world. Industrial emissions combine with vehicle exhausts to cause air pollution, while concentrations of heavy metals and ammonia loads are often high enough to cause major fish kills downriver from industrial areas. The lack of hazardous waste facilities compounds the problem, with industrial wastes often discarded on fallow or public lands, in rivers, or in sewers designed to carry only municipal wastewater. The future scale of environmental and health problems from industrialization in developing countries will depend greatly on policy actions taken today. The potential the developing countries have to leap-frog to cleaner production is enormous, given gains in technology as well as the levels of private capital now flowing into these countries. In Indonesia, for instance, in the first half of 1997, petrochemicals represented almost one half of the US$16.2 billion in foreign investments. Decisions regarding the location sites of those industries, the technologies used and the type of precautions for occupational safety could have a tremendous impact on the future health of the people who live and work there (World Resources Institute, 1999).

It is all due to haphazard industrialization that the effluent from the industries could not be managed properly. And as there are thousands of new chemicals which have been involved in various manufacturing processes, the waste, whatever the nature of it may be, is full of hazardous chemicals. All these new chemicals pollute the atmosphere in one way or the other and once exposed to nature, it is carried to farther distances through air and water. Main industries which are flourishing in developing countries are agriculture and dairy based, which include, Textile, leather and food industries.

Fig 1.1: World map of Arsenic affected aquifers (British Geological Survey, 2017)

1.2 Industrial Pollution Perspective of Pakistan

Prior to 1960, the industries were only a few in number, thus the problem of pollution had not arisen. The industrialization boom commenced in the 1960s and the manufacturing units are being added at a rapid rate. It is ironic to note that while installing the industries the “Environmental Impact Assessment” (EIA) had not been carried out and the safety measures ignored. The process of conducting EIAs started in 1970s in the developed countries and Pakistan in late 1980s.

With a view to assess the extent of pollution a detailed survey was carried out in the year 1982. Similarly a project titled “Hazardous Chemical Industries and Safety Measures in Pakistan” was completed in 1987 by Pakistan Council of Scientific and Industrial Research (PCSIR). It is felt that growth of manufacturing and the pollution will occur simultaneously yet one should not be allowed to develop at the cost of other. It has been estimated that total numbers registered industries in Pakistan is 6634 out of which 1278 are considered highly toxic (Khan, 1998). However, little attention has been given to proper disposal of industrial waste. Recently it has been realized that there is a significant threat of water borne diseases, degradation of fresh water quality, environmental depletion and soil deterioration from the effluent and toxic emission of industries. Based on the source, wastewater/effluent may be a potential source of heavy metals e.g., Cd, Cr, Cu, Li, Ni, Pb, and Zn contamination. Different toxic and poisonous substances are used in the process of different Industries. For example, lead is used in battery industry; chromium is used in tannery industry and cyanide in metal finishing industry. These toxic compounds are the major source of contamination and pollution in developing countries as shown in Fig. 1.1 and 1.2, describing critical areas with polluted aquifers by arsenic and chromium.

Fig 1.2: World map of chromium pollution due to tanneries (Pure Earth, 2011)

Table 1.1 shows the amount of toxic substances being imported every year in Pakistan. (Mubin et al., 2002). Severe issues related to improper waste management are in common practice throughout. It is all due to severe negligence of the organizational authorities that the existing rules and regulations are not being implemented in their true spirit.

1.2.1 Examples of Industrial Pollution

Karachi – There are three industrial areas namely Sindh Industrial Trading Estate (SITE), Landhi Industrial Area (LIA) and Korangi Industrial Area (KIA). The wastes and effluents from SITE and LIA/KIA fall into rivers Lyari and Malir respectively and ultimately find their way into the Arabian Sea. Overall share of SITE towards industrial pollution is 51 % and on account of textiles (89 %) and chemicals (8 %). Daily production of BOD load by SITE and LITE is 615 and 550 tonnes respectively. SITE wastes include 400 tonnes dissolved solids, 50 tonnes suspended solids and 5 tonnes Ammonium Oxide. From River Lyari Karachi Harbour receives 376 tonnes dissoloved solids and from Manora Channel 35 tonnes suspended solids per day. Korangi Creek is the recipient of heavy loads of tannery, organic wastes and metals (Hussain, 2000). Based on the statistics of Pakistan Statistics Bureau Table 1.1 illustrates the immense quantities of hazardous materials being imported in Pakistan on yearly basis.

Table 1.1: Toxic substances imported every year in Pakistan (Mubin et al., 2002)

Sr. No	Name of Substances	Quantity (Tons/year)
1	Chromium	2866.08
2	Lead	839.95
3	Mercury	33.35
4	Arsenic	23.19
5	Cadmium	22.62
6	Cyanides	2.10

Kasur:- The tanneries discard 150 tonnes of wastes and 13,000 cubic meters of the effluents daily. Effluent amounting 2,500 cubic meters flows in Rohi Nallah and the remaining quantity is allowed to form three stagnant ponds covering an area of 132 hectares. Chromium sulphate, lime, sulphides and animal tissues are the main pollutants. Daily discharge of poisonous Chromium in the effluent is 300 kilograms (Hussain, 2000).

Faisalabad: - The city houses textile, chemical, fertilizer, leather, sugar and metal industries. The wastes and effluents from 500 industries are mostly thrown away, without prior treatment (Hussain, 2000). The chemical rich wastes have turned the surrounding land unfit for agricultural purposes (Fig 1.3).

***Kala Shah Kaku:* -** This complex is situated at a distance of 12 kilometers from Lahore on both sides of Grand Trunk Road. There are 150 industrial units which deal with pesticides, chemicals, textiles, ceramics, metals, paper etc. The untreated effluents are allowed to flow in the nearest water channels e.g. Deg Nallah. This water channel originating from Kashmir passes through many districts in Pakistan like, Sheikhupura, Gujranwala, Sialkot, before it finally falls in the Upper Chanab Canal ultimately joining the Ravi River. Before the establishment of industrial area at Kala Shah Kaku this Deg Nallah was considered to be clean and annual catch of fish from this nallah was around 600,000 kilograms (Husain, 2000).

After receiving huge bulks of industrial wastes this Nallah lost its cleanliness and there were no more fish in it onwards. The daily flow of 30 million liters of extremely polluted wastewater finally goes into the River Ravi (Hussain, 2000).

Fig 1.3: Untreated effluent disposal into nearby drains from textile & chemical industries

All these major industrial pollutants, along with other sources of contamination, are affecting the human health and environment in one way or the other. There are three main media through which any type of industrial caused pollution is exposed directly to the habitat or the inhabitants and i.e. subsurface contamination, land or surface contamination and air contamination. Before going into details, it’s better to throw light on what really contamination means. It is also very important to understand the characteristics of significant media, water and soil, so as to understand the path followed by the contaminant in the whole hydrologic cycle.

1.3 Groundwater Resources and Groundwater Flow

There are precious resources of water present in the hydrosphere. Also, an immense quantity of groundwater resources lying under the continental earth can be recovered more easily with the help of the modern technologies today. However only a small part of the water present on the earth is of any use to mankind as 94% of total water on earth is salt water, filling the oceans and seas. Out of the remaining, 99% of water is out of reach as it is frozen in ice caps and glaciers or buried deep underground. Groundwater serves as a sink tank of all kinds of wastes which may be industrial or domestic. These wastes sunk into the groundwater because of the percolation through the unlined channels when they are on their way to the main streams, rivers and seas. It may also be due to leachate through the landfills or leaky sewer as well as septic tanks. All this addition of wastes, constituting the harmful chemicals and organic and inorganic matters, results into the degradation of the quality of the water and thus making the groundwater contaminated (Nielsen, 1991).

While specifically discussing about groundwater contamination, which is equally hazardous as surface water contamination, the understanding of the role of subsurface strata and groundwater flow pattern is very significant. Water transmitting properties which must be considered while describing the groundwater movement or flow include hydraulic conductivity and trasmissivity. The terms permeability (p) and hydraulic conductivity (K) are often used interchangeably to refer to the ease with which water moves through soil or an aquifer under saturated conditions. A precise definition of hydraulic conductivity is the quantity of water that will flow through a unit cross sectional area of porous material per unit of time under a hydraulic gradient of 1.0 (measured at right angles to the direction flow) at specified temperature.

ASTM defines hydraulic conductivity measured from field aquifer tests as follows. The volume of water at existing kinematics viscosity that will move in a unit time under unit hydraulic gradient through a unit area measured at right angles to the direction of flow (ASTM). Transmissivity (T), a term derived from hydraulic conductivity, describes the capacity of an aquifer to transmit water. Transmissivity is equal to the product of the aquifer's saturated thickness (b) and hydraulic conductivity (K). It is commonly measured in units of gpd/ft of aquifer thickness. Darcy's law, expressed in many different forms allows calculation of the quantity of water flowing through defined areas of an aquifer, provided that the hydraulic conductivity and the hydraulic gradient are known. One means of expressing Darcy's law is: $Q = KiA$; where; Q = quantity of flow per unit of time, in gpd, K = hydraulic conductivity, gpd/ft^2, i = hydraulic gradient, A = cross sectional area through which the flow moves ft^2. To determine the flow from one aquifer to another via a confining unit, a slightly modified form Darcy's law can be used;

$Q1 = (p/m)\, A\triangle h$

$Q1$ = quantity of leakage, in gpd

p = vertical hydraulic conductivity of the confining unit, in gpd/ft^2

m = thickness of the confining unit, ft^2

$\triangle h$ = difference in head between the two aquifers

A = cross sectional area in ft^2

The time groundwater takes to travel a specified distance is particularly important in studies of contamination. Time of travel can be estimated using the form of Darcy's Law that describes average linear velocity.

$$\bar{v} = K \, {}^{i}\!/_{n}$$

v = average interstitial (linear) velocity

K = horizontal hydraulic conductivity

i= horizontal hydraulic gradient

n = porosity

Once average velocity is known, the time of travel over given distance can be easily calculated;

$$T = {}^{d}\!/_{\bar{v}} = {}^{dn}\!/_{Ki}$$

Where:

t = time of travel

d = distance

1.3.1 Groundwater Availability

Under the crust of the earth, groundwater is found in a very large area, and according to estimates the amount of groundwater in the world is about 500,000 Million Acre Feet (MAF). One fifth of this source lies in the active zone, within a depth of 2,500 feet of the surface. It is more than 30 times the water contained in all fresh water lakes and is more than 3,000 times the average volume of water flowing through rivers and streams (Kahlown et al., 2005)

1.3.1.1 Availability of Groundwater in Pakistan

Pakistan is blessed with extensive groundwater resource, which has been built due to direct recharge from natural precipitation, river flow and the continued seepage from the conveyance system of canals, distributaries, watercourses and applications losses in the irrigated lands during the last 90 years. This groundwater source has a potential of about 55 Million acre feet (MAF), out of which about 48.69 MAF is being exploited by over 661, 853 private tube wells, and about 18,620 public tube wells for domestic, agricultural and industrial purposes. Province wise groundwater usage is 42.69 MAF in the Punjab, 3.5 MAF in Sindh, 2 MAF in Khyber Pukhtoonkhawa, and 0.5 MAF in Balochistan. The potential of groundwater exploitation in Azad Jammu Kashmir is only 16800 AF while usage is above 4300 AF. The Northern areas, the potential for groundwater exploitation is virtually none. Groundwater use is nearing the upper limit in most parts of Pakistan. In Balochistan the water table has been declining continuously. A number of studies have estimated that the deficit in

Quetta sub-basin is about 21,000 AF per year and the aquifer storage will be exhausted in 20 years (Kahlown et al., 2005). Different provinces of Pakistan are shown in Fig. 1.4.

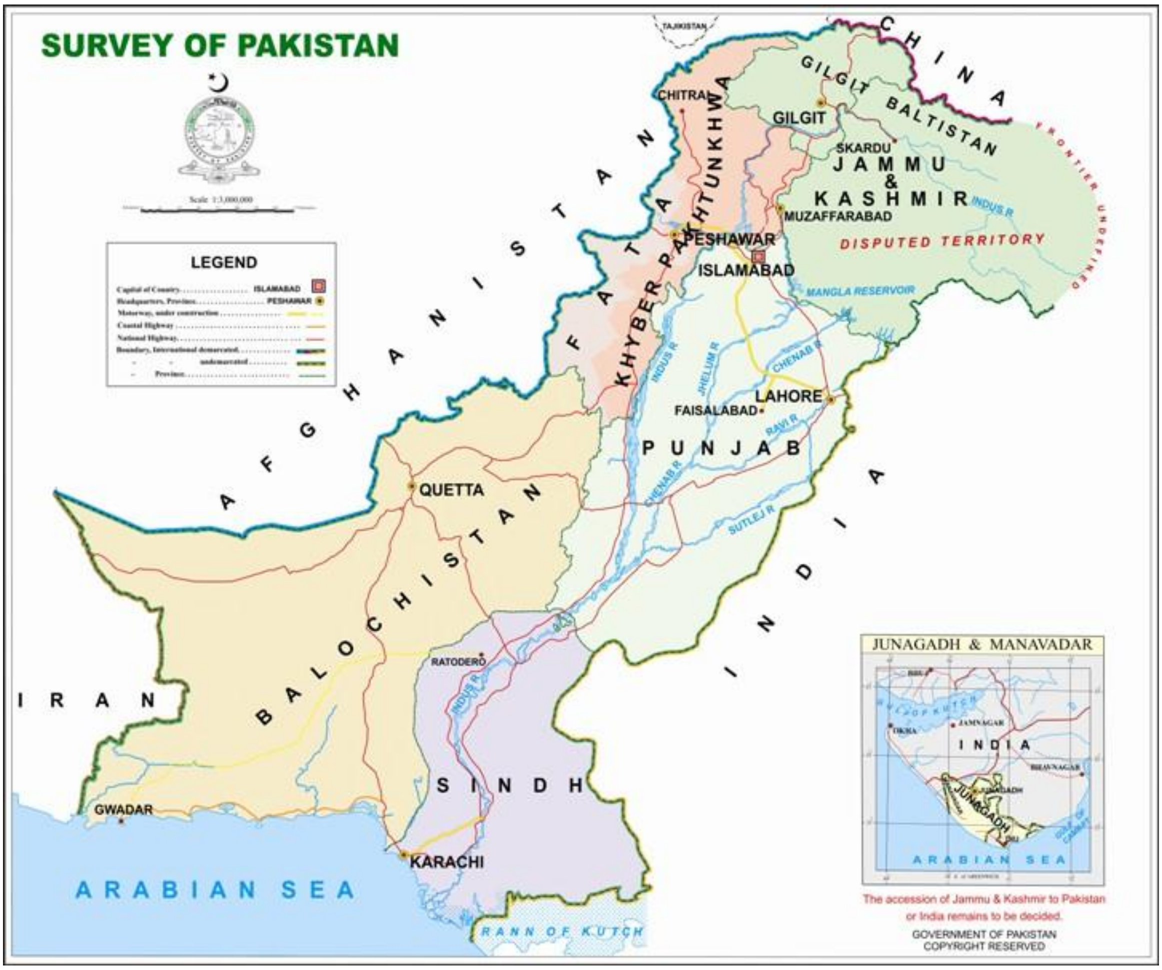


Fig. 1.4: Map of Pakistan showing provinces (www.surveyofpakistan.gov.pk)

For the purpose of drinking water sources, Pakistan can be divided into five major zones: 1) the sweet groundwater areas where water is easily accessible for human consumption; 2) the brackish groundwater areas where canal or river water is available; 3) the mountainous and hilly areas in the north where spring water is frequently available; 4) the eastern desert belt where groundwater may be available only at greater depth and 5) coastal belt of Pakistan where, generally, saline water is available. However, recent estimates of the availability and use of groundwater of an acceptable quality indicate that this resource has been heavily overexploited and has affected both the quality and quantity of the groundwater (Kahlown et al., 2005).

1.3.2 Groundwater Contamination

The Safe Drinking Water Act (SDWA) of 1974 defines the term “contaminant” broadly to include “any physical, chemical, biological or radiological substance or matter in water” (Boulding and Ginn, 2003).

This definition draws no distinction between contamination from natural and anthropogenic sources, nor does it distinguish between acceptable and unacceptable levels of contamination. Definitions of contamination from several other sources give some useful additional perspectives on the meaning of terms.

Groundwater contamination is the degradation of the natural quality of groundwater as a result of human activity (Boulding and Ginn, 2003).

Contaminants are all solutes introduced into the hydrologic environment as a result of human activity regardless of whether or not the concentrations reach levels that cause significant degradation of water quality, pollution results when contaminant concentrations reach levels that are considered to be objectionable (Boulding and Ginn, 2003).

Boundaries of polluted groundwater zones are the lines at which the concentrations of all pollutants have fallen below the maximum permissible concentration for potable water or where all water properties have taken on the normal values of the environment concerned (Boulding and Ginn, 2003).

A substance is any organic or in organic chemical, microorganism, radionuclide, or other material, such as sediment. Whether or not a substance is a contaminant depends on its association with adverse impacts and on other site-specific factors such as hydrogeology (Boulding and Ginn, 2003).

The term “contamination” is referred for degradation of natural water quality because of human activity definition of contamination (Boulding and Ginn, 2003).

1.3.3 Sources of Groundwater Contamination

It is a natural phenomenon that the water present on the surface or in the rivers, canals and drains is to percolate through the soil and ultimately it is to mix with the groundwater. If this water contains any type of impurity then it is also to be carried by that percolating water to the groundwater. Consequently these impurities contaminate the groundwater and hence it is termed as groundwater contamination.

There is a large number of sources causing contamination which includes industrial wastes, fertilizers, agri-chemicals i.e. pesticides and herbicides etc., household wastes, hospital wastes and sludge.

The industrial wastes contain many harmful and toxic chemicals are of not any use, they are wasted into the sewage tanks and then later on to the rivers and seas via drains.

These harmful wastes may be in the form of gases which are disposed off along with smoke and thus polluting the atmosphere. These pollutants in the air may travel back to earth being carried by the precipitation mixing ultimately with groundwater and making groundwater contaminated.

The effluent of the industries, on its way to the major disposal place, sea, passes through canals and rivers, which are unlined. Here the pollutants, whatever they may be, in the mixed form with water percolate into the soil. This is the easy way in which groundwater is influenced by the harmful wastes of the industries.

Another major source of groundwater contamination is the fertilizers used and chemicals used as pesticides. Pesticides can be classified into four large groups according to their use: herbicides, insecticides, fungicides and soil fumigants which control weeds, insects, plant pathogens and soil microorganisms. Pesticides are applied before, during and after crop emergence and harvest. Part of the does reaches the soil and then groundwater.

Landfills are another source of polluting the groundwater. A landfill is defined as "any land area dedicated or abandoned to the deposits of urban solid wastes regardless of how it is operated or whether or not a subsurface excavation is actually involved". These solid wastes may include household, industrial and hospital wastes of which the public sector assumes responsibility for the collection and disposal.

A term "LEACHATE" is used to describe the groundwater contamination due to landfills. It can be properly defined as the contaminated waste which is produced when water percolates through wastes in land disposal sites. Leachate is not produced in a landfill until filled materials reach the water saturation point. For landfill leachate to enter underlying groundwater areas it depends upon several factors. Possible sources of water in landfills include precipitation, moisture content of refuse, surface water infiltrating the fill, percolating water entering from adjacent land areas, or groundwater coming into contact with the fill material.

Groundwater is being contaminated by sewage irrigation as well. The use of wastewater for irrigation is rapidly becoming a more attractive alternative as groundwater and fresh surface water supplies are decreasing. Wastewater can be used for additional irrigation and to promote greater use of crop and the wastewater can potentially supply plant nutrients to crops or landscape production, and, if fertilizers cost is reduced consequently, this is an added incentive. However, the irrigation of specific crop with raw or primarily treated sewage although inducing potential savings, has been shown to cause deterioration of groundwater and soil quality. It is because that it however, contains pathogenic organisms, refractory, organics (surfactants, phenols and agriculture pesticides) which tend to resist their removal by conventional methods of wastewater treatment, heavy metals and dissolved inorganic. (Boulding and Ginn, 2003).

The presence of microorganisms including bacteria, viruses, fungi and protozoa's in the groundwater renders it polluted. The presence of such organisms is the major reason of causing the water borne diseases. Irrigation and disposal of sewage effluent into soils then contributes enormous number of gram-negative bacteria.

Tank and pipeline leakage is another source of groundwater contamination. Many industries employ underground collection pipeline devices to move process fluids and wastes within a plant or to move materials to storage areas or ship them out. The material, whatsoever it may be, will leave its effects on the groundwater. In case of petroleum and other oil leakage, the water has been reported objectionable and not recommended to be used as potable water. A schematic diagram for various sources of groundwater contamination is shown in Fig.1.5.

The extent to which a contaminant moves in groundwater depends on its behavior in relation to various processes, which facilitate transport, and those, which serve to resist the movement.

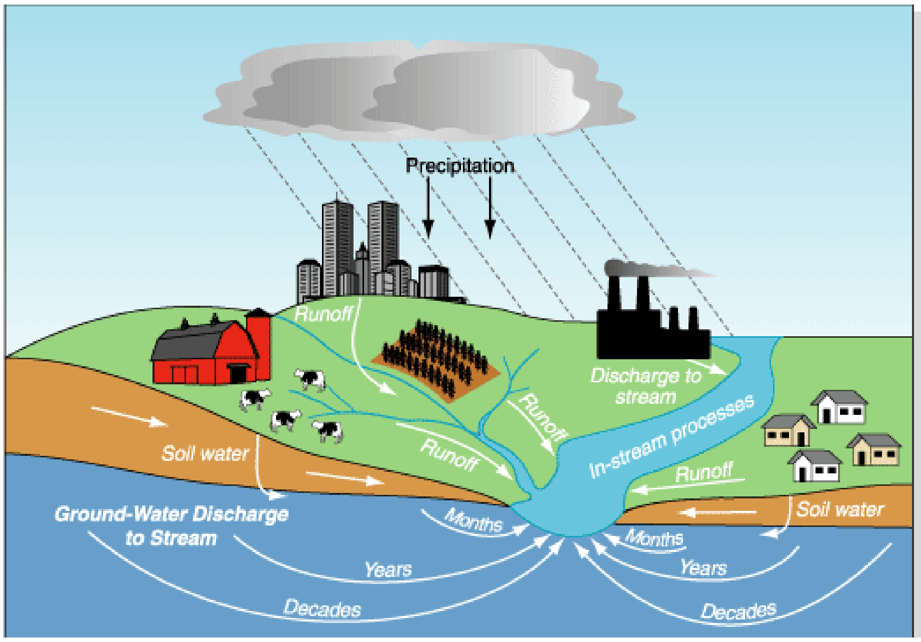


Fig 1.5: Different sources of groundwater contamination (Phillips et al., 1999)

1.3.4 Contaminant Transport Process

Groundwater in its natural state is constantly in motion, although in most cases it is moving very slowly, typically at a rate of inches or feet per day. This movement of groundwater governs the extent to which chemical constituents migrate in groundwater. The contaminants, which are dissolved in groundwater, travel along with the flow of groundwater. This groundwater flow can be calculated using Darcy's law.

Contaminants having density lower than groundwater tend to concentrate in the upper portions of an aquifer, while those having a higher density concentrate in the lower portions. Viscosity of a fluid is the measure of its resistance to shear. The viscosity of specific contamination affects their rate of migration through soil and within an aquifer (Boulding and Ginn, 2003).

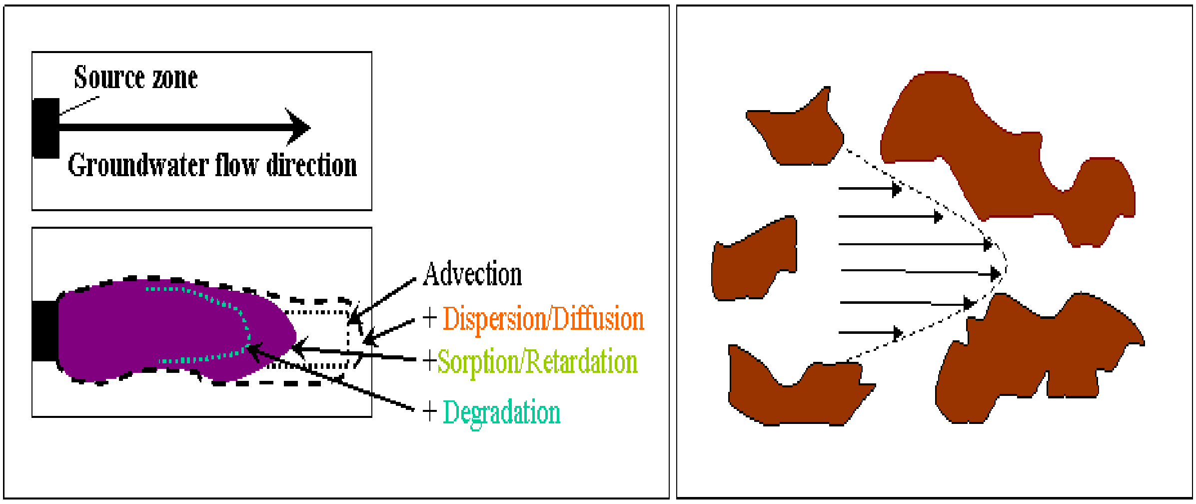


Fig.1.6: Transport process of contaminants in groundwater and velocity variations within an individual pore (EUGRIS, 2017)

Different processes involved in the movement of contaminants in groundwater and their velocity variations based on the existing geological formations and groundwater flow are shown in Fig. 1.6 (EUGRIS, 2017). Dispersion and density or viscosity differences may accelerate the movement of contaminants in groundwater. While retardation due to biological degradation or other factors slow down the contaminant velocity.

1.3.5 Mathematical Modeling for Groundwater Flow and Contaminant Transport

Mathematical models of groundwater flow have been used since the late 1800s. A mathematical model consists of differential equations developed from analyzing groundwater flow (or solute transport in groundwater) and are known to govern the physics of flow (and transport). The reliability of model predictions depends on how well the model approximates the actual situation in the field. Inevitably, simplifying assumption must be made in order to construct a model, because the field situation is usually too complicated to be simulated exactly. In general, the assumptions necessary to solve a mathematical model analytically are very restrictive. For example, many analytical solutions are developed for homogeneous, isotropic, and/or infinite geological formations where flow is also steady-state (hydraulic head and groundwater velocity do not change with time). To deal with the more realistic situations (e.g., heterogeneous and anisotropic aquifer in which groundwater flow is transient), the mathematical model is commonly solved approximately using numerical techniques. In the case of groundwater flow, the relevant physical principles are Darcy's law and mass balance. By combining the mathematical relation describing each principle, it is possible to come up with a general groundwater flow equation, which is a partial differential equation (PDE). Since in groundwater studies, the fluxes (Darcy flux, average linear velocity) are macroscopic quantities which are related to the head gradient and hydraulic properties of the aquifer (i.e., porosity, permeability, hydraulic conductivity) by the Darcy's law, the PDE developed for the general groundwater flow is thus established for macroscopic flow in porous media. (Zhang, 2016)

1.4 Drinking Water Quality and Water Borne Diseases

The population of Pakistan is expected to grow to 221 million by the year 2025. This increase in population will have direct impact on the water sector for meeting the domestic, industrial and agricultural needs. Pakistan has now essentially exhausted its available water resources and is on the verge of becoming a water deficit country. The per capita water availability has dropped from 5,600 m^3 to 1,000 m^3 since the independence in 1947. The quality of groundwater and surface water, which are the main sources of water, is low and is further deteriorating because of unchecked disposal of untreated municipal and industrial wastewater and excessive use of fertilizers and insecticides (Kahlown, 2005)

Pakistan has already fallen in the category of water stressed country and if the situation continues it would degrade into water scarce country. As per USAID report, an estimated 250,000 child deaths occur each year in Pakistan due to water-borne disease. The links between water quality and health risks are well established. Inadequate quantity and quality of potable water and poor sanitation facilities and practices are associated with a host of illnesses such as diarrhoea, typhoid, intestinal worms and hepatitis (WWF, 2007). A report of World Health Organization (WHO) said diseases associated with contaminated water kill more than 25,000 people every day and about 10 million each year in the world (SPECTRUM, 2004). In Pakistan around 30 to 40 % of all the reported diseases and deaths are attributed to poor quality respectively. Moreover, the leading cause of deaths in infants and children up to 10 years age as well as mortality rate of 136 per 1000 live births due to diarrhea is reported while every fifth citizen suffers from illness and diseases caused by polluted water. In Karachi only, 10,000 people die annually of renal infection due to the polluted drinking water (Kahlown et al., 2005).

1.5 Tannery Industry and Environmental Issues

Leather industry has been characterized as one of the highly polluting industries and their concerns that leather making activity can have adverse impact on the environment. The global production of about 24 billion meter square of leather by 2005 presents a considerable challenge to the industry considering the harmful nature of some of the chemicals used in leather processing. The tannery effluents are characterized by high contents of dissolved, suspended organic and inorganic solids giving rise to high oxygen demand and potentially toxic metal salts and chromium metal ion. The disagreeable odor emanating from the decomposition of proteinous waste material and the presence of sulphide, ammonia, and other volatile organic compounds are also associated with tanning activities. Solid wastes generated in leather industries contribute mainly skin trimmings, Keratin wastes, fleshings wastes, chrome shaving wastes and buffing wastes. They constitute protein as the main component. If these protein and other chemicals, which are present in the chemically treated protein, are not utilized properly it will pose hazardous pollution problem to the environment. Raw material for leather industry is raw hide or skin. The salt used for preserving the skin/hide discharges huge amount of pollution load in terms of total dissolved solids (TDS) and chlorides. Other major polluting chemicals used in tanning industry are lime, sodium sulphide, ammonium salts, sulphuric acid, chromium salts and vegetable tanning materials (Table 1.2) (Kanagraj et al., 2006).

Table 1.2: Typical waste emission factors associated with leather processing

	Soaking	Liming	Deliming	Pickling	Chrome tanning	Dyeing and Fat liquoring	Composite (incl. washing)
BOD$_5$	8.3-18.8	17.5-35.0	1.5-4.5	0.3-0.5	0.5-1.2	1.5-3.0	35.0-105
COD	22.5-45.0	35.0-87.5	3.8-10.5	0.8-2.3	0.5-3.8	3.8-10.5	87.5-280
Total solids	262.5-415	105.0-175	6.0-15.0	6.3-52.6	5.0-90	6.0-15.0	528.0-875
Solids Suspended	22.5-52.5	21.0-70.0	2.3-6.0	0.8-2.3	0.5-3.8	0.9-1.5	70.0-140
Solids chloride Cl-	112.5-225	14.0-28.0	1.5-3.0	0.5-3.8	3.0-38	0.8-1.5	210.0-332.5
Chromium as Cr	-	-	-	-	5.0-7.5	-	3.5-8.8

All values expressed in kg/tone of hide processed

Currently, about 6.5 million tons of wet salted hides and skins are processed worldwide annually. About 3.5 million tons of various chemicals are used for leather processing. A variety of chemicals is used in the tanning process along with large quantities of water which are discharged as effluents, containing a huge bulk of liquid and solid wastes, and substantial quantities of Cr and other heavy toxic trace metals, organic matter, lime and sulfide (Kanagraj et al., 2006).

1.5.1 Chromium as Major Contaminant from Tannery Industries

Tannery effluents are ranked as the highest pollutants among all industrial wastes. They are especially large contributors of chromium pollution. For instance, in India alone about 2000–3000 tone of chromium escapes into the environment annually from tannery industries, with chromium concentrations ranging between 2000 and 5000 mg/l in the aqueous effluent compared to the recommended permissible discharge limits of 2 mg/l. There are two types of tanning systems which are vegetable tanning, which does not contain chromium, and chrome tanning. However, due to the high pollution load and low treatability, conventional vegetable tanning can't be considered more environment friendly than chrome tanning. Moreover, vegetable tanned leathers have different physical properties and specific applications, but is biodegradable. Currently more than 90% of global leather production of 18 billion sq. ft is through chrome-tanning process. Chromium salts (particularly chromium sulphate) are the most widely used tanning substances today. Hides tanned with chromium salts have a good mechanical resistance, an extraordinary dyeing suitability and a better hydrothermic resistance in comparison with hides treated with vegetable substances. Unfortunately only a fraction of the chromium salts used in the tanning process react with the skins. The rest of the salts remain in the tanning exhaust bath and are subsequently sent to a depuration plant where the chromium salts end up in the sludge. One of the major emerging environmental problems in the tanning industry is the disposal of chromium contaminated sludge produced as a by-product of wastewater treatment. Tannery effluents severely affect the mitotic process and reduce seed germination in extensively cultivated pulse crops.

Major problem is the scarcity of data in every respect. There is no authenticity of the statistical figures or health reports or analysis findings of different chemical parameters in different media. Furthermore situation becomes worse when the problem is not being prioritized by the government either. All the tiny efforts made by government or individual stakeholders are only under the influence of strict international rules and regulations for export and import of commercial products. Thus the government along with other stakeholder is bound to meet the WTO requirements.

This is the major incentive which compels them to make necessary arrangements regarding environmental considerations. Mainly it includes wastewater treatment plant in order to meet the standard requirements set by National Environmental Quality Standards (NEQS). It will help in proper control of effluent quality which is being disposed into the drains. Basic requirement fulfills the compliance of environmental standards for controlling the surface water quality so as to control the hazardous effects of industrial effluent on flora and fauna.

Chromium is a naturally occurring heavy metal which is used extensively in different industries particularly in tannery industries.

1.5.2 Chromium Toxicity and its Accumulation

Industrial activities like electro plating, metal cleaning and dyeing processing, cement, and leather tanning are the major sectors that play role in releasing chromium into the environment. A study done by Marchese et al. (2008) about the rate of accumulation of chromium in four fresh water plant species, clams, crabs, and fishes showed that, all the four fresh water species and animals were found with high concentration of chromium which is an indication of its high accumulation potential. This clearly indicates that this problem become more serious and toxic to human beings which are found at the top of the food web due to its toxicity and bio accumulation effect. Tanning agents could help permanent stabilization of the skin matrix against biodegradation. This industry has gained a negative image in society with respect to its pollution potential and therefore is facing a severe challenge. Basic chromium sulfate (BCS) is a tanning agent, which is employed by 90% of the tanning industry. Conventional chrome tanning results in wastewater containing as high as 1500−3000 ppm (parts per million) of chromium; however, the present day high-exhaust chrome tanning methods lead to a wastewater containing 500−1000 ppm of chromium. But, the discharge limits for trivalent chromium vary broadly ranging from 1 to 5 mg/l in the case of direct discharge into water bodies and 1 to 20 mg/l in the case of discharge into the public sewer system. Therefore, the treatment plant used by the tanning industry needs to treat the influent by 200 fold to send to water bodies, which is not practical in most of the cases (Belay, 2010).

Chromium can exist in air, water, soil, and food, and common exposure pathways include ingestion, inhalation, or dermal contact. Chromium is commonly found in two forms: trivalent chromium (chromium III) and hexavalent chromium (chromium VI). Chromium III is the most stable form of the element, and occurs naturally in animals, plants, rocks, and soils. Chromium VI rarely occurs in nature, and is usually the product of anthropogenic activities.

The health effects of chromium depend on the route of exposure and the form of the chromium. For example, inhaling chromium can cause damage to the respiratory system, whereas neither dermal nor oral exposures generally affect the respiratory system. Gastrointestinal effects are generally associated with oral exposure, but not with dermal exposure. In addition, chromium VI typically causes greater health risks than chromium III. The reasons for the increased danger of chromium VI versus chromium III are complex, and relate in part to the varied paths of cellular uptake between the two forms.

The primary health impacts from chromium are damage to the gastrointestinal, respiratory, and immunological systems, as well as reproductive and developmental problems. Chromium VI is a known human carcinogen, and depending on the exposure route, can increase the rate of various types of cancers. Occupational exposure to chromium VI, which often occurs through inhalation, has been linked to increased rates of cancer in the respiratory system. According to the WHO, over 8,000 workers in the tanneries of Hazaribagh, India suffer from gastrointestinal, dermatological, and other diseases, and 90% of this population die before the age of 50 (Maurice, 2001). Separate studies in Kanpur, India also show that there is a significantly higher prevalence of morbidity in these workers, mostly from respiratory diseases owing to chromium exposure (Rastogi et al., 2008)

Chromium III is considered to be less dangerous than chromium VI, although some investigations have demonstrated that chronic exposure to this form, especially in occupational settings, can significantly damage lymphocyte DNA (Medeiros et al., 2003) Studies have also indicated that the broader category of chromium accumulation in the human body can have an adverse effect on the ability to metabolize iron, it is important because iron is essential to red blood cells. (Kornhauser et al., 2002). As most of the human body's iron is contained in these cells, iron deficiency anemia can occur when the body cannot absorb enough of the metal.

1.5.3 Chromium and its behavior in the environment

Chromium is present in the environment predominantly in one of the two valence states: trivalent chromium Cr (III), which occurs naturally and is an essential nutrient, and hexavalent chromium Cr (VI), which is highly toxic and is classified as a human carcinogen. Trivalent chromium Cr (III) exists as a cationic species (Cr^{3+}) and can be easily removed from solution by precipitation in alkaline media. Hexavalent chromium however exists in the anionic form and is soluble in both acidic and alkaline media, in aqueous solution, Cr (VI) exists in the form: chromate CrO_4^{2-}, dichromate $Cr_2O_7^{2-}$ and hydrogen chromate $HCrO_4^-$ .The form of anion which predominates will depend primarily on the pH of the medial and the respective chromium concentration (Neil, 2001). There is a weak adsorption of chromate anions by natural clay minerals due to negative charges (Benhammou et al., 2006).

1.6 Problem Statement

In Pakistan but there was no focused legislation regarding Environment before 1983. There was no observation of any standards in order to maintain the maximum contaminant level in the environment. Even in 1983 an Environmental Ordinance was passed constituting the basic structure of Pakistan Environmental Agency and it lacked any strict implementation from industrial waste perspective.

All this encouraged haphazard industrialization, without any proper planning, drainage system and any initial environmental examination reports. There were no wastewater treatment plants and industries disposed off their waste in open fields and natural drains finally disposing in the main rivers.

With this background, introduction of chemicals to enhance the industrial processes made the situation worse. Particularly talking about the two major sectors in which industries groomed exponentially, i.e. textile and leather, the areas with large clusters of these industrial units, not only water resources but overall environmental conditions are highly vulnerable and reported to be adversely affected.

Focusing on tannery units; there are three main clusters of industrial units, situated in Karachi, Sialkot and Kasur. At Korangi Industrial Site in Karachi there are 170 tanneries with daily solid waste load of 90 – 200 tonnes. And there are 135 tannery units in Sialkot, disposing off their waste in two drains, which pass by. In Kasur area there are more than 237 tanneries which are disposing off their waste first in Rohi Drain and then into the River Chenab through another main drain. History of tanneries in Kasur dates back about 100 years. But initially it was not wide spread and there was no use of harmful chemicals. With the passage of time chrome tanning became popular and chromium sulphate was started as a chemical to help improving the finishing of leather (Hussain, 2000)

375 kilogram of chromium sulphate is being used in these tanneries on daily basis. 150 tonnes solid waste load is being disposed on daily basis. More than 13,000 cubic meters per day is being discharged from these tanneries on daily basis. Before year 2000 there was no treatment plant and all the waste was disposed into the drain or left over in open fields. From the drain the wastewater was used for irrigation purposes as well. The effect of use of hazardous wastewater for irrigation is also questionable. Besides more than 400 acres area in the surroundings of the tanneries was completely soaked with tannery wastewater for decades, creating a very unaddressed environmental issue, preferably considered as a very significant

matter regarding the health hazards and environmental impact on the whole area and the inhabitants (Fig 1.7). Not only, directly the soil but the subsurface is also severely affected by the continuous percolation of the hazardous chemical containing wastewater directly from the open fields and also from the unlined channels (Rehman, 2004).

This improper disposal and drainage of the tannery waste ultimately became havoc for the inhabitants of the Kasur district. This resulted in the severe unhygienic conditions in the vicinity, contamination of the groundwater by the toxic chemicals, contamination of the crops growing in the area due to the heavy concentrations of the hazardous materials, in the soil and groundwater. As the groundwater is the major source for the drinking purpose and for agricultural purposes as well, thus the rate spreading of the risk to public health and environment is also many folds high, due to direct exposure to the source of contamination. Due to the unhygienic conditions the people of the area are suffering from a number of serious diseases and unexpected diseases have also been observed in the region. The major diseases in the area are typhoid, hepatitis and stomach related diseases, with children, women and elderly people among patients. In 2005, about 10 percent of Kasur's population was infected with hepatitis, 20 percent of the town's children had diarrhea, and 70 percent of diseases were due to the contaminated water.

Fig 1.7: Areas adjacent to the tanneries soaked in tannery effluent due to direct disposal

Fig 1.8: Tannery industry workers handling hazardous waste

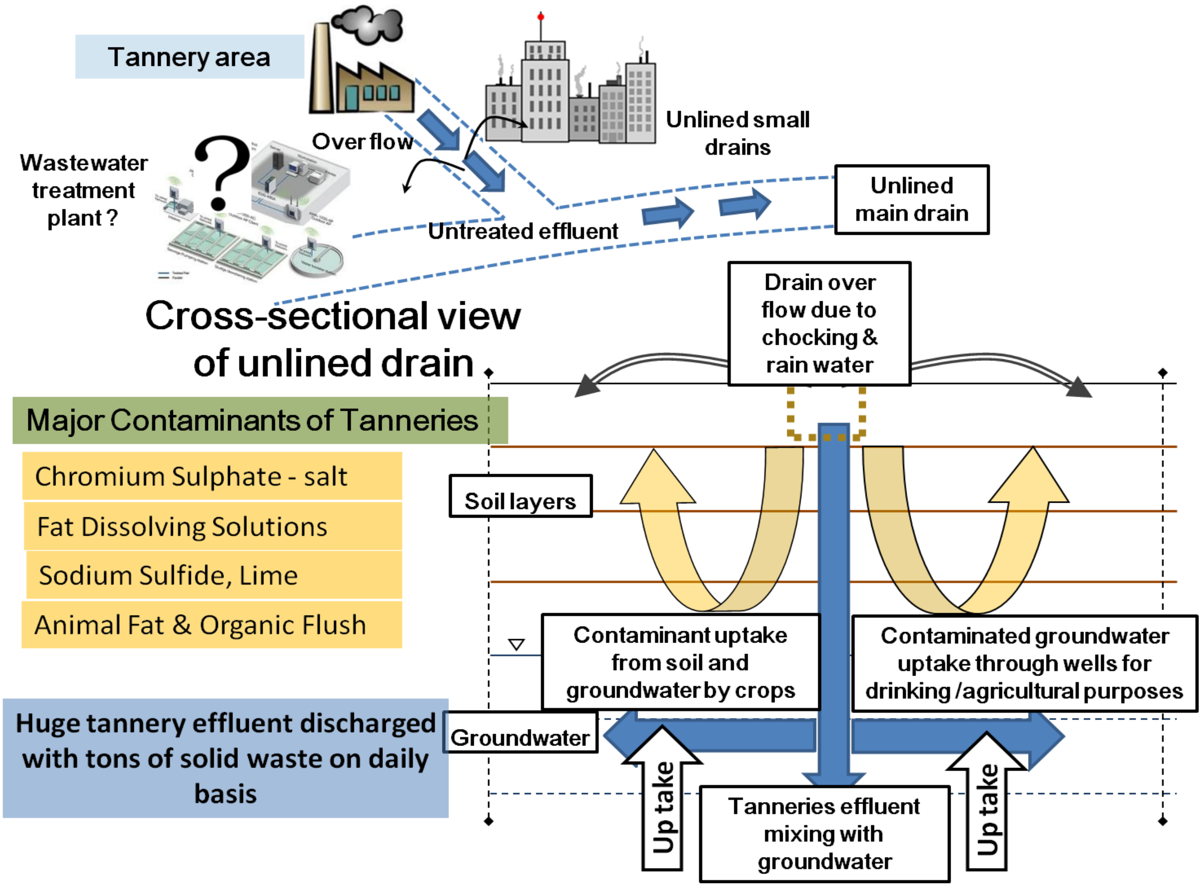


Fig 1.9: Schematic diagram of tannery management situation at research area representing the research concept

On the basis of the previous studies conducted, it has been observed that heavy metal concentration is found in excess in the groundwater of the Kasur district. The concentration level of Arsenic, Fluoride and Chromium has reached to an alarming extent. 75, 000 people who are directly related to tannery industries are vulnerable to risk of harmful effects of hazardous chemicals being used in chrome tanning (Fig 1.8).

Furthermore there has been massive shift of population in the nearby areas of the tanneries which are directly exposed to all the hazardous effects from tanneries. There are so many hygienic issues associated with that of tanneries effluent and poor sanitation conditions prevailing in the research area. Initially the effluent was not in excessive quantities therefore the practice to dispose the effluent in open areas was not as harmful as it became with the immense increase in the tannery industries due to high demand of raw leather.

Table 1.3: Comparison of the quality of raw effluents from tanning industries in Kasur with National Environmental Quality Standards (NEQS) (Rehman, 2004)

Parameters	Raw Effluents in 1989*	Raw Effluents in 2002**	NEQS***
Suspended Solids (mg/L)	2,025	2,700	1,150
Total Dissolved Solids (TDS)	5,390	7,500	3,500
Sulphates	438	2,000	600
COD	3,427	3,100	150
BOD5	1,423	1,600	80
Sulphides	50	120	1.0
Chromium	17.5	90	1.0

**Pakistan Council of Scientific and Industrial Research (PCSIR), 1989*
***Kasur Tanneries Waste Management Agency (KTWMA), 2003*
****National Environmental Quality Standards (NEQS) of Pakistan*

According to the report of Environmental Protection Department (EPD) Punjab, in 1997 the groundwater in Kasur has been detected extremely polluted with chromium as compared with WHO standards. Chromium (VI) is termed as carcinogenic (cancer causing). Its presence in the air as aerosols of chromium and in groundwater can result in several chronic diseases leading to cancer (EPD, 1997). The results obtained showed higher concentration of total chromium in drinking water from tube well sources which were at depth of 100 meters, as high as 0.25 mg/L while the standard for Chromium in drinking water by WHO is 0.05 mg/L.

In 1988, the highly contaminated and untreated industrial effluents discharged from these tanning factories had rendered around 1,250 acres of fertile agricultural land into lakes of stagnant wastewater. In 1989, Pakistan Council for Scientific and Industrial Research

(PCSIR) analyzed the untreated industrial effluent and results showed significantly high values of BOD_5 (1423 mg/L), COD (3427 mg/L), total solids (7415 mg/L), total dissolved solids (5390 mg/L), suspended solids (2025 mg/L), chromium (17.5 mg//L), chlorides (1100 mg/L), Sulphides (50 mg/L) and sulphates (438 mg/L). In 1993, International Union of conservation of energy (IUCN) estimated that around 120 tanneries discharging daily 9,000 cubic meter of polluted effluents which carried around 74 kg of Chromium and more than 200 kg of Sulphides per day (Rehman, 2004). Since 1989, the quantity and toxicity of the industrial effluent has been increasing tremendously in terms of concentration level and its impact on health and environment has obviously increased. The comparison of quality of raw effluents during different years has been shown in Table 1.3.

1.7 Objectives of Study

In the year 2000, when the health situation became severe in Kasur city and the surrounding villages and localities, the number of people sick from water borne diseases increased alarmingly, the government and international agencies like UNDP, became active. The major steps taken to combat the adversity of the situation include the lining of drain, development of biological wastewater treatment plant and two parallel drains across the road to carry to untreated effluent from the tannery area to the treatment plant.

However, the drain passing through the center of the city is still not completely lined and only the portion which passes through congested streets was lined at that moment. But the stagnant ponds of untreated effluent were left open and ultimately they percolated down into the soil shifting the problem from the surface to the subsurface, where it is more complex in nature to be addressed and to be solved out.

Even after decades since the problem was at its peak, the ground reality is still as adverse as it was on day one. The overflowing drains with untreated effluent, blocked drains and heaps of solid waste including tannery waste are clear evidence of adverse environmental conditions. The wastewater treatment plant is no more capable of handling the excessive loads of tannery effluent, which, therefore is diverted to another drain without treatment.

In order to address this critical environmental issue and investigate the ground situation to find out the regions of high subsurface contamination and the extent of groundwater contamination due to chromium as major target contaminant from tanneries, this research was initiated. A schematic diagram of the existing situation and tannery waste management related issues, which lead to the motivation of this research are presented in Fig. 1.9.

With this background, this research work was planned, with major objectives considered to be as follows:

- to investigate the soil & groundwater contamination due to chromium from untreated effluent of tanneries
- Study of the Health Hazards: Community based survey and data collection so as to study the health hazards in the research area due to the chromium contamination of groundwater.
- Development of contaminant transport model to study transport and fate of chromium in subsurface within the predefined boundary in the study area. This model will be developed using FEMWATER - GMS software.
- To provide a workable site management plan to eradicate the hazardous effects due to improper waste management

The research work basically constitute of extensive field investigations, soil and groundwater explorations, determination of impact of tannery effluent in drains on soil and groundwater, followed by monitoring of groundwater for chromium concentrations and simulation of chromium in subsurface for a certain time period and health impact of chromium on the residents. Based on the result and field investigation findings and their analysis, a dynamic plan was produced by developing a framework to cope with the adverse scenarios related with tannery waste management in order to effectively control the complex contamination situation at on site.

1.8 Environmental Standards for Chromium in Different Phases and Media

An environmental standard is a policy guideline that regulates the effect of human activity upon the environment. Environmental standards are a set of quality conditions that are adhered or maintained for a particular environmental component and function. Different environmental regulatory authorities have developed environmental standards for all the chemical and biological parameters, based on vast investigations and experimentation under different conditions for different media i.e. air, soil, water and wastewater.

There are different international organizations and institutes which have developed different standards pertaining to a wide range of parameters and pollutants existing under different environmental conditions and media

Ministry of Environment, Japan has developed and issued Environmental Quality Standards for groundwater in 1997, which are described in Table 1.4. Now they are required to be maintained in order to protect human health.

According to additions made in 1999, 2000, 2001, 2011, 2012, EQS now regulate 28 hazardous substances including heavy metals, volatile organic carbon, etc. According to these standards the Standard value for Cr (VI) in groundwater should not exceed 0.05 mg/L.

Table 1.4: Environmental quality standards for groundwater pollution (MOE Japan, 2012)

Items	**Standard Values**
Cadmium	0.003 mg/liter or less
Total Cyanogen	not detectable
Lead	0.01 mg/liter or less
Chromium (VI)	0.05 mg/liter or less
Arsenic	0.01 mg/liter or less
Total mercury	0.0005mg/liter or less
Alkyl mercury	not detectable
PCB	not detectable
Dichloromethane	0.02 mg/liter or less
Carbon tetrachloride	0.002 mg/liter or less
Vinyl chloride monomer	0.002 mg/liter or less
1,2-dichloroethane	0.004 mg/liter or less
1,1-dichloroethylene	0.1 mg/liter or less
1,2-dichloroethylene	0.04 mg/liter or less
1,1,1-trichloroethane	1 mg/liter or less
1,1,2-trichloroethane	0.006 mg/liter or less
Trichloroethylene	0.03 mg/liter or less
Tetrachloroethylene	0.01 mg/liter or less
1,3-dichloropropene	0.002 mg/liter or less
Thiram	0.006 mg/liter or less
Simazine	0.003 mg/liter or less
Thiobencarb	0.02 mg/liter or less
Benzene	0.01mg/liter or less
Selenium	0.01mg/liter or less
Nitrate nitrogen and nitrite nitrogen	10 mg/liter or less
Fluoride	0.8 mg/liter or less
Boron	1 mg/liter or less
1,4-dioxane	0.05mg/liter or less

Similarly the standards defined for soil quality examination through leaching and content test are described in Table 1.5, as issued by Ministry of Environment, Japan. These were issued in 1991 with addition in 1994, and regulating 25 substances.

National Environmental Quality Standards were developed and issued for municipal and industrial effluents by PEPC (Pakistan Environmental Protection Council) as a revised version in year 2000 (GOP, 2000). These are presented in Table 1.6. Only the component of the standards related to industrial and municipal effluents is mentioned here.

Table 1.5: Environmental quality standards for soil pollution (MOE Japan, 1994)

Substance	**Target level of soil quality examined through leaching and content tests**
Cadmium	0.01 mg/l in sample solution and less than 0.4mg/kg in rice for agricultural land
Total cyanide	not detectable in sample solution
Organic phosphorus	not detectable in sample solution
Lead	0.01 mg/l or less in sample solution
Chromium (VI)	0.05 mg/l or less in sample solution
Arsenic	0.01 mg/l or less in sample solution, and less than 15 mg/kg in soil for agricultural land (paddy fields only)
Total mercury	0.0005 mg/l or less in sample solution
Alkyl mercury	not detectable in sample solution
PCBs	not detectable in sample solution
Copper	less than 125 mg/kg in soil for agricultural land (paddy fields only)
Dichloromethane	0.02 mg/l or less in sample solution
Carbon tetrachloride	0.002 mg/l or less in sample solution
1,2-dichloroethane	0.004 mg/l or less in sample solution
1,1-dichloroethylene	0.02 mg/l or less in sample solution
cis-1,2-dichloroethylene	0.04 mg/l or less in sample solution
1,1,1-trichloroethane	1 mg/l or less in sample solution
1,1,2-trichloroethane	0.006 mg/l or less in sample solution
trichloroethylene	0.03 mg/l or less in sample solution
tetrachloroethylene	0.01 mg/l or less in sample solution
1,3-dichloropropene	0.002 mg/l or less in sample solution
Thiuram	0.006 mg/l or less in sample solution
Simazine	0.003 mg/l or less in sample solution
Thiobencarb	0.02 mg/l or less in sample solution
Benzene	0.01 mg/l or less in sample solution
Selenium	0.01 mg/l or less in sample solution

Pakistan Environmental Protection Council (PEPC) is an apex organization at the National level for formulation and implementation of the national environmental policy and programs. It was set up in 1984 under section 3 of the Pakistan Environmental Protection Ordinance. During the first ten years of its existence only one meeting of the PEPC had been held under the Caretaker Prime Minister of Pakistan who decided to establish the National Environmental Quality Standards. The standards were related to:

- Municipal and liquid industrial effluent
- Industrial gaseous emissions and
- Motor vehicle exhaust and noise.

These standards were notified in the Gazette of Pakistan on 29 August 1993. The approved NEQS were uniform standards applicable to all kind of industrial and municipal effluent. There are 32 parameters prescribing permissible levels of pollutants in liquid effluent while 16 parameters for gaseous emission. In April 1996, the PEPC set up an Environmental Standards Committee (ESC) to review, among other things, the NEQS and suggest changes where necessary, based on conditions in Pakistan. The committee realized that some of the parameters were more stringent than other countries of the region, so the task of the rationalization of NEQS was referred to an Expert Advisory committee to review and suggest changes, if and where required. Ten parameters were identified by committee, eight (8) liquid effluent viz. BOD, COD, TDS, Chloride, Sulphide, Chromium, Ammonia, and Temperature, and two (2) gaseous emissions viz. SO_2 (Sulphur di oxide) and Oxides of Nitrogen for review. Finally after the Environmental Standards Committee endorsed the proposed revised NEQS, the Pakistan Environmental Protection Council was recommended to approve the revised draft NEQS.

In December 28, 1999, PEPC approved the revised NEQS. The revised version of NEQS is presented in Table 1.6. It is worth mentioning that dilution of liquid effluents to bring them to the National Environmental Quality Standards (NEQS) limiting values is not permissible through fresh water mixing with the industrial effluent before discharging it in to drains or water bodies.

The direct discharge of effluents from tanneries into water bodies has become a growing environmental problem in these days. Most of these waste waters are extremely complex mixtures containing inorganic and organic compounds that make the tanning industry potentially a pollution-intensive sector (Akan et al., 2007). Statutory limits have since been set for chrome discharge and disposal, and relevant guidelines have been drawn up throughout the world. Due to high correlation between chrome tanning and its environmental impact, checking of the efficiency of processing operations and treatment plant takes on prime importance.

Table 1.6: National Environmental Quality Standards (of Pakistan) for municipal and industrial liquid effluents (mg/L)

S. No.	Parameter	Existing Standards	Revised standards		Into Sea
			Into inland waters	Into sewage treatment	
1	Temperature or temperature increase*	40°C	=<3°C	=<3°C	=<3°C
2	pH value	6-10	6-9	6-9	6-9
3	BioChemical Oxygen Demand (BOD)5 at 20°C	80	80	250	80**
4	Chemical Oxygen Demand (COD)	150	150	400	400
5	Total Suspended Solids (TSS)	150	200	400	200
6	Total Dissolved Solids (TDS)	3500	3500	3500	3500
7	Grease and Oil	10	10	10	10
8	Phenolic Compounds (as phenol)	0.1	0.1	0.3	0.3
9	Chloride (as CI')	1000	1000	1000	SC***
10	Fluoride (as F')	20	10	10	10
11	Cyanide (as CN') Total	2	1.0	1.0	1.0
12	An-ionic Detergents (as MBAs)	20	20	20	20
13	Sulphate (SO")	600	600	1000	SC***
14	Sulphide (S')	1	1.0	1.0	1.0
15	Ammonia (NH3)	40	40	40	40
16	Pesticides	0.15	0.15	0.15	0.15
17	Cadmium	0.1	0.1	0.1	0.1
18	Chromium (Trivalent and Hexavalent)	1.0	1.0	1.0	1.0
19	Copper	1.0	1.0	1.0	1.0
20	Lead	0.5	0.5	0.5	0.5
21	Mercury	0.01	0.01	0.01	0.01
22	Selenium	0.5	0.5	0.5	0.5
23	Nickel	1.0	1.0	1.0	1.0
24	Silver	1.0	1.0	1.0	1.0
25	Total Toxic Metals	2.0	2.0	2.0	2.0
26	Zinc	5.0	5.0	5.0	5.0
27	Arsenic	1.0	1.0	1.0	1.0
28	Barium	1.5	1.5	1.5	1.5
29	Iron	2.0	8.0	8.0	8.0
30	Manganese	1.5	1.5	1.5	1.5
31	Boron	6.0	6.0	6.0	6.0
32	Chlorine	1.0	1.0	1.0	1.0

The effluent should not result in temperature increase of more than 3°C at the edge of the zone where initial mixing and dilution takes place in the receiving body. In case zone is not defined use 100 meters from the discharge: Value for industry is 200 mg/L*

**** Discharge concentration at or below sea concentration (SC)*

1.9 Summary of Chapter 1

This chapter constitutes introduction to both sides of the picture of industrial revolution, the positive and negative impacts on the human lives, followed by a brief introduction to environmental hazards caused by the improperly managed industrialization in Pakistan, where this research was conducted.

This chapter also includes basic sources of groundwater contamination and how it is carried away by groundwater flow and basic equations and law for groundwater flow.

With the basic purpose of bringing the groundwater contamination due to tannery industries in limelight, tannery industry in Pakistan and the hazardous effects of major pollutants released from these industries are described briefly. The Environmental standards for industrial effluents and other environmental quality standards for groundwater and soil are mentioned.

Finally the motivation for the research, the problem statement, and how the adverse environmental and health conditions are prevailing in the research area due to tannery waste are described in the end of the chapter. The problem statement is followed by specific objectives based on the existing situation are put forward to help in developing a strategy to cope this environmental hazard, in order to conduct the research work.

CHAPTER 2

TANNERY INDUSTRIES IN PAKISTAN AND THE STUDY AREA

2.1 Tannery Industry in Pakistan

Being an agricultural economy, Pakistan has a natural advantage in the area of immense livestock population, which is the major input (hides & skins) of the industry. Estimated livestock population comprises of cattle, 22 million; buffalo 23 million; sheep 24 million and goat 49 million. At present, the country produces 7.8 million hides & 38 million skins per annum. Although the local production of hides & skins used in the tanning industry has been increasing, the supply has been insufficient to keep up with growing demand. Therefore, industry has to import raw hides & skins from international market to keep its tanning industry remaining. Pakistan imported 13.6 million worth of raw hides and skins in the year 2002-2001. Hides and skins are mainly imported from Iran, Afghanistan, and Africa. (Zaman, 2001)

In the past few decades, developing countries have witnessed a sharp increase in leather production because such activities have declined in the developed world due to more stringent environmental pollution control requirements and high labor costs. Accordingly Pakistan witnessed a rise in its leather export from US $ 672 million in 2002 to 1.13 billion in 2007, which indicates an increase of 68 % in a short span of 5 years (Haydar and Aziz, 2009). The leather industry contributes 17.61% of the country’s total exports. Most of the Industry has been located in clusters or industrial zones in the cities of Karachi, Lahore, Kasur, Multan, Faisalabad, Peshawar, Gujranwala and Sialkot. Leather in Pakistan is primarily sourced from 725 small and medium size tanneries located in Karachi, Lahore, Multan, Kasur, Faisalabad, Peshawar, Gujranwala and Sialkot. (SMEDA, 2003)

2.2 Leather Manufacturing Process at Kasur Tanneries

The leather and leather product sector represents one of the most labor intensive industrial commodities. It is estimated that this sector directly employs more than 200,000 workers and it is believed that earnings of over one million people are dependent on leather sector. Out of total more than 600 registered tannery units in Pakistan, Kasur Tannery area has more than 50 % of this share, being the biggest tannery industry area. Vegetable tanning method being the old method of tanning has been replaced by chrome tanning in Kasur Tannery area as finer quality results could be achieved by using chrome tanning. Therefore presently chrome tanning method is the most widely used process in Pakistan’s leather sector.

Vegetable tanning method and a combination of both chrome and vegetable tanning are also used in some tanneries. In conventional chrome tanning processes, chromium salts are used in an amount of 1.5-2.5% by weight of Cr (III) oxide, based on pelt weight, to obtain leather which resists the boiling test. A considerable portion of the offered Chromium is neither bound nor incorporated in the hide tissue and as a result passes into the wastewater (Saadia et al., 2009). The production process consists of a number of steps involving the application of large quantities of water and chemicals to the raw skins. About 130 different types of chemicals are used in leather manufacturing process ranging from inexpensive common salt (Sodium chloride) to expensive Chromium sulphate. Leather manufacturing process consists of following major steps (Khan, 1996)

- Pre-Process
- Pre-tanning Process
- Tanning Process
- Wet Finshing Process
- Dry Machining
- Finishing

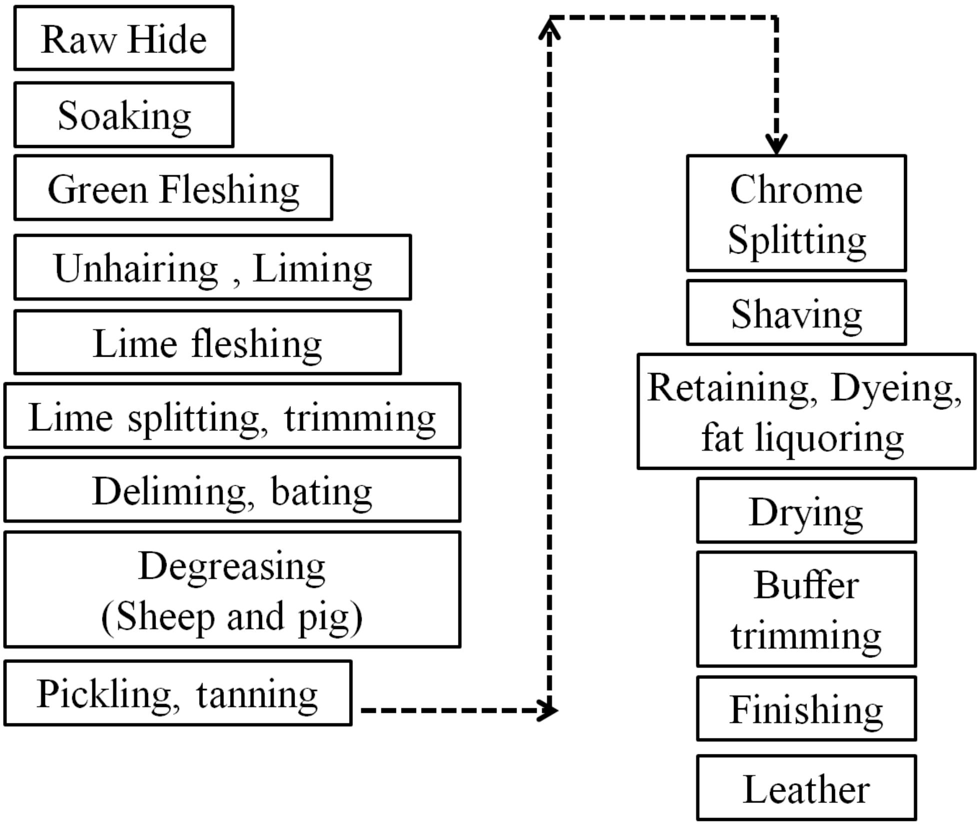


Fig. 2.1: Flow chart for leather processing (Dasanayaka and Sardana, 2009)

Table 2.1: Composition of Solid Waste Generated from a Typical Tannery (ETPI, 1999)

Type of Solid Waste	**Rate of Generation**	**Characteristics of Solid Waste**	**Remarks**
Dusted Salt	0.1 kg/skin	Contains around 120 gm/kg of moisture, 120 gm/kg of salt	Contaminated with blood, hair, dirt and bacteria. Partly reused in curing and the rest is indiscriminately dumped in undeveloped lands near the tanneries.
Raw Trimmings	0.024 kg/skin	Proteins	The skins are trimmed in order to give smooth shape. The trimmings are usually sold to soap and poultry feed productions
Fleshing	0.25 kg/ skin	Contains around 240 gm/kg of proteins, 30 gm/kg of fats, 15 gm/kg of chromium oxide	After chrome tanning, skins or split hides are shaved to proper thickness. This operation produces solid waste containing chrome. Secondary users including poultry feed manufacturers usually collect these shavings from the tanners.
Dry Trimmings/ Dry shaving/ Buffing Dust	0.06 kg/ skin	Contains around 300 gm /kg of proteins, 130 gm/kg of fats, 30 gm /kg of chromium oxide	Secondary users, including poultry feeds makers, collect cuttings and dry trimmings and buffing dust of the leather from the tanneries.
Assorted Refuse	No consistent quantity	Primarily cartons, bags, drums, etc.	This is normally sold separately (in bulk)
Wet Trimming/ Wet Shaving	0.14 kg/skin	Contains around 240 gm/kg of proteins, 30 gm/kg of fats, 15 gm//kg of chromium oxide	After chrome tanning, skins or split hides are shaved to proper thickness. This operation produces solid waste containing chrome. Secondary users including poultry feed manufacturers usually collect these shaving from the tanners.

In pre-processing, skin/hides are received and salt is applied on the flesh side of the skins/hides, skin trimming is done to remove unwanted parts. After pre-processing, the pre-tanning process starts with the soaking process in which skins are made flaccid by soaking them in water. After soaking, the hair is removed. Lime is used for the dehairing process. Unwanted flesh is removed with the help of fleshing machines after the liming process. To prepare limed skin for tanning, the skins are de-limed using Ammonium Sulphate and then are washed. Bating is done for further purification of the hide. As a next step, degreasing is carried out with the help of detergents.

Tanning process starts with pickling which is the treatment of skin with acids and salts to bring it to the desired level of pH. Tanning may be defined as the treatment of skin for preservation. Chrome tanning used Chromium Sulphate as a tanning agent. Tanning process stabilizes the collagen network of skin. After tanning, skins are called wet blue and are stored for sometimes and thereafter they are sorted out according to quality. If hides of cows or buffaloes are being used for leather manufacturing, these are sliced to get desired thickness. This process is not carried out on the skins of goats, camel or sheep. Thereafter, the hair side of the wet blue is shaved to give the desired thickness. In order to give desired softness, color, strength, and quality to the leather, wet blue skins are processed further through a wet finishing process. A fat liquoring process is carried out to impart desired softness and dyeing is done to give it a colour. After wet process, different drying processes are carried out to dry the processed leather. These processes consist of setting, vacuum drying, stacking/toggling, buffing/shaving, nailing/trimming, processing, and segregation of the leather. Finally, finishing processes are carried out to impart durability and beauty to the leather (Dasanayaka and Sardana, 2009).

2.3 Description of Kasur Study Area

2.3.1 Geographical and Topographical Details of Kasur

Kasur is situated in Punjab province, adjacent to the eastern border of Pakistan with India, which is only 12 kilometers from the city. It is only at distance of 55 kilometers towards south east of the second largest city of the country, Lahore, which is educational and cultural center of country. The geographical coordinates of Kasur are 31°6’56” North, 74°26’48” East.

From Fig. 2.2, looking at the magnified image of Punjab province, it can be observed that Kasur lies in alluvial plain of two main rivers the Ravi and Sutlej. Both these rivers originate from the Himalayas in India and then entering Pakistan territory and make their path to Arabian Sea.

2.3.2 Demographics and Administrative Structure of Kasur

District Kasur was declared as independent district in 1976 after being detached from District Lahore. Now district Kasur has further 3 tehsils included in administrative boundary of it. These three tehsils are Kasur, Chunian, Pattoki, spreaded over total area of 3,995 square kilometer. According to Punjab Development Statistics, total population in whole Kasur district is 2,918 thousand, out of which 1,528 thousand are males and 1,390 thousand are females. Density of population is 706 per square kilometer. Further breakdown of population for urban and rural localities on tehsil level is mentioned in Table 2.2.

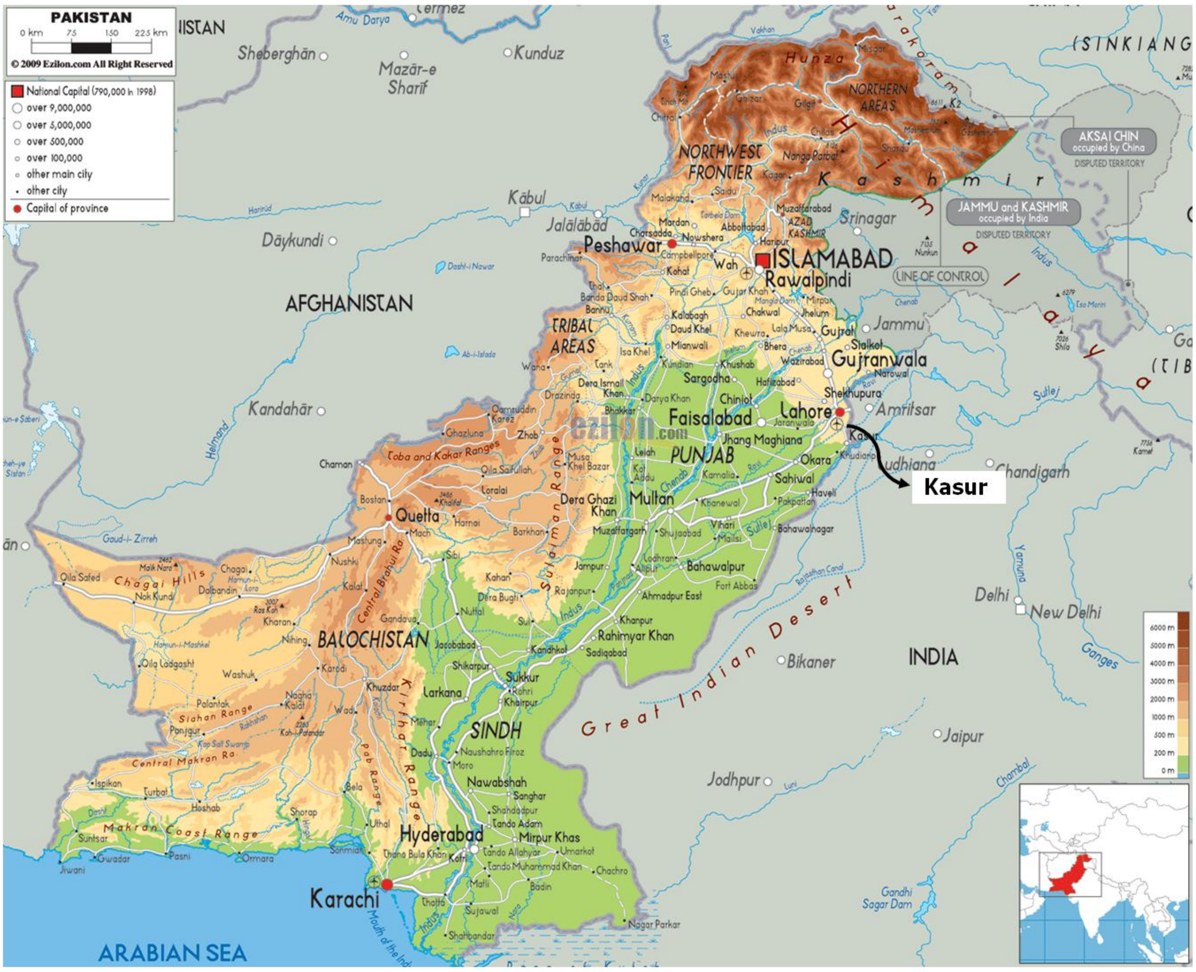


Fig.2.2: Geographical map of Pakistan (Edited) (www.ezilon.com)

Table 2.2: Town Wise Distribution of Urban and Rural Population (Directorate of Industries Punjab Lahore, 2012)

Name of Town	POPULATION THOUSAND PERSONS		
	URBAN	RURAL	TOTAL
KASUR	450	978	1428
CHUNIAN	75	632	707
PATTOKI	141	642	783
TOTAL	666	2252	2918

2.3.3 Climate of Kasur

Kasur area falls under semi arid sub tropical climate zone with intense summer heat and cold winters. In April the temperature rises fast and May and June are the hottest months with temperature rising up to 45°C. Mean annual maximum temperature recorded from May to June is 41°C and mean annual minimum temperature is 4°C from December to January (Abida et al., 2007). The monsoon season starts at the end of June and remains until the middle of September. January is the coldest month with a mean minimum temperature of about 15°C. The rainfall in the area is subject to large variation from year to year. The average annual rainfall is about 500 millimeters, while yearly evaporation is 1500 mm having a deficit of 1000 mm. In winter season the wind direction is north and northwest and in summer, southeast. Westerly storms or cyclones usually disturb the wind direction (PDRC, 2000).

2.3.4 Geology of Kasur

The study area lies in alluvial plain which is largely flat and featureless and it is formed of the Pleistocene and the sub-recent alluvium deposited by the rivers of the Indus system (Fig. 2.2 & 2.3). It is product of alluvial formation by the Ravi and Sutlej rivers consisting mainly of fine-medium sand, silt and clay. Coarser sands and gravels occur in parts (WAPDA/EUAD, 1989). It constitutes of unconsolidated surficial deposits of silt, sand and gravels (Fig. 2.3). In many respects soil shows a high degree of similarity throughout the area. The soils are reddish brown to grayish brown, mostly moderately coarse and medium textured soils, containing high percentage of fine to very fine sand and silt. The clay part consists of non-swelling materials, which may account for the generally favourable permeability characteristics of the soil. Most soils in the Punjab are moderately to highly permeable; only some have low permeability. The lime content is also observed to be high in subsurface soil (Abida, 2007).

The lithology in the north east and central parts of Bari Doab (Plain between the River Ravi and Sutlej) has been described as consisting of fine textured silt and silty clay, mixed with “kankar”(fine gravels), silt stone and mudstone. Sand is found commonly in thin layer of limited extent. Studies of landscape and soils revealed that superficial sediments in different parts of the plain represent various depositional environments of different ages from Pleistocene to Late Holocene (Soil Survey of Pakistan, 2004).

According to WAPDA (1964), the area is underlain to depths of 300 meters or more by unconsolidated alluvium, which is saturated with groundwater to within a few meters of the surface. The alluvial deposits can be considered to form one single aquifer in which groundwater is generally under water conditions (unconfined). Because of the high evaporation rate, the slow circulation and poor underground drainage, groundwater in the area is considerably mineralized. This mineralized water has been diluted to different degrees and depths by the rivers and canals wherever free circulation of water from these sources is possible. The thickest body of good quality groundwater is found in a strip adjacent to the rivers. In the center of the alluvial plain, in between the two rivers, highly mineralized water is occurs even at shallow depths (Soil Survey of Pakistan, 2004).

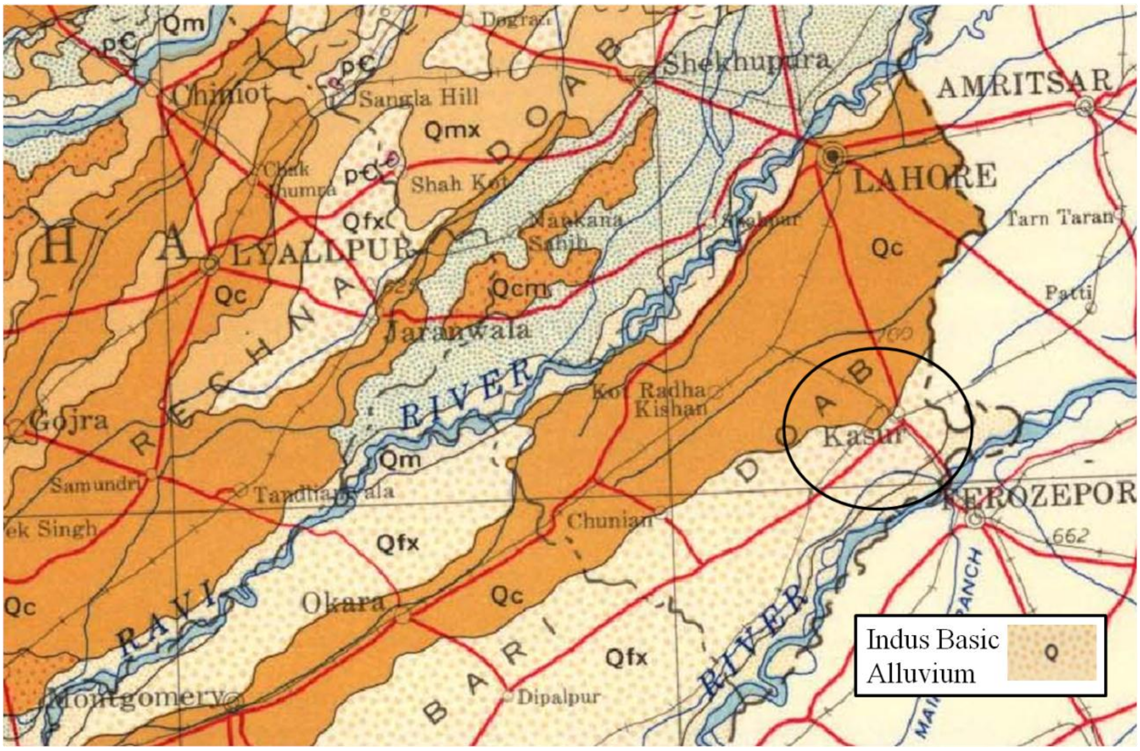


Fig. 2.3: Geological formation map of study area - scale 1:2000 000, prepared by Geological Survey of Pakistan – Edited (GSP, 2012)

2.3.5 Tanning Industries in Kasur

Tanning has a long standing tradition in Kasur. Initially rather primitive tanneries existed in the Din Garrh area on the eastern bank of Drain Rohi, a former river meandering through the old town. All the operations were carried out manually, and tree barks were used for tanning. Subsequently, tanneries started spreading over a wider area towards south of the river and Kot Molvi Abdul Qadir, Niaz Nagar and Younus Nagar agglomerations were gradually developed. Today Kasur is the biggest tanning concentration in the country. They now number over 237 individual factories varying in size from large to small (PDRC, 2000). These industries are operating with estimated average daily input of over 180 tons of wet salted weight, comprising some 8,000 hides (cattle, buffaloes), and between 12,000 and 15,000 skins (sheep and goats) per day. According to United Nations Industrial Organization (UNIDO), at present tanneries in Kasur discharge around 13,000 m^3/day of heavily polluted wastewater. Every year, an estimated amount of 4,000 tons of BOD_5, 11,000 tons of COD, 10,000 tons of suspended solids, 160 tons of chromium and 400 tons of sulfides are discharged to the environment (Rehman, 2004).

History of tanning processing in Kasur dates back to about 100 years. Earlier these tanneries were combined with residential area and were present in the same compound. All the operations were carried out manually, and tree barks were used for tanning. This type of tanning is called vegetable tanning. But gradually for the last 40 years, especially since the process of tanning became more technical process and also when the use of chemicals increased, the tanneries were separated from household units. Most of the tanning units were initially was concentrated at Din Garrh area, on the south bank of the Rohi Drain. Subsequently, tanneries started spreading over a wider area towards south of the drain and Kot Molvi Abdul Qadir, Niaz Nagar and Younus Nagar agglomerations were gradually developed. Today Kasur is the biggest tanning concentration in the country.

Here, in the outer region of the city wide space required for different tanning processes is spaciously available. In the beginning there was no such issue of tannery waste due to its lesser amount of discharge and availability of vast open fields. Looking at the map of Kasur city (Fig. 2.4), it can be observed that there is a drain, named Drain Rohi passing through the center of city. It is basically an abolished river, existing decades back, lately converting to a seasonal drain to carry surplus water flow in the rainy season and monsoon. The recently grown tannery area is also mentioned in Fig. 2.4. It includes all those areas where now tanneries are spread all over. This Tannery area is in southern side of the main and old city wall. This is the new direction of the expansion of the city.

Initially when there was not drainage of the industrial waste. The tannery effluent was directly thrown into the open fields. In Fig. 2.4 the agricultural lands can be viewed which were once adversely affected by the tannery waste disposal. Even now after the construction of drain and the treatment plant, the tannery waste over flows into the fields and destroys the agricultural crops (Fig. 2.4). Later on in year 2002, after the constrution of Wastewater treatment Plant and the Drains, the open fields were dried by continuous pumping.

2.3.6 Significant Components in the Research Area

The main areas which were focused particularly during the research for site investigations, sampling and experimentations are shown in Fig. 2.5 and are described as follows.

- Tannery area

- Wastewater treatment plant
- Drains in the area
- Residential localities and villages in the area

These are the components which were thoroughly surveyed and investigated followed by sampling, monitoring of wastewater, groundwater and soil. These areas were important in order to conduct thorough site characterization, so as understand the present contaminant condition in the tannery area and to understand the scenario, how the surrounding areas are being influenced by the tannery effluent seepage into soil and surface flow.

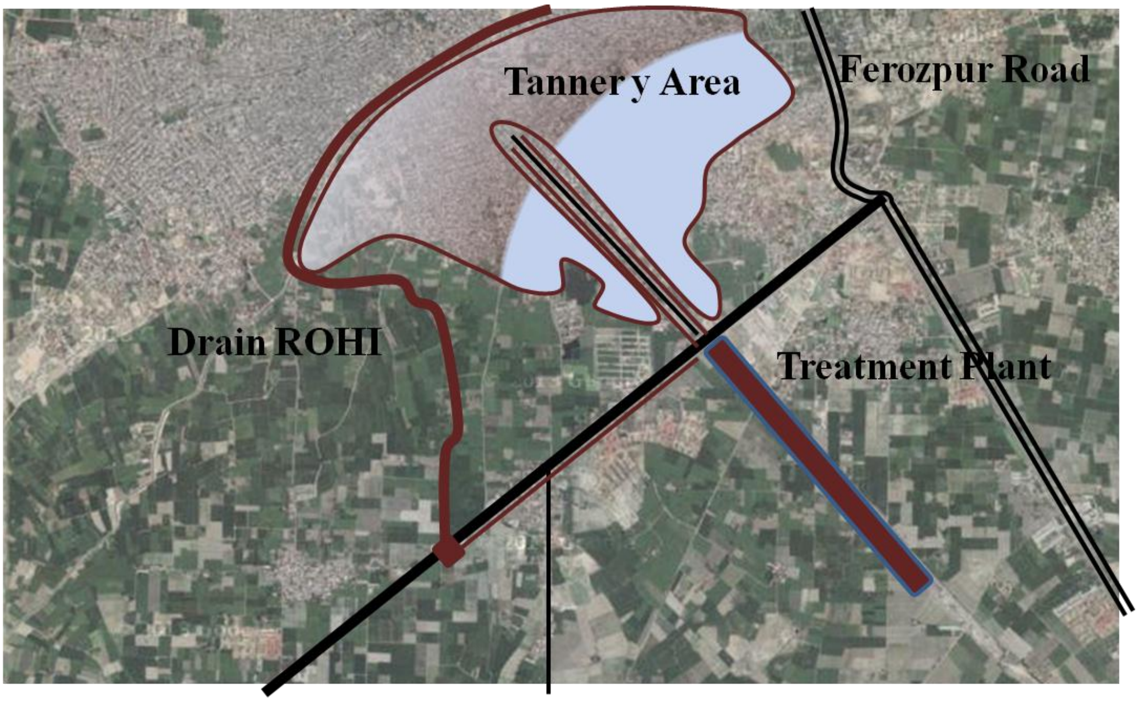


Fig. 2.4: Satellite image showing tannery area, treatment plant and adjacent agricultural lands – Edited (Google earth)

2.3.6.1 Tannery Area

Tannery area, which developed on the south-eastern side of the main old city wall, include Din Garrh, Kot Molvi Abdul Qadir, Niaz Nagar, Younas Nagar. It is encompassed by two highways, one is Ferozpur Road, linking Lahore (Pakistan) and Ferozpur Road (India) and second one is Debalpur Road which links Kasur city with other Tehsils of Kasur District. From Fig. 6 areas included in Tannery area can be observed. Niaz Nagar is the densest area regarding tanneries and occupies the maximum share of total tanneries in the whole area, reaching the figure of 100 tanneries. The second densest area is Din Garrh having around 50 tanneries. In order to carry the tannery effluent from tannery area to the Common effluent pretreatment plant (CEPTP), two pumping stations were installed in tannery area and two drains were constructed to carry the pumped tannery effluent (Rehman, 2004). There are still open fields which remain pounded due to overflow of tannery effluent from these drains. However the construction of these drains and treatment plant has helped in elimination of stagnant ponds formed due to direct disposal of tannery effluent. Now this space is used in different tannery activities, mainly in drying raw skin and hides. Besides new localities are also being formed in the tannery area in order to control the usage of open fields.

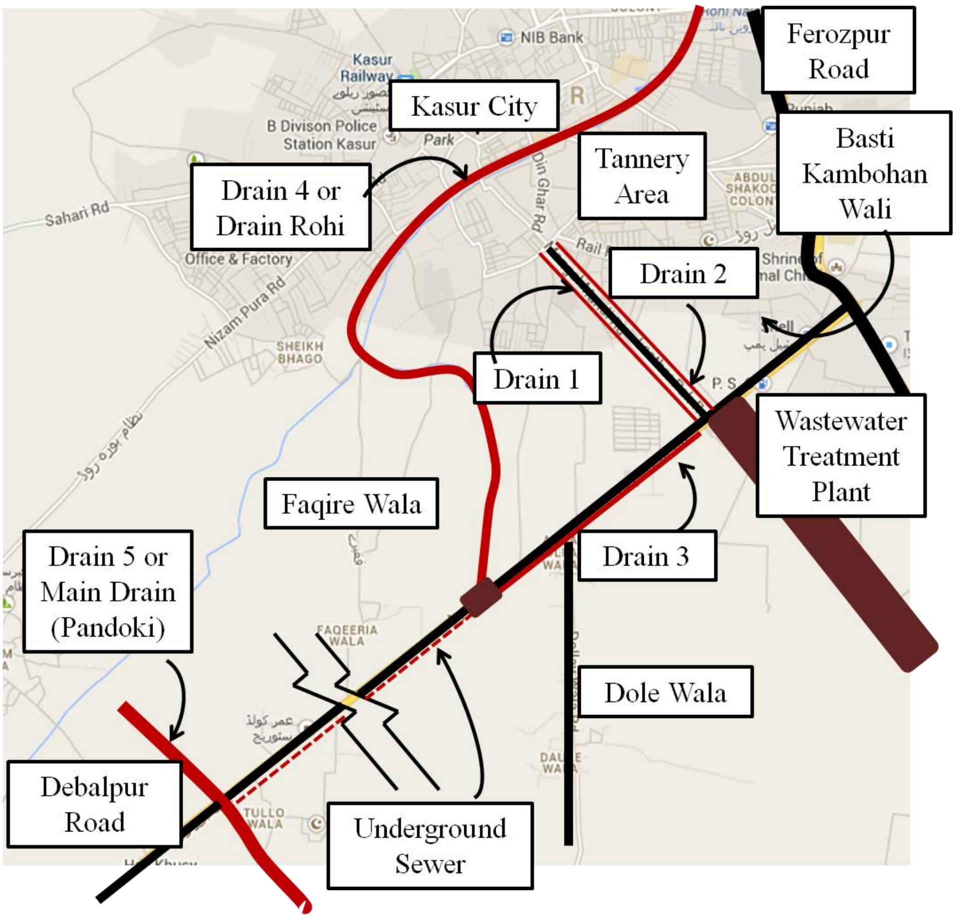


Fig. 2.5: Major components of Kasur study area (google earth – Edited)

2.3.6.2 Wastewater Treatment Plant

Establishment of Wastewater Treatment Plant in Kasur is one of the three major components of Kasur Tanneries Pollution Control Project (KTPCP).This project was initiated by government of Pakistan to tackle with the environmental issues in Kasur, in collaboration with UNDP and UNIDO for technical and financial assistance. UNDP was partial donor of the project while UNIDO was the consultant of UNDP for design and implementation of the project. An autonomous agency named Kasur Tanneries Waste Management Agency (KTWMA) was established to execute the project. Tanners associations are project partners according to the rule of “polluters pay principle”. Tanners Associations share 5 % cost of construction of the project and 50 % cost of operation maintenance of the project. The work on the project started in January 1996 and was completed in March 2002.

According to Kasur Tannery Waste Management Association (KTWMA), Common Effluent Pre-Treatment Plant (CEPTP) is comprised of coarse and fine screens, equalization tanks, sedimentation tanks, facultative ponds, and permanent sludge lagoons. After screening the effluent enters equalization tank where it is homogenized with surface aerators. The homogenized effluent is uniformly pumped into sedimentation tanks equipped with sludge and scum scrappers. The settled sludge is discharged in to the sludge tanks and from there pumped into permanent sludge lagoons (Rehman, 2004).

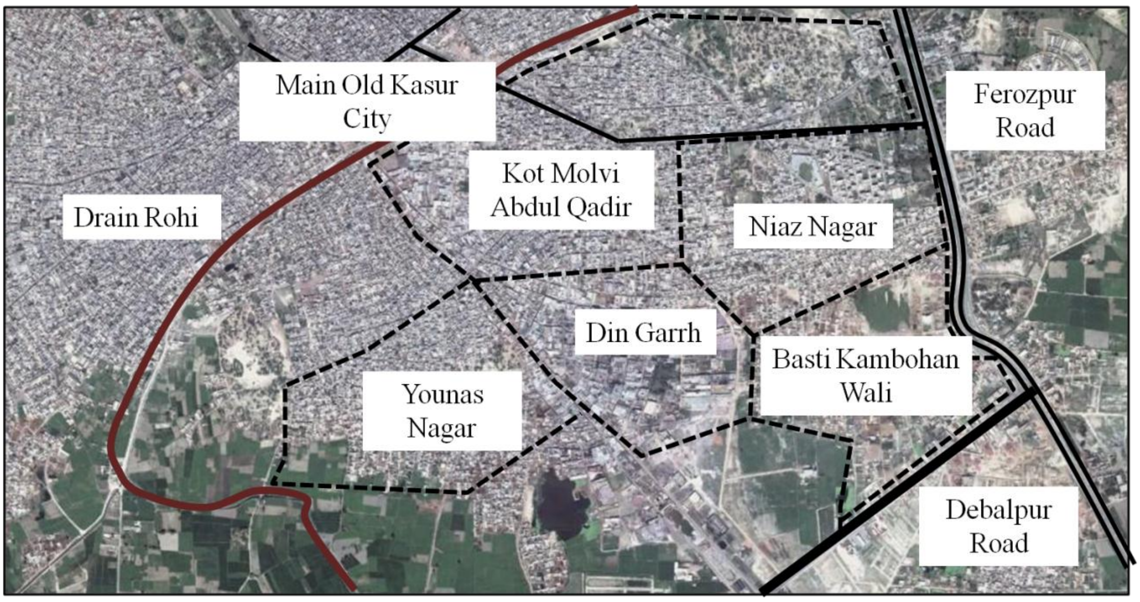


Fig. 2.6: Tannery area details and area wise distribution (google earth - Edited)

The clarified effluent overflows through the weirs into facultative lagoons. After zigzagging through lagoons, the purified effluent is discharged into Drain 5, Main Drain (Pandoki) via outfall channel (Drain 3). From Drain 5, main drain, it is carried to the River Sutlej. The two pumping stations installed in Tannery area pump out the wastewater into two channels, named Drain 1 and Drain 2, which carry the untreated effluent to the Common Effluent Pre treatment Plant (CEPTP). With the construction of Drain 1 and Drain 2, 400 acres of land has been reclaimed from tannery effluent. As part of the project, a chrome recovery plant was also constructed which started operation from September 2000 and has operational capacity of 20 m^3/day. This plant caters for the need of 35-40 tanneries.

The overall impact of treatment on the quality of effluents as described by KTWMA is mentioned in Table 2.2. The difference between the influent and effluent quality from CEPTP is also quite obvious from direct observation in Fig.2.7.

Table 2.3: Impact of treatment on Effluent Quality at CEPTP in year 2003

Parameters	**Effluent Quality Before Treatment (mg/L)**	**Maximum Reduction**	**Effluent Quality achieved after Treatment (mg/L)**	**NEQS mg/L**
Suspended Solids (mg/L)	2700	98%	58	1,150
Total Dissolved Solid (mg/L)	7500	30%	5250	3500
Sulfate$(SO^4)^{-2}$	2,000	35%	1,300	600
BOD_5	1,600	75%	400	80
Sulfide S^{-2}	120	75%	30	1.0
Chromium	90	98%	1.8	1.0

Source: (Rehman, 2004)

2.3.6.3 Drains in Kasur Study Area

There are five drains included in the research area. Each drain has different characteristics and wastewater carrying nature. For simplification, all the drains are numbered and sometimes referred with their local name as well. All the drains are shown in Fig 2.8, while their location is mentioned in the sketched diagram in Fig. 2.5 showing all the major components involved in the research. Drain 1 and Drain 2 (Fig. 2.5) carry untreated tannery effluent from the main tannery area to wastewater treatment plant. Depending upon the tannery effluent discharge, the flow in these drains is variable. These are recently constructed drains, after the establishment of wastewater treatment plant in year 2000, so as to carry untreated effluent to the treatment plant and also to pump out the stagnant ponds which before year 2000 were immensely visible all around the tanneries. The concentration of effluents is very high in these two drains. Drain 3 (Fig. 2.5) is basically constructed to carry the treated effluent from the treatment plant for final disposal into the main drain. However its capacity and wastewater characteristics are questionable. Drain 4 or Drain Rohi (Fig 2.5) is basically a storm water drain presently carrying untreated domestic and municipal waste from the city along with tannery waste as well of a few industries.

There is junction of Drain 3 and Drain 4 (Fig. 2.5) at a distance of about 2.5

kilometers from the treatment plant. From where onwards the wastewater, whether it is treated or untreated is carried to Main drain, Drain 5 for final disposal through underground sewer pipe (Fig. 2.5). All these drains are a part of research and were used for periodic sampling and monitoring of wastewater quality.

Before the construction of wastewater treatment plant there was only one drain and that was Drain 4 (Drain Rohi). All the tannery effluent was directly disposed into the open fields adjacent to the tanneries. Whole the periphery was soaked with tannery effluent.

It was not until year 2000 that any practical efforts were made out to relieve the inhabitants of the area from this miserable environmental and health conditions. According to reports of International Union of Conservation of Nature (IUCN) in 1993, at least 50,000 workers and inhabitants living in and around the polluted areas are at direct risk of cancer and other chronic diseases associated with pollution caused by tannery industry in Kasur. In the report, IUCN alarmed that the citizens exposed to this toxic environment will result in increased number of incidents (or an epidemic) of cancer, renal pathology, or other systematic diseases (Rehman, 2004).

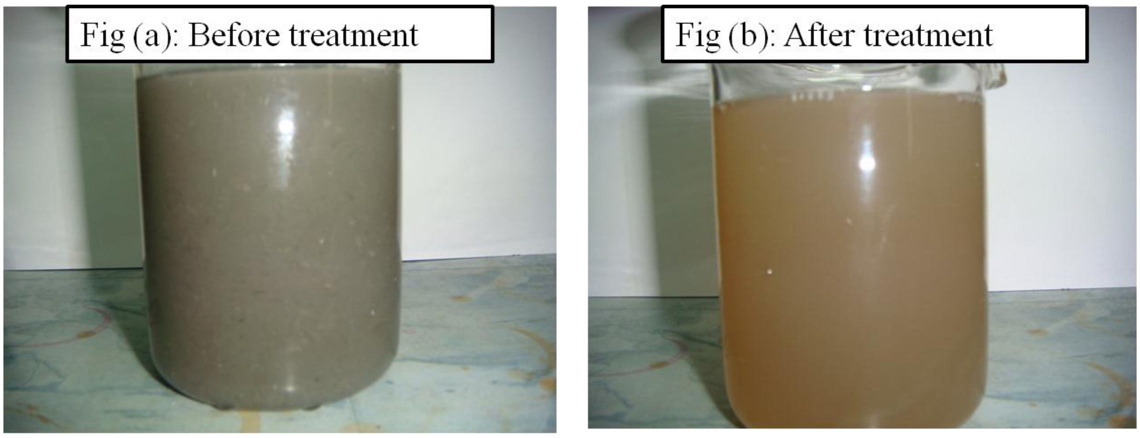


Fig. 2.7: Wastewater quality comparison before and after treatment at CEPTP (picture taken in 2008)

2.3.6.4 Residential localities and Villages in the Study Area

The Study area in Kasur mainly focused on the peripheries and surroundings of the main Kasur city so as to achieve the objectives set for the research. Following are the main localities and villages in the Kasur study area.

Basti Kambohan Wali: This locality is the nearest residential area from the tanneries and the wastewater treatment plant. This area has very recently been developed as a consequence of the government scheme to utilize the vacant area adjacent to the tanneries, where once all the tannery effluent had been pounded. Still stagnant fields can be observed in this area and there were not any necessary measures taken before accommodating new residents in this place (Fig. 2.9).

Fig. 2.8: Five drains and underground sewer in Kasur study area (picture taken in 2008)

Dole wala: This place is at a distance of 2.5 kilometers from the tanneries and the main significance of this locality is that it is and old locality which has observed all the draw backs of pounded tannery wastewater in their agricultural fields. Even now due to over spillage of Drain 3 the agricultural land in this locality is completely soaked with tannery effluent. Another significance of this locality is its position with reference to drains and treatment plant. This residential area is circled by treatment plant on one side and drains on the other. This area directly comes under effect whenever there is overflow in the drains or in treatment plant ponds. It is due to the reason that it lies on the downstream side of the drains flow (Fig. 2.10)

Faqire wala: This is the third main locality included in the study area due to its significant location as it lies on the left bank of Drain 4 (Drain Rohi), as shown in Fig. 4, at a distance of just 200 meters. It has always been the primarily affected locations, since the problem of tannery waste has become severe. Earlier, when there was no treatment plant and no drains were constructed, the open fields adjacent to this locality were all pounded due to tannery effluent. Nowadays as the other drains have been constructed and the load in Drain 4 has reduced and now it is only used for domestic and some of the tanneries effluent existing on the bank of it, there is not much exposure to tannery effluent left, except the overflow of Drain 4 during monsoon season or heavy rains. But due to existence on downstream side there is a great possibility of leakage of tannery effluent from Drain 4 into the groundwater and presence of high concentrations of chemicals in the subsurface and particularly in the groundwater.

Fig. 2.9: Stagnant ponds existing in Basti Kambohan Wali (picture taken in 2010)

Fig. 2.10: Dolewala Village: open fields pounded due to overflow from Drain 3 and treatment plant ponds at 1 km distance from this location (Picture taken in 2011)

2.4 Summary of Chapter 2

This chapter mainly has two components. The first one is related to major tanning processes taking place in an average tanning unit, typically with reference to Kasur tanneries. It describes the amount and sources of raw material used for leather processing and tanning.

Besides, the chemicals and their average quantities required for the process of tanning is also mentioned. Being the backbone of Pakistan trade, tanning industries are supposed to be given due focus on all the issues related to industry on priority basis so as, not only to flourish the trade but also provide healthier environment for the inhabitants and workers in the tannery areas.

The second component of Chapter 2 constitutes the description of detailed information about the Kasur study area. It starts with basic information about Kasur district, its location, geographical significance, followed by the description about climate and geological details. Information about the demographics and administrative structure of Kasur district has also briefly included in this chapter.

Basically the land surface is more or less flat in the whole area, and being alluvial soil carried by the river water, there is high proportion of sand in the soil texture, indicating high probability and rate of percolation. The natural topography of the area depicts an assumed natural groundwater flow from north towards south (ocean), parallel to the flow of the rivers in Indus plain. However the rainfall, only 500 mm average on annual basis, which is not that much high, indicates periodic and unpredictable water seepage into the soil. A strong bonding of coarse materials existing in subsurface indicates increased possibility of retention of adsorbed ions in soil as well. Mainly it is found that the whole Kasur area and its surroundings is a fertile land being exploited by the tannery wastewater, especially the presence of harmful and carcinogenic chemicals in the effluent is a matter of great concern. However the land reclamation and proper tannery industrial management have already been initiated by the government, all what is required is to further enhance the efficiency of all the activities to come out with more fruitful results, rather than making the situation adverse.

The main objective of this chapter is to build foundation for upcoming chapters in which focus is intended to lay on research activity taken place in this research area.

CHAPTER 3

LITERATURE REVIEW

3.1 Introduction

This chapter includes the literature reviewed in order to facilitate and support conduction of current research work. Literature related to research work comprise of a wide range of subjects being incorporated and chained in such a way to help in coming out with a solid and productive research outcome.

3.2 Worldwide Tannery Waste Management Issues and Subsequent Subsurface Contamination

Reviewing the literature about tannery waste contaminated sites globally, Dhaka, Bangladesh is facing serious threats regarding tannery waste. Industrial waste generated from tanneries located in the southwestern part of Dhaka, pose serious threats to the environment. Surface accumulation of trivalent chromium, as high as 28,000 mg/kg, has been encountered at 1 km distance from waste lagoon. In contrast, maximum concentration of hexavalent chromium is about 1 mg/kg, and is very irregularly distributed all over the area. Although soil pH is alkaline in general, a sharp drop of pH down to 3.4 has been observed at some locations. Furthermore high chloride (Cl) and lead (Pb) concentrations pose risk for city's groundwater quality. The waste, both organic and inorganic, and wastewater generated from the industrial activities of Hazaribagh tannery area are discharged into the low lying areas in the surroundings. There is Chromium discharge in to the river water, approximately 1.25 tons per day, whereas the chromium discharge from tannery effluent is approximately 1.6 tons / day, considering a peak discharge of 21,000 m^3/day and 80 mg/L of Cr, in other words, an estimated 0.35 tons of chromium are settled in the lagoon and are suspected to be the source of chromium contamination. In three deep tube wells water tested for chromium showed concentration variation from 0.002 to 0.003 mg/L (Shams et al., 2009).

Similarly, a site investigation at leather tannery district in Italy reveals a very scattered distribution of Chromium in soil, with a mean Cr concentration in soils, 210 mg/kg (ranging from 50 to 10,000). Most of the investigated site present surface Cr concentrations higher than subsurface, suggesting local sources of Cr to be responsible for soil contamination (Bini et al., 2008).

A case study regarding tanneries conducted in Albania, in southeastern Europe, by Floqi et al. (2007) evident hundreds of thousands ton wastewater effluent into water basins discharged from all processing leather factories and tanneries. The physical and chemical indicators of tanneries effluent depend from the capacity of production. BOD5 varies at limits of 965 – 1631 mg O_2/L, COD from 6168-11032 mg O_2/L, Total suspended solids (TSS) at limits of 1264-9984 mg O_2/L, total sulphides 21-380 mg O_2/L, total chromium 4.75-49.2 mg/L, Ammonia ions 10-102 mg O_2/L. Municipalities dump sites and riversides are used for solid waste disposal.

Groundwater pollution by chromium has been reported in the Leon Guanajuato valley in the center of Mexico (Armienta et al., 1996). Tannery wastes, dust from a sanitary landfill of chromate compounds and transport of chromium products are the sources of chromium at other sites. Chromium is fixed preferentially in hydrous Fe and Mn oxides in the more polluted soils. Less polluted soils have a high proportion of chromium associated with the sulphide and organic fraction. Cr (III) is retained in the physical characteristics of the soil, relative abundance of the various soil components and characteristics of the contaminant source, give rise to differences in chromium soil concentrations with depth. The weathering of ultramafic rocks in the northwest of valley has produced hexavalent chromium concentrations in the groundwater between 0.004 mg/L and 0.015 mg/L. Buenavista, the most polluted area with water Cr (VI) concentrations upto 50 mg/L, is located southwest (13 km) of Leon city. The source of chromium in this area, approximately 5 km square, is leakage from an improper, disposal of solid waste from the chromate factory (Armienta et al., 1996). Total, hexavalent and trivalent chromium were determined in surface and 30 cm depth soil samples from a highly chromium polluted area in Guanajuato state, central Mexico. Nearly 0.9 kilometer square out of 8 kilometer square are sampled was polluted with chromium, at concentrations up to 12,960 mg/kg, mostly as Cr (III), concentration of Cr (VI) were lower than 0.5 mg/kg in most sampled points, with the exception of one, where the concentration was found to be 65.14 mg/kg (Armienta et al., 1996).

3.3 Previous Research Studies Conducted in Kasur Study Area

Similar research conducted in Pakistan also reveals critical situation regarding subsurface contamination due to untreated and improper industrial wastewater disposal in general and tannery effluent in particular.

In January 1997, the Environmental Protection Department, Government of the Punjab, conducted a baseline survey, in order to sample drinking water quality from 21 sources from different locations in and around Kasur, The samples were taken from different sources, mainly from tube wells, domestic motor pumps, and hand pumps, with varying depths ranging from 12 to 165 meters. More than 50 % of these samples were found polluted with chromium as compared with the minimum permissible level of 0.05 mg/l prescribed by the World Health Organization (WHO), irrespective of their depth and location, with maximum value of 0.25 mg/L (EPD, 1997).

According to United Nations Industrial Development Organization, at present the Kasur tanneries in Kasur discharged, around 13,000 m^3 per day of heavily polluted tannery wastewater and on average 160 tons of chromium is discharged on daily basis from tanneries (Rehman, 2004). Initially more than 400 acres of agricultural land was devastated by pounding of tannery effluent directly into adjacent fields and chromium concentration in wastewater was observed to be as high as 147 mg/L (Wattoo et al., 2000).

In another study, effluent and relevant soil samples from 38 tannery units housed in Kasur were obtained for metal analysis. The study evidenced enhanced levels of Cr, 391 mg/L and 16.7 mg/L, in tannery effluent and relevant soil, respectively. The effluent versus soil trace metal content relationship confirmed that effluent Cr was strongly correlated with soil Cr. The study exhibited a gross pollution of soils with Cr at levels far exceeding the stipulated safe limit defined for tannery effluents. The maximum value of chromium in tannery effluent observed was 3,956 mg/L (Saadia et al., 2005).

Similar kind of research work conducted by Saadia et al., (2008) explored groundwater quality of Kasur area and it showed that Na, Ca, Mg, K, Fe and Cr were present as major pollutants in groundwater with alarmingly high concentration levels, while Co, Pb and Zn merged as minor pollutants. Principal Component Analysis (PCA) and Cluster Analysis (CA) identified industrial effluents, particularly from tannery effluent to be the probable source of the observed metal pollution of the groundwater. Comparison with international standards for water quality evidenced that Cr and Fe levels were in far excess of the recommended safe limits. The recorded higher levels of Cr were of major concern, since the metal originates from the tanning industry where Cr compounds are extensively used. Overall, the influx of industrial metal contaminants in effluent discharged indiscriminately into open land in Kasur has already started showing its impact on the aquifer and the maximum value for chromium observed in groundwater samples is 9.8 mg/L (Saadia et al., 2008).

Similarly comparative study of Cr in soil from Kasur tannery area with background values depicted enhanced levels of Cr than its background concentration due to adoption of chrome tanning. The surface accumulation of chromium indicates the maximum value of chromium retained in soil to be 26 mg/Kg (Saadia et al., 2009).

3.4 Chemistry of Chromium in Soil and Leaching and Retention Behaviour

3.4.1 Chromium

CHROMIUM
ATOMIC NO. 24
ELECTRON IN SHELLS: 2 - 8 - 13 - 1

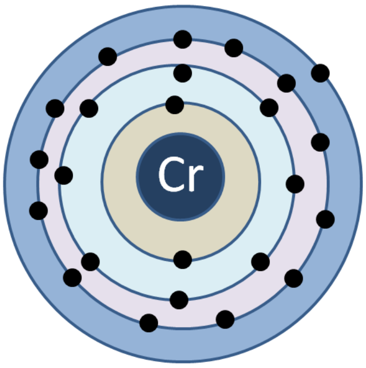


Fig. 3.1: Electron shell of chromium atom (www.wikkipidia. Com)

Fig. 3.2: Silvery metallic chromium as it exists in nature (www.wikipidia.com)

Chromium (Cr), the 17th most abundant element in the earth's mantle, is used in many industrial processes such as plating, alloying, tanning of animal hides, water corrosion inhibition, textile dyes and mordants, pigments, ceramic glazes, refractory bricks and pressure treated lumber. Chromium was discovered by Louis Vauquelin in year 1797 in France.

Chromium metal exhibits immediate reaction with atomospheric oxygen resulting in the formation of strong dense and noporous dichromium trioxide (Cr_2O_3) thus confirming high reactivity of the metal. Chromium oxide passivates the metal from any further reaction with oxygen. This is the reason that Chromium is resistant to corrosion and the metallic sheen is retained. Cr, a solid at room temperature, generally reacts with halogen gases such as fluorine at high temperatures of 400∞C and pressures of 200 to 300 atm. Cr also reacts with the other halogen gases such as chlorine, bromine, and iodine to form a variety of brightly colored compounds. Cr metal dissolves in dilute hydrochloric acid and sulfuric acid. Cr does not appear to react with nitric acid, most likely owing to the result of passivation by surface chromium oxides. Many of the Cr compounds are toxic. Chromium is one of the chief ingredients in mineral and metallic colors, being responsible for the color of some gem stones. Among the gem stones colored by Cr are emeralds, ruby, alexandrite, chrome garnet, and some sapphires (Jacques et al., 2004). Other basic properties of Chromium and technical data related to physical properties are described in Table 3.1 and 3.2 respectively.

Table 3.1: Basic properties of chromium (www.wikipedia.com)

Name	**Chromium**
Symbol	Cr
At. No.	24
At. Wt.	51.9961
Density	7.14 g/cm^3
Melting point	1970°C
Boiling point	2671°C

Table 3.2: Technical data for chromium (www.wikipedia.com)

THERMAL PROPERTIES		**BULK PHYSICAL PROPERTIES**	
Phase	Solid	Density	7.14 g/cm^3
Abs. Melting Point	2180 K	Density(Liquid)	6.3 g/cm^3
Abs. Boiling Point	2944 K	Molar Volume	7.2824 x 10^{-6}
Heat of Fusion	205 KJ/mol	Brinell Hardness	1120 MPa
Heat of Vaporization	339 KJ/mol	Mohs Hardness	8.5 MPa
Sp. Heat	448 J/(Kg.K)	Vickers Hardness	1060 MPa
Neel Point	393 K	Bulk Modulus	160 GPa
Thermal Conductivity	94 W/(mK)	Shear Modulus	115 GPa
Thermal Expansion	4.9 x 10^{-6} K^{-1}	Young Modulus	279 GPa

3.4.2 Chromium, its Application and Existence in Environment

Chromium is a lustrous, brittle, hard metal. Its color is silver-gray and it can be highly polished. It does not tarnish in air, when heated it burns and forms the green chromic oxide. Chromium is unstable in oxygen, it immediately produces a thin oxide layer that is impermeable to oxygen and protects the metal below (LENNTECH, 2017).

Chromium main uses are in alloys such as stainless steel, in chrome plating and in metal ceramics. Chromium plating was once widely used to give steel a polished silvery mirror coating. Chromium is used in metallurgy to impart corrosion resistance and a shiny finish; as dyes and paints, its salts color glass an emerald green and it is used to produce synthetic rubies; as a catalyst in dyeing and in tanning leather and to make molds for firing bricks. Chromium (IV) oxide (CrO_2) is used to manufacture magnetic tape.

Chromium is mined as chromite ($FeCr_2O_4$) ore. Chromium ores are mined today in South Africa, Zimbabwe, Finland, India, Kazakihstan and the Philippines. A total of 14 million tonnes of chromite ore is extracted. Reserves are estimated to be of the order of 1 billion tonnes with unexploited deposits in Greenland, Canada and USA. (LENNTECH, 2017).

3.4.3 Leaching and Retention Ability of Chromium in Subsurface

Contamination of soil with heavy metals is a common environmental problem related to industrial activity and agricultural practices i.e. wastewater irrigation and composts, application of fertilizers, and agro – chemicals, disposal of sewage sludge (Punning and Varvas, 1993). Sorption and precipitation are fundamental chemical reactions of trace elements that greatly affect metal availability in aerobic terrestrial systems. Retention and release reactions of solutes in soils, include precipitation/dissolution, ion exchange and adsorption/desorption reactions (Irha et al., 2009). Metal leaching through the boundary between topsoil and subsoil increases soil bound and /or dissolved metal in subsoil. If subsoil has a high affinity for a metal, the retention of the metal leached from the surface soil is efficient and its further penetration to groundwater could be prevented. On the contrary, if the adsorption is low, subsoil is an inefficient barrier against groundwater contamination. Finally if the adsorption capacity of both topsoil and subsoil is low, soil as a whole offers low protection against groundwater contamination by metals deposited to the soil surface from air pollution, fertilizer application, or other sources (Irha et al, 2009).

Study of the literature reveals that clay has very low permeability. Many researchers used clay as a liner material in their studies relating to retention of heavy metals from leachates. Earlier studies showed that clay surface prefers high valency cations to low valency cations. Yong et al. (1993) evaluated the role of various clay soil solids in heavy metal retention capability. Bandyopadhyay et al. (2000) performed experiments on the retention of hexavalent chromium in a natural clay liner in a sanitary landfill and found that clay had considerable retention capacity for hexavalent chromium. The present investigation was carried out in especially designed column experiment with kaolin as the clayey material to adsorb chromium Cr^{6+} from a synthetic chromium solution in order to assess the potential of the clay bed as liner material. In this column study, metal concentrations in the effluent from the clay bed were analyzed to ascertain the adsorptive behavior of the clay bed and exchange potential of ions. Besides, change in pH in the effluent samples and permeability of the bed was also studied. Break-through curves developed through the column study revealed that chromium Cr^{6+} was exchanged for Ca^{2+} and Mg^{2+} ions. The role of Na^{+} and K^{+} ions appeared to be insignificant in the retention of chromium Cr^{6+} by clay. It was also noted that pH of the column effluent showed an initial jump into alkaline condition which came down to a value in close proximity of the chromium-bearing acidic feed solution. Based on the findings, it may be concluded that the clay-bed has considerable retention capacity for higher valency chromium ions. Hence, the clay bed as liner can be effectively used as a potential barrier to the passage of hexavalent chromium resulting in lesser permeation of this hazardous material into the groundwater (Bandyopadhyay et al., 2005).

In a batch study conducted by Choppala et al. (2010), to investigate sorption and mobility of chromium species in various soil types, there was no significant effect of soil properties on the adsorption of Cr (VI), however its adsorption was high in soils with high iron content. In all soils, the amount of adsorption, as measured by K_f value was higher for Cr(III) than Cr(VI). The amount of Cr (III) adsorbed increased with an increase in pH and CEC (cation exchange capacity) of soils. The adsorption data were fitted to Freundlich equation and the adsorption parameters, K_f and n were calculated. Soil properties, including pH, CEC, OM (organic matter), clay, water extractable SO_4^{2-} and PO_4^{3-} were investigated on adsorption of Cr(III) and Cr(VI). While Cr (III) is strongly retained onto soil particles, Cr (VI) species such as chromate (CrO_4^{2-}), bichromate ($HCrO_4^{-}$) and dichromate ($Cr_2O_7^{2-}$) are weakly sorbed to soils under alkaline to slightly acidic conditions, leading to their movement to sub surface environments. Oxidation-reduction (redox) reactions are largely controlled by the adsorption of Cr species in soils, the supply of redox compounds are microbial activity. The detoxification of Cr (VI) through reduction to Cr (III) and its subsequent adsorption has been considered as an effective method for remediation management of Cr contaminated soils (Choppala et al., 2010).

Masuda et al. (2010) conducted research in the area near Kasur and investigated geochemical characteristics in sediments of fluoride and arsenic contaminated groundwater aquifer. Subsurface geology of the area was studied using data from drilled cores by conducting soil bores. It was found that residential and industrial areas including research area were covered with Pleistocene aeolian deposits. These sediments cover two aquifers intercalated by a less permeable layer. Most polluted groundwater appears in the first aquifer at 15 to 25 m depth beneath the center of the village of Kalalanwala. A considerable amount of anthropogenic fluoride contaminates the aquifer along an ancient river channel. Arsenic might derive from anthropogenic sources such as industrial waste.

3.5 Health Impacts of Chromium from Tannery Industries

Inspite of having adverse toxicities, chromium is intensely used in many industrial processes particularly in tannery industries and electroplating industries. Chromium has been announced to be carcinogen, mutagen, and thyroid disrupter. Trivalent chromium Cr(III) is widely employed as supplement and is used in glucose/insulin homeostasis, maintains metabolism, regulates body composition, and acts as antidepressant in diabetes. Cr (III) complexes have remarkable antibacterial activities. Chromium (III) decreases glucose concentration in the blood. Various pediatric syrups in Nigeria have been reported to be composed of higher concentrations of different heavy metals including chromium. It has a long list of toxic effects. Some categories of the metal toxicities which are of immediate concerns to the scientists and public health officials are narrated by the researcher (Andleeb, 2014). Chromium along with cobalt toxicity results in inner retinal dysfunction. Hypersensitivity induced by chromium results into allergic inflamed skin, or allergic contact dermatitis. Cr(VI) affects adversely the survival, growth, reproduction, fecundity and fertility and causes ovarian inflammation, disrupted ovarian histoarchitecture and fibrosis. The Cr (VI) causes various health problems including menstrual disorders, endocrine disruption, mutation and infertility. Hexavalent chromium disturbs metabolism and arrest p53-dependent cell cycle in hepatocytes which inhibit mitochondrial respiratory chain complex activity leading to apoptosis. Biomarkers of liver injury such as aspartate and alanine transaminases, lactate dehydrogenase activities, bilirubin, albumin and glucose levels increased, whereas triglyceride and cholesterol levels decreased following the metal induced disturbances. Cr (VI) is a carcinogen of liver in human. Being contaminant of water and soil, corrosive and cytotoxic, it can induce inflammatory response, acute and chronic lung tissue toxicity resulting in cancer. Cr(VI) is also a human carcinogen of kidney. It reduces total protein, hemoglobin, packed cell volume, total erythrocyte count, mean corpuscular volume, mean corpuscular hemoglobin, total leukocyte count, whereas alanine transaminase, blood urea nitrogen and creatinine increase in response to the toxic effects the metal leading to renal failure. Gestational exposure to Cr (VI) resulted in increased Cr concentration in the placenta, increased germ cell apoptosis, accelerated germ cell cyst (GCC) breakdown; advanced primordial follicle assembly and primary follicle transition. Cr (VI) induces oxidative stress in radish and retards growth of radish seedlings, inhibits photosynthesis in algae, decreases growth performance of Catharanthusroseus and other various plants by affecting enzymes. Besides its important role with its very minute quantities in biological systems, industrial use of Cr has contaminated our environment and has created diverse health issues. (Andleeb, 2014).

Ahsan et al. (2006) conducted study in Kasur Tannery area and found that values of liver function tests of factory workers in tanneries of Kasur were to be within the normal range in all age groups except for the albumin content and alkaline phosphatase activity, which were higher in younger age group. The total chromium content in the blood of workers of 1 – 20 years working period was significantly higher (24%), when compared with the same age group amongst the non-workers. The mean cell volume, packed cell volume and platelet counts in the workers were generally lower, whereas the haemoglobin, mean corpuscular haemoglobin and mean corpuscular haemoglobin concentration values were higher in the workers than non-workers. The white blood cell counts decreased in the workers up to the age of 40 years, whereas in older population it showed slight increase. The albumin, alkaline phosphatase, alanine aminotransferases, aspartate aminotransferases and total protein showed higher values, whereas the total bilirubin, direct bilirubin and blood serum glucose contents showed lower values in blood sera of the factory workers, both male and female, when compared with those of the control population. The total chromium (56%) and hexavalent chromium (78%) were significantly higher in the blood of exposed male and female worker population as compared with the control population. No definite pattern was observed in different haematological and biochemical parameters, when comparing the workers with non-workers. Slight variation may be due to multitude of factors in addition to possible effects of chromium toxicity. (Ahsan et al., 2006).

Naz et al. (2016) conducted research work to evaluate human health risk of Cr (VI) and Cr (III) via oral and dermal exposure of drinking water in groundwater samples of nearby Sukinda chromite mine. Mathematical models were used to carry out risk assessment as per IRIS guidelines and the input parameters were taken according to the Indian context. The concentrations of TCr and Cr (VI) were found in the range of 48.7–250.2 and 21.4–115.2 µg/l, respectively. In the maximum locations, TCr and Cr (VI) concentrations were found 2.3–6 times and 2.1–11.5 times higher, respectively, than the permissible limit as per standard statutory bodies. The total cumulative average cancer risk and non-cancer risk (Hazard Quotient) was found 2.04E-03 and 1.37 in male and 1.73E-03 and 1.16 in the female population, respectively, which indicated 'very high' cancer risk and 'medium' non-cancer risk as per USEPA guideline. Male population was found 1.2 times higher cancer and non-cancer risk than females, because of the higher water ingestion rate in male. The obtained health risk via dermal route was found 6 times lesser than the oral ingestion due to very less dermal exposure time (0.58 h/days). As a consequence, 'high' cancer risk also recorded in one of the locations where TCr concentration was within permissible limit which is because of the higher proportion of bioavailable Cr (VI). Sensitivity analysis of input parameters towards cancer and non-cancer risk revealed that Cr (VI) and Cr (III) concentrations were the main predominant parameters followed by exposure duration, body weight, average time, and dermal slope factor. This research work also revealed that the maximum cancer and non-cancer risk is due to oral exposure of Cr (VI), rather than dermal, due to the lower exposure time of dermal pathway. It was observed that the male population had higher cancer and non-cancer risk than the females at all the locations.

3.6 Geographical Information Systems (GIS) and Groundwater Modeling Systems (GMS) Software

Morishita et al. (1998) a Professor from Aichi Gakuin University Japan, with his team members, worked on the Participatory GIS for Health Impact Assessment of Arsenic-contaminated Water in Pakistan: A Case of Chahklalanwala Village, District Kasur in the year 2005. According to his observations drinking the arsenic-contaminated groundwater has recently imposed severe health impact both in rural and urban areas of Punjab. Considering the importance of community participation in the preparation of GIS database, the approach of participatory GIS was developed to involve local communities in the process of building a comprehensive health database. To experiment the concept of participatory GIS, the village Chah klalanwala in Kasur district of the Punjab province was selected. This village can be called as 'little Minamata of Pakistan' in terms of water related diseases. Through participatory GIS, local communities will be able to get access to reliable information that may enable them to play an active role for environmental self-governance. Based on the outcomes of the participatory GIS, the researchers intend to formulate a participatory action plan to provide arsenic-free safe drinking water in this village. This publication aimed to discuss the nature of participation for the preparation of Health GIS database, nature of arsenic-contamination related diseases and initial findings of the on-going research work by the authors in the village Chahklalanwala. The research team found that the participation of rural communities for preparation of health database was very helpful to interlink ground realities with the use of GIS technology for health impact assessment. Additional major finding is that participatory GIS is cost-effective approach for the training of young GIS professionals who are engaged in this survey through internship offered by the Pakistan Society of Geographic Information Systems (PSGIS). Participatory GIS also helps to strengthen technical capacities of the local communities for future actions in health sector. Participatory GIS approach for data collection reduces the cost of physical and social surveys. It increases reliability and accuracy of data. Our water filter units are in experimental stage, however preliminary results have shown that these filter units are efficient to remove arsenic and fluorides from drinking water. We are in the process of developing participation models based on our experiences of working in low income and low literacy society in rural areas of Pakistan.

GIS based modeling approach (Shukla et al., 1998) was applied for the evaluation of the groundwater quality regarding pesticide pollution. According to the attenuation factor AF, a screening model, was used to evaluate the relative degree of vulnerability of groundwater to pesticide contamination in Louisa County, Virginia. For evaluating the contamination potential of pesticides, three scenarios of pesticides leaching represented by high, moderate and low cases of degradation and sorption in soil were considered. Data layers were overlaid within a geographical information system (GIS) for the spatial computation of AF, for the actual and 2 meter groundwater depths. This spatial data base was divided into five contamination potential categories namely high, medium, low, very low, unlikely, based on the numerical values of the AF for each cell (1/9 ha) the results for the three most mobile pesticides are presented in this paper. The model AF was evaluated by comparing its predicted results with the field data from an experimental watershed. The AF model was able to identify most of the frequently detected pesticides in the watershed. A sensitivity analysis was also performed. The results of this study provide information about the potential groundwater threat by pesticides to the citizens and the decision makers of the country can also be use this research to formulate an appropriate land use management plan to protect the groundwater quality.

Livingston et al. (1998) found and evaluated current environmental policy governing nitrates contamination of groundwater and its relationship to optimal policy design, in the context of the South Palette alluvial aquifer in the western United States. The contribution of the agriculture to nitrate pollution of surface and groundwater is a growing concern throughout the world. The best management technique is assessed in its relationship to optimal policy design. First the current physical environmental problem and existing institutional arrangements are described. Second, legal and economic criteria are brought to bear on the question of appropriate policy design. Finally, the strengths and weaknesses of the existing policy are evaluated in this context and changes in policy that would increase effectiveness are recommended. Considerable justification is found for state initiated control because victims of groundwater pollution are dispersed and risk assessment is technically demanding. However ex post elements of existing policy must be improved, perhaps through targeting and some devolution in monitoring and enforcement responsibilities.

The paper presented by Jawed Ali Khan (Khan, 1998), Director, Ministry of Environment Islamabad, attempts to highlight the importance of GIS as a tool for measuring Environmental Impact and builds a theoretical framework for studying the Impact of Lahore-Islamabad Motorway on the natural eco-system as well as on the cities, towns, village and hamlets located within the threshold of the Motorway. The findings reveal that the impact of the Motorway particularly on the natural eco-system would be most pronounced along the immediate peripheries in the near future. The worst affected areas are found to be located in the salt range region because of the consequential disturbance in the fragile ecological balance of this area. The natural eco-system in other area would also be affected due to disruption in the natural drainage pattern as well as aquifer recharge. As regards the human environment, adverse impact on hamlets and scattered settlements would be visible due to loss of complimentary between settlements, while the strong pull factors at the “Exit Points” as well as within the threshold would lead to rapid land-use-conversion and loss of scarce fertile agricultural land. Based on the findings, the paper advocates for timely intervention through advance planning of entire threshold area so that adverse impact of the Motorway could be minimized and advantages of strong magnetic pull sparking the engine of development could be positively guided and benefits fruitfully distributed.

Hideharu Morishita and Muhammad Nadeem (Morishta and Nadeem, 2005), presented a paper representing the designing cropping pattern under saline condition using GIS this study was conducted in district Kasur, seriously affected by salinity. Out of a total irrigated area of 165 million hectares in Pakistan, about twenty five percent is fully or partially affected by excessive salts. The salt-affected areas have been created by seepage of water from canals as well as from saline ground water. In these areas soluble salts have been accumulated on the soil surface and in the root zone. Agricultural productivity in these areas has seriously been affected. The capabilities of GIS were applied in the study area, Kasur district, to compare the salinity over different periods of time and to find the change in level of salinity with the passage of time. The increasing trends of salinity were found where the ground water quality was inferior. About twelve percent of the study area is under slightly to strongly saline conditions. Sixty two percent (62 %) groundwater is marginal for crop production and about seven percent ground water is hazardous for crop production. The GIS was further used to design cropping patterns for ground water irrigated as well as surface water irrigated parts of the study area. The results of the study indicate that GIS applications to agriculture would provide decision support systems especially for finding the land capabilities for growing different kinds of crops.

Laurent et al. (1998) proposed a method for water resources protection based on the spatial variability of vulnerability. The vulnerability of a water resource is defined as the risk that resource will become contaminated if a pollutant is placed on a surface, in comparison to another. A spatial modeling method was defined in this research to estimate a travel time between any point of catchment and a resource (river or a well). This method is based on the spatial analysis tools integrated in Geographical information system. The method is illustrated by an application to an area of Massif Central (France) where three different types of flow appear: surface flow, shallow subsurface and permanent groundwater water flow (base flow). The proposed method gives result similar to that of classical methods for the estimation of time of travel. The contribution of GIS is to improve the mapping of vulnerability by taking the spatial variability of physical phenomenon into account.

Allah Bakhsh (Bakhsh, 2005) worked in collaboration with Dr. Ramesh S. Kanwer, on the application of the GIS technique in order to obtain the spatial clusters of Nitrates as a result of leachate from the Agricultural fields. They published their research work in the paper titled “Spatial Clusters of Subsurface Drainage Water NO3-N Leaching Losses”. This grouping of nitrate-nitrogen (NO3-N) leaching losses from agricultural fields into spatial clusters can help determine the cause/effect relationships for their occurrence. This study was designed to investigate the spatial relationships of low, medium, and high NO3-N leaching losses clusters with soil and landscape attributes using cluster and discriminant analysis and the map overlay capability of a geographical information system (GIS). Field measured data of a six-year (1993 through 1998) study on NO3-N leaching losses from 36 experimental fields at the Iowa State University's northeastern research center near Nashua, Iowa, were normalized on an annual basis to compare over the years. The cluster analysis resulted in the formation of three clusters based on the satisfactory evaluation criteria of pseudo-F statistic, cubic clustering criterion, and R^2 values. The discriminate analysis, carried out on the basis of clusters, identified elevation and subsurface drainage as the factors that contributed significantly ($p < 0.01$) in discriminating among these clusters. The verification of discriminant functions developed on these factors predicted the cluster membership for all the groups with an overall accuracy of 86 percent. The map overlay analyses of GIS showed that spatial occurrence of the clusters transporting high NO_3-N (nitrate-nitrogen) leaching losses was affected by the interaction of soil type and elevation levels.

According to Dev Das (Das, 2000) GIS is a tool for storing, manipulating, retrieving and presenting both spatial and non-spatial data in a quick, efficient and organized way. Since most land information elements have a geographic connotation, geographically referenced data with GIS techniques come to the fore in such and application. The term 'geographic' in GIS refers to the location attributes which define the spatial positioning of the piece of information on the face of the earth. Preparation and maintenance of data in the form of maps and referenced tabular files itself can be considered as a primitive form of GIS. However, with the advent of digital computers, with high data processing speed and the development of analytical tools thereon to handle geographically referenced data with ease and flexibility, computer aided GIS has become a reality of late. Such systems generally deal with data classified/segregated into the spatial type (location referenced) attribute type (without locational connotation) and the time variant or repetitive types of data. Using of GIS in hydrogeology is only at its beginning, but there have been successful applications that started to develop. As an example there is the Sali river basin, Bankura district, West Bengal, where sites for groundwater exploration and artificial recharge have been demarkated applying GIS technique using ARC/INFO and ILWIS 2.1 Software.

Dr. Abraham Thomas (Thomas et al., 2001) worked on assessing the spatial distribution of pollutant fluxes reaching an urban unconfined aquifer system in Birmingham, United Kingdom by the use of GIS Urban groundwater recharge and pollution is a complex and poorly understood process. No suitable method is available for assessing the amount of recharge and pollutant fluxes reaching in urban aquifers of the UK. As part of a large project on the Birmingham urban aquifer studying long-term urban aquifer sustainability, a desktop GIS (ArcView GIS and the ArcView Spatial Analyst extension)-based runoff-recharge-pollutant flux model has been developed to estimate the potential recharge and pollutant fluxes to an urban unconfined aquifer system. This paper explains how an integrated approach (involving analysis of various thematic maps and other attribute information of a UK urban area using the above-mentioned desktop GIS-based recharge pollutant flux model) could help in assessing the amount of groundwater recharge and pollutant fluxes (currently a few chosen pollutant species such as nitrate, chloride, and BTEX compounds) reaching to the groundwaters of the Birmingham area.

Bilgehan Nas and Ali Berktay (Nas & Berktay, 2006) worked on the groundwater contamination in the city of Konya, Turkey. They used GIS modeling in order to evaluate

Nitrate data. Approximately 75% of the city's water consumption has been supplied from 198 groundwater wells for the last six years. Nitrate is one of the important water quality parameters and was measured in the water samples taken from 139 wells in 1998 and from 156 wells in 2001 within the study area of 427.5 km^2. To evaluate the nitrate data, a vector-based GIS software package ArcView GIS 3.2 was used. A hardcopy map of the city was digitized in the UTM projection system. The locations of the wells were obtained by a hand-held Global Positioning System (GPS) receiver. According to the maps produced, nitrate concentrations generally tend to increase in the city center, the average concentrations being 2.2 and 16.1 mg/L for the years of 1998 and 2001, respectively. A statistical correlation procedure was also applied to well depths and nitrate concentrations. As a result, correlation coefficients of 0.259 and 0.261 were obtained for data collected in 1998 and 2001. It is concluded that the distribution of nitrate concentrations is not correlated with well depths within the study area.

According to Babikar et al. (2007), assessing the quality of groundwater is important to ensure sustainable safe use of these resources. However, describing the overall water quality condition is difficult due to the spatial variability of multiple contaminants and the wide range of indicators (chemical, physical and biological) that could be measured. This contribution proposes a GIS-based groundwater quality index (GQI) which synthesizes different available water quality data (e.g., Cl^-, Na^+, Ca^{2+}) by indexing them numerically relative to the World Health Organization (WHO) standards. Also, introduces an objective procedure to select the optimum parameters to compute the GQI, incorporates the aspect of temporal variation to address the degree of water use sustainability and tests the sensitivity of the proposed model. The GQI indicated that the groundwater quality in the Nasuno basin, Tochigi Prefecture, Japan, is generally high (GQI < 90). It has also displayed the natural (depth to groundwater table, geomorphologic structures) and/or anthropogenic (land-use and population density) controls over the spatial variability of groundwater quality in the basin. Temporally, groundwater quality is more variable in the upper and lower parts of the basin (variation, *V*, 15-30%) compared to the middle part (*V*, <15%) probably attributed to the seasonality of precipitation and irrigation of rice. In the lower southeastern part of the Nasuno basin and the vicinity of the Naka and Houki rivers the sustainable use of groundwater is constrained by the relatively low and variable groundwater quality. The model sensitivity analysis indicated that parameters which reflect relatively lower water quality (high mean rank value) and those of significant spatial variability imply larger impacts on the GQI and must be carefully and accurately mapped. Optimum index factor technique allows the selection of the best combination of parameters dictating the variability of groundwater quality and enables an objective and fair representation of the overall groundwater quality (Babikar et al., 2007).

Groundwater modeling has a wide range of applicability in addressing complex natured environmental and geotechnical issues. The use of advanced groundwater modeling software has helped in site characterizing and sub-surface explorations and made it possible to achieve far higher degree of efficiency and accuracy than ever.

Researcher Yang et al. (2009) studied the impact of tunneling construction on the hydrological environment of Tseng Wen Reservoir Transbasin Diversion Project in Taiwan, using GMS, FEMWATER groundwater modeling software package. MODFLOW was then applied to simulate the hydrological conceptual model in the tunnel area. The automated parameter estimation method was adopted to calibrate groundwater level fluctuation and hydrogeological parameters in the region. Calibration of the model demonstrated that errors between simulated and monitored results are smaller than allowable errors. The study also observed that tunneling excavation caused groundwater to flow towards tunnel (Yang et al., 2009). Furthermore FEMWATER, code for solving 3 – D groundwater flow problems in which hydrogeological characteristics are integrated into GIS, is applied to evaluate the impact of tunnel construction on an adjacent hot spring area. Finally the groundwater flow obtained via, GMS indicated that the hydrogeological conceptual model can estimate the possible quantity of tunnel inflow, and the impact of tunnel construction on the regional and local groundwater resources regime of the transbasin diversion project (Yang et al., 2009).

In another similar study by Spengler et al. (2012), the impact to groundwater quality in a coastal limestone aquifer caused by injection of reclaimed water was simulated using a three-dimensional numerical groundwater model. Numerical transport simulations conducted for a 18.9 ML day^{-1} injection scenario indicate that a non-reactive constituent will take between 100 and 200 days to reach the shoreline from an injection point located in the vicinity of the Honouliuli Wastewater Treatment Plant. The increase in concentration of non-reactive constituents at the shoreline resulting from the injection of reclaimed water will stabilize after roughly four to five years. The mass flux rate of nitrogen entering the near-shore environment for this future injection scenario is roughly 150% higher than current estimated flux rates but 75% lower than estimated flux rates during the era of furrow irrigated sugarcane cultivation. The concentration of the recalcitrant microbe Clostridium perfringens is estimated to increase from a baseline concentration of 0.20 to 0.34 CFU per 100 ml within groundwater entering coastal waters immediately down-gradient of the injection sites

(Spengler et al., 2012).

Another researcher Dr. Rojas (2002), used GMS – FEMWATER to analyze Payatus landfill site in Manila for pump and treatment remediation technique to decontaminate the contaminant plume in underlying groundwater. The 22-hectare Payatas Dumpsite is the largest and oldest among the existing dumpsites in Metro Manila. The potential contamination of the underlying aquifer system due to the leachate percolating from the old dumpsite is investigated through a three-dimensional unsaturated-saturated flow and solute transport model using the FEMWATER module of the Groundwater Modeling System (GMS). The conceptual Payatas FEMWATER model is a two-layer model covering an area of about 7.6 square kilometers. The leachate flux beneath the dumpsite was estimated using the Visual HELP, a quasi- two-dimensional hydrologic model that is used for evaluating landfill designs. The results of the 50-year simulation were analyzed. Pump-and-treat remediation schemes were also simulated and analyzed using FEMWATER.

Insigne and Kim (2010) studied groundwater exploitation by continual extraction and indiscriminate use of groundwater by residential sector, causing decrease in groundwater level in Paranaque and Las Pinas city, which results salt water to penetrate into the aquifer due to the proximity of Manila Bay. This study modeled the present condition and extent of saltwater intrusion in the aquifer bounded by Paranaque River and Manila Bay. The model was simulated using a 3D finite element modeling software (FEMWATER) that is capable of modeling the groundwater flow condition in the aquifer. The output of model was intended to be used for prediction of the future condition of the aquifer for better groundwater management. FEMWATER, a three-dimensional finite element-based, transient, density-driven flow and transport groundwater model of the United States Environmental Protection Agency (EPA), is incorporated to simulate the coastal aquifer under study mathematically. This simulates the flow and transport in both saturated and unsaturated media. Furthermore, the density-dependent problems such as salinity intrusion can be simulated by the coupled flow and transport motion. The collected data were utilized to develop and implement the 3D finite element simulation model. During the in-situ groundwater testing there was no existing evidence of saltwater intrusion in the study area. However, to predict the response of the aquifer system to future withdrawal scenarios, both the flow and transport processes were subsequently modeled using FEMWATER. The simulation model was not calibrated due to insufficient available data for satisfactory calibration and validation of the model. The given parameter values and boundary conditions were utilized as representative information for the study area. In addition, the basic study objective was to predict the extent and degree of the salinity concentration in the study area. To meet these study objectives, the simulation model was used to simulate the aquifer conditions for the present discharge scenarios, and five other scenarios to forecast the possible condition of the aquifer in ten years. The research work was concluded that this model can be used as a basis to provide reliable data for projecting saltwater contamination for the management and development of groundwater resources (Insigne and Kim, 2010).

3.7 Summary of Literature Review

This chapter focused on significant literature review related to proposed research work, covering a wide range from tannery waste management case studies to groundwater simulations for contaminant transport.

Surface accumulations of trivalent chromium have been found always higher and that of hexavalent chromium accumulations are always very minute and irregularly distributed in most of the sites reviewed. Similarly inspite of heavy accumulations at surface, not very serious groundwater contamination has been observed at most of the sites. Similarly effluent discharge with high chromium concentrations is a common observation at most of the sites.

Literature available regarding Kasur Study area shows provides no serious and detailed research conducted so far particularly regarding site characterization and subsurface contamination. Whatsoever data available, only comprises of random groundwater sampling and even this groundwater data has not been properly analyzed with point of addressing the main source of groundwater contamination. No such information about the hydrogeological features and their impact on groundwater or contaminant flow could be obtained from existing data. Maximum surface accumulations of chromium are found upto 26 mg/kg, while maximum level of chromium in groundwater samples out of 64 samples have been found to be 9.8 mg/L and maximum chromium levels in tannery effluent up to 3,956 mg/L. All these higher value of chromium in different media, evident the adverse situation regarding chromium contamination in the area, not only in surface but also in subsurface. However information about the location of these sampling points and their correlation with sources of contamination has not been discussed in these available research studies. Furthermore there is huge variation in the existing data related to soil, groundwater contamination and wastewater characteristics in the research area Kasur. As the data available is uncertain and not reliable due to its unexpected variance, reliable and logical site investigation is the only option to obtain rationalized site characterization of the study area.

Leaching and retention abilities of soil mainly depend upon the subsoil characteristics, particle size distribution and other existing organic or inorganic compounds in soil. If subsoil has high affinity of a metal, the retention of metal leached from surface will be efficient and consequently most of the metal will be retained in the soil, preventing further carriage of metal to groundwater. But on the other hand if soil is not efficient in retaining the metal higher concentrations could be observed in groundwater. No significant effect of soil properties on the adsorption of Cr (VI) could be observed. On the contrary Cr(III) has higher adsorption at higher pH and CEC (cation exchange capacity). Partitioning coefficient plays a significant role in determining adsorption efficiency of a soil. Higher the portioning coefficient higher rate of retention of soil.

Literature studies regarding application of GIS and GMS software for analysis of an environmental investigation depicts a wide range of applicability of both. Literature studies related to GIS reveals its diverse usage for spatial variation analysis in every kind of scenario, while application of GMS – FEMWATER and MODFLOW help in conducting contaminant transport simulations for recommending remediation techniques. MODFLOW package for GMS is commonly practiced in order to simulate groundwater flow in saturated zone while FEMWATER is more precisely used for simulation of groundwater including modeling of salinity intrusion and other density dependent contaminants. FEMWATER is an ideal 3 D finite element model used to simulate density driven coupled flow and coupled flow and contaminant transport in saturated and unsaturated zones. There are always some limitations while simulating for flow and contaminant transport using FEMWATER and it is about the inadequacy and unreliability of field information for which the model is being used. Due to this reason it becomes difficult to accurately calibrate and validate the model therefore changes of error are always there.

Research methodology for this study was based on the reviewed literature and available information. The main points which led to plan research methodology are as follows.

The discrepancies in available information, which were necessary in order to properly investigate the environmental issue and to conduct a more detailed research and site characterization, were highlighted and were included in the research plan. The main features required to be addressed and to be brought under limelight include the substrata information and geological cross sectional details; chromium concentrations in subsurface and its distribution; seasonal groundwater monitoring and the studying the variation trends regarding groundwater contamination due to chromium; identification of point sources of contamination.

Main task was not only to obtain field data and monitoring but to integrate all the research components to correlate the subsurface contamination with the source of contamination and obtaining maximum subsurface geological structure formation so as to understand the behavior of contaminant in soil and study the extent of contamination so as to predict the fate of contaminant in subsurface.

CHAPTER 4

SITE INVESTIGATION STRATEGY AND METHODLOGY

4.1 Introduction

This chapter comprises of site investigation strategy and the research methodology adopted to conduct field and laboratory based investigations so as to obtain the proposed objectives.

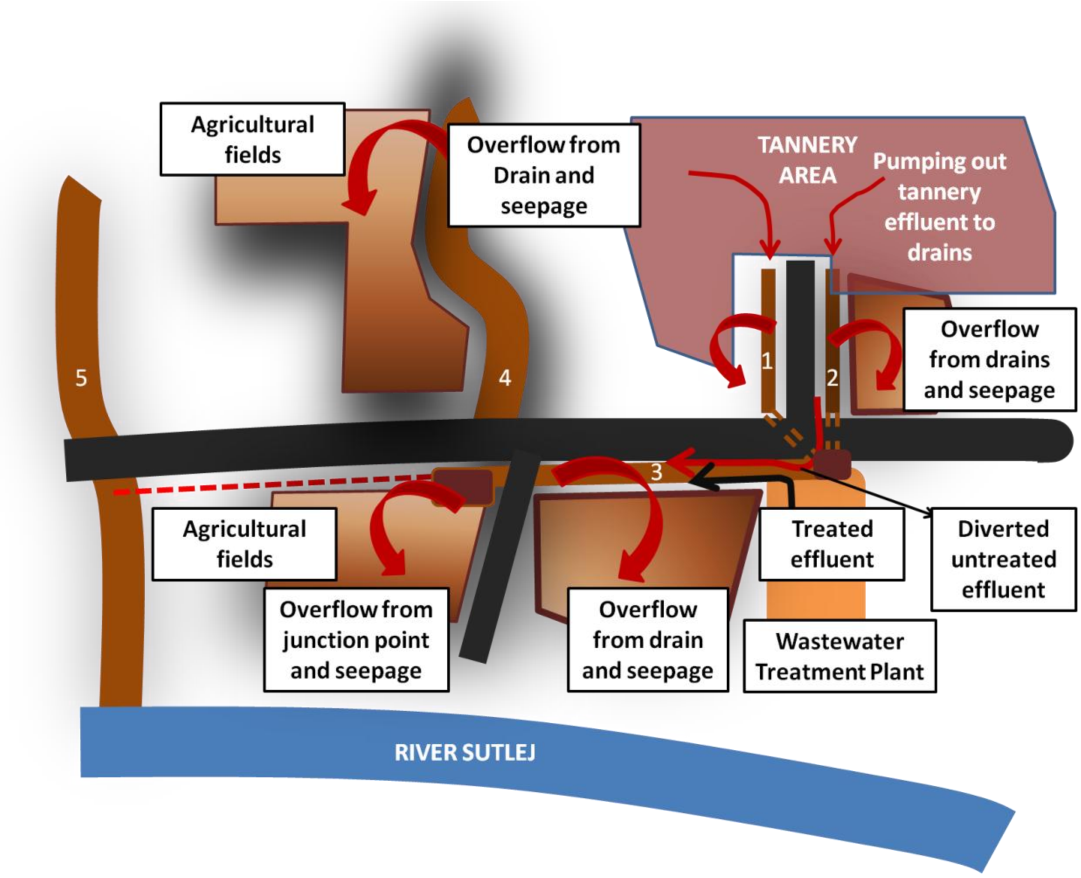


Fig. 4.1: A modeled sketch for existing pollution scenario at Kasur study area

A schematic diagram showing existing situation of possible pollution spreading scenario is shown in Fig. 4.1. From this figure the significant locations of study area can be highlighted. Site investigation strategy includes detailed field survey of tannery area and the adjacent peripheries on the basis of which whole research plan was framed. Meetings and discussions with officials of city management and waste handling agencies were also part of this section.

4.2 Strategy for Site Investigations – Detailed Field Survey

Basically the identification of significant sources of contamination and their role in spreading pollution needs to be focused on the preliminary stage of research so that detailed investigations could be conducted in those regions. In this regard the tannery area, wastewater treatment plant, solid waste dumping site, drainage in the area, peripheral residential localities were surveyed so as to observe on site conditions.

Plan view of significant locations in research area are drawn in Fig. 4.2 as it shows complete map of all the components included in the proposed study area. During the initial field surveys an attempt was made to reach and visit each and every part as shown in Fig. 4.2 so as to observe the existing situation of pollution.

Total area included in Fig. 4.2 is about 24 km square and it is encompassed by two main roads Ferozpur road and Debalpur road, outside the boundary of city Kasur. While conducting survey initially the area surrounding the tannery units was the major focus due to overflowing drains and stagnant ponds in open spaces adjacent to tannery units. This problem is almost persistent throughout the year however it becomes worse during the rainy seasons.

More or less whole district Kasur and nearby villages are the victim of the groundwater contamination. It’s due to the years of uncontrolled tannery units waste disposal into open fields, which resulted in enhanced problem of soil and groundwater contamination. Possible paths and ways of carrying tannery pollution to subsurface and at farther distances could be explained as follows on the basis of field observations.

It is also important to mention that no reliable information was available from the literature reviewed so far. All the information was revolving around the concentrations of chromium in groundwater, wastewaters and surface soils. It also emphasizes the need of conducting a field survey which may help in most suitable site selection for further groundwater, wastewater and soil sampling and analysis.

In order to further analyze the results modeling software were used to interpret the existing situation. In this case different scenarios were conceptualized based on rational situations throughout the time frame during which industrial pollution from tanneries was continuously deteriorating the environmental conditions of the region. Furthermore the tannery owners and residents, due to lack of education and awareness, were not familiar with the means to properly dispose the solid waste and tannery effluent. These factors further enhanced the adverse conditions in the study area.

4.2.1 Sources of Contamination within Tannery Units

Tannery area in Kasur can be approached from Debalpur road (Fig. 4.1 & 4.2) as well from center of city. The main areas include Din Garrh, Kot Abdul Qadir, Niaz Nagar and Younas Nagar which were visited in detail. Main focus was laid on confirming the tannery waste handling situation inside the tannery unit and then its final disposal into the drain. There were different types of pollutions which were observed at tannery area, originating within the tannery units.

Bulks of solid waste were being produced at every tannery unit visited and it was also found that every process taking place in tannery unit generates huge amount of solid waste. There was no procedure being adopted to handle these excessive amounts of solid waste, even there was no awareness about the segregation of industrial waste from domestic waste. Here and there casual dumps of solid waste were not only causing hindrance in performing different activities but were also source of bacterial growth and unhygienic conditions within the tannery units. This situation can be observed in Fig. 4.3. There was no segregation activity in practice for tannery waste and it was almost disposed with domestic waste or it was flushed with the wastewater. It not only caused increase in the waste loads in effluent but also caused hindrance in smooth flow of wastewater in the drains.

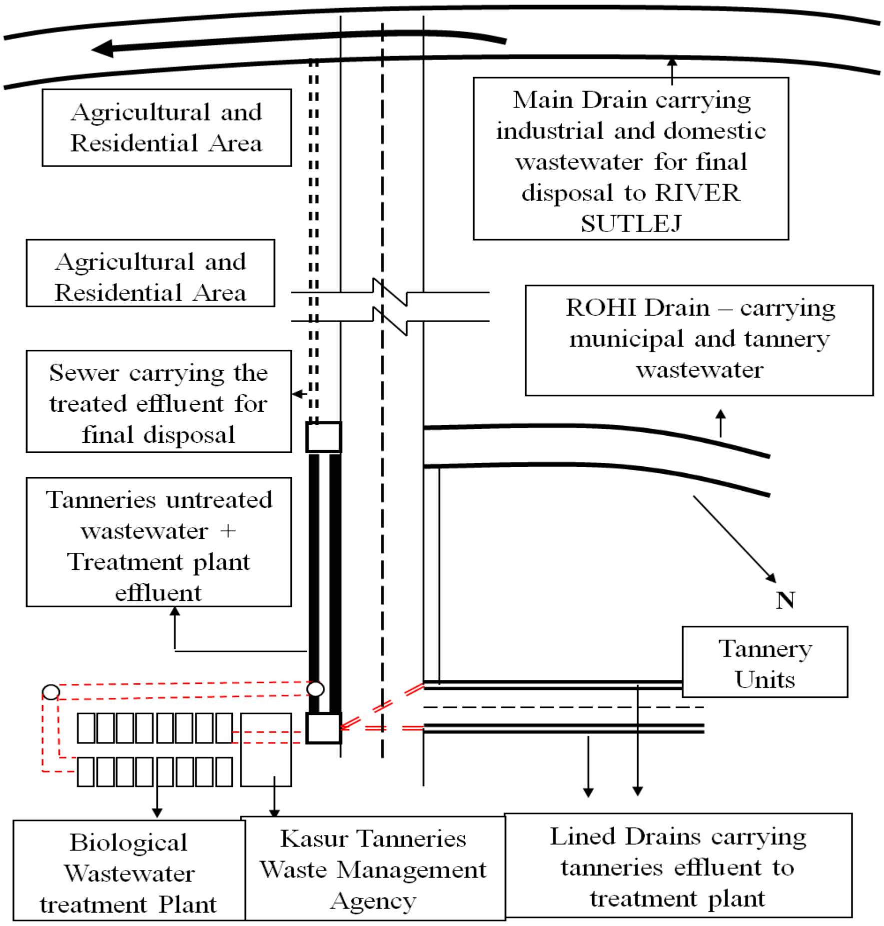


Fig. 4.2: Plan view of detailed map of significant locations in Kasur study area

Hardly in any tannery unit, was pretreatment facility found for removal of large particles of solid waste from tannery wastewater which may help in ease of flow in drains. Although pretreatment is not so expensive and it can be done on individual basis yet there was no awareness about its significance. Even if there are some screens available for segregation of large solid waste particles in wastewater, which are no more able to be used due to clogged waste. On a proposal by the government to all the tannery owners to have a grit/grease chamber and coarse screening, only 56 out of 237 provided this facility in their tannery units and even this installed equipment is out of use due to unawareness. Resultantly wastewater flowing in the small drains in the streets is heavily loaded with solid waste and most of the time they remain choked as it can be observed from Fig. 4.4. Improper tannery solid waste management was found be one of the major environmental hazards at each industry. There was no segregation which led to bulk of hazardous solid waste into the effluent carrying drains, thus further enhancing the issues with wastewater handling approaches and creating operational disorders in the wastewater treatment plant.

Stagnant ponds of the tannery effluent persistently existed on the vacant plots even after the lining of the effluent carrying drains due the choking and overflowing of the drains (Fig. 4.5). This situation becomes adverse during rainy season, when the discharge in open drains increases, resulting in heavy discharges in the drains. These stagnant ponds were a continuous source of bacterial growth and mosquitoes breeding, resulting in sickness of a large number of inhabitants, especially children.

4.2.2 Wastewater Treatment Plant Facility

Biological wastewater treatment plant, currently managed by Kasur Tanneries Waste Management Agency (KTWMA) was established in year 2002, and playing a major role to improve the waste management situation in Kasur. However there are a few drawbacks which can be observed in proper functioning of this treatment plant. Provided those short comings in treatment are completely overcome, this treatment plant can play a very vital role in eradicating the problem of pollution in Kasur from the roots.

Fig. 4.3: Situation of improper handling of solid waste (Picture taken in Nov 2008)

Fig. 4.4: Wastewater containing heavy loads of solid waste (Picture taken in Nov 2008)

Fig. 4.5: Stagnant ponds existing in vacant open fields in adjacent areas of tanneries (picture taken in Nov 2008)

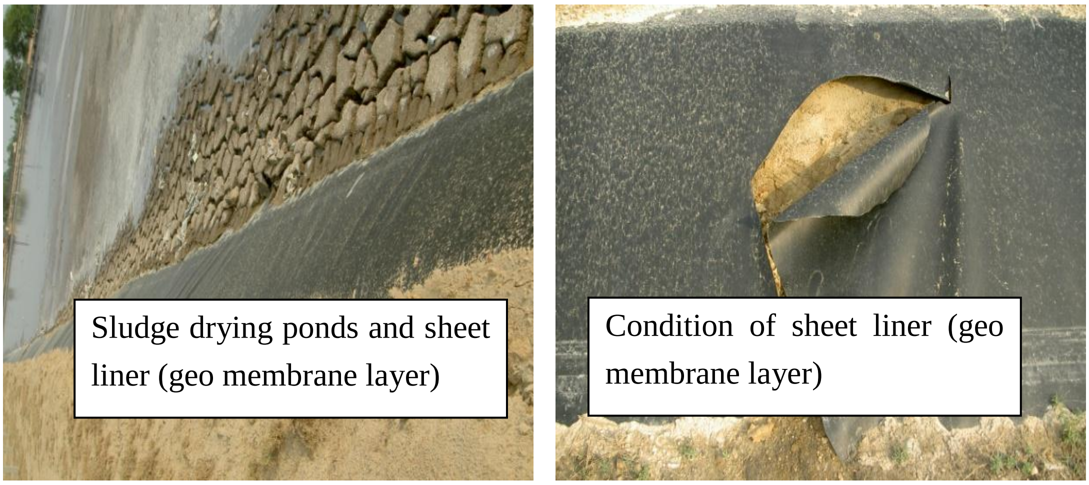
Two pumps installed in tannery area pump untreated effluent into two drains which carry wastewater to treatment plant facility. The effluent stays there for about three weeks (21 days) and somewhat contaminants are removed due to the natural process of sedimentation and BOD and COD loads are reduced.

Inadequacy of treatment plant is one of the major issues related to wastewater treatment plant. Capacity of the plant needs to be increased in order to compensate the excessive discharge from the tanneries. The influent and effluent from the treatment plant are periodically monitored at KTWMA facility and these results indicate that outflow concentrations of the contaminants are far less than that of the inflow concentrations. Due to excessive discharge from tanneries, it can be observed that there is a diversion of untreated effluent before it enters the treatment plant into Drain 3 which usually carries treated effluent from the treatment plant to final disposal in Main drain (Drain 5) through an underground sewer.

Drains 1 & 2 carry untreated effluent from the tannery area to the treatment plant. After passing through the physical treatment in the form of screening the wastewater is taken to two concrete aeration tanks in which there are 8 aerators in each (Fig. 4.6). Thus all the 16 aerators take air from atmosphere and mix to the wastewater for aeration. Total depth is 4.7 meters, width is 32.5 meters, and water depth is three (3) meters with total volume of 6333.5 cubic meters. The retention time of wastewater in these aeration tanks is 1 day after which the wastewater is carried to clarifiers which consist of half span bridge equipped with sludge scrappers for scum collecting and sludge scrapping. The diameter of the bridge is 18 meters. The equalized wastewater enters the clarifier for settling under gravity and settled sludge is scrapped from bottom of tank with the help of sludge scrapper. From the clarifiers the wastewater enters wastewater stabilization lagoons. There are 32 wastewater lagoons, 16 on each side and wastewater retained in these lagoons for a retention time of 5 to 7 days. During this time various organic and inorganic chemical reactions takes place and organic matter settles down in the form of sludge. Geo membrane sheet lining is laid at the bottom of the ponds to avoid percolation of harmful contaminants contained in the sludge. Sludge collected from the clarifiers is very toxic as it contains harmful chemicals including chromium. The sludge is pumped to sludge drying lagoons through a pipe line where it is dried for permanent disposal. De-sludging period of clarifiers is one to one and half years. The use of geo membrane layer although very useful for preventing seepage of chemicals, however the present situation of this sheet lining is adverse as it is torn out from most of the places and unreliable to control the subsurface seepage as shown in Fig. 4.7.

Fig. 4.6: Main processes at treatment plant showing aeration tanks, clarifier and wastewater lagoons (pictures taken in Nov 2008)

These conditions are prevailing since unknown time duration and thus their precise impact on the environmental conditions cannot be determined. However from the findings of the site investigations and conduction of survey these severe conditions can be correlated to the deteriorating subsurface soil and groundwater aquifers. It can be confirmed from the intense and repeated groundwater sampling and analysis for different basic parameters and total chromium levels showed considerable concentrations of these contaminants, however not in alarming levels to exceed the permissible limits. Still there existence in soil and groundwater need to be investigated so as to evaluate the risk associated and future contaminant transport patterns in the study area.



Sludge drying ponds and sheet liner (geo membrane layer)

Condition of sheet liner (geo membrane layer)

Fig. 4.7: Different components of biological wastewater treatment plant (pictures taken in April 2011)

Fig. 4.8: Soil waste disposal site used for both domestic waste and tannery waste disposal (Picture taken in April 2011)

The solid waste disposal site is shown in Fig. 8, which is present on the back side of wastewater treatment plant just adjacent to a residential locality. At solid waste disposal facility both domestic and hazardous industrial waste are disposed together without any segregation or taking any especial measures. Adverse site conditions can be observed at soil waste disposal site posing open threat to public health and environment. Although this a new disposal site developed after the treatment plant construction as a replacement to previous solid disposal site, situated inside the tannery area near Din Garrh yet there is no proper waste handling approach in practice.

4.2.3 Situation of Tannery effluent Carrying Drains

Drains 1 & 2 are lined and carry the pumped tannery effluent from the tannery area to the treatment plant. The width of these drains is 1.2 meters and the depth is 1.5 meters. There are two pumping stations to facilitate tannery effluent discharge into two drains from where it is carried to the treatment plant. Tannery wastewater from two pumping facilities in two main tannery areas clusters Din Garrh and Younas nagar are disposed in these two drains 1 & 2. Due to inadequacy of the treatment plant the wastewater in excess is diverted to Drain 3 where it gets mixed with the treatment plant effluent. From there onwards the wastewater is carried to junction point of Drain 3 and Drain 4 (Drain Rohi). Thus the total length of Drain 3 is about 1.5 kilometers and an average width is 3 meters. The diversion of untreated effluent can be observed into Drain 3 (Fig. 4.9, 4.10, 4.11).

The discharge in Drain 3 is mostly in excess and overflowing on the sides. But at particular times along the year, when the industries are having their peak production duration i.e. from May to September, and during the rainy season, heavy discharges and overflows can be observed as it is obvious in Fig. 4.12. Adjacent fields are flooded with tannery effluent which is heavily polluted. This immense overflow disturbs the lives and ruins the crop cultivations in the adjacent areas. Another main reason of such heavy overflows is the blockage of the drain by soil waste especially at the end point of Drain 3 as shown in Fig. 4.14 & 4.15. Furthermore the underground sewer is incapable of handling such heavy discharges from Drain 3 and 4. Inadequacy of the underground sewer combined with the blockage of drains and sewer make the situation adverse.

Fig. 4.9: Diversion of untreated effluent before it enters treatment plant (Nov 2008)

As the flow of wastewater in the drains is dependent upon the operational activities of the tannery units therefore consistently overflow out of the drains could not be observed. There is irregular repetition of the overflowing of drains and it particularly varies along with the seasonal impacts on the industrial production. Thus in winter season when the tanneries are not working at their peak production, the rate of overflow has been observed to be much lesser and in winter season it is mainly subjected to rains which are only observed in February. Otherwise mostly winter season is dry and effluent overflow from all the drains. However this reduced flow rates result into higher rates of industrial solid waste depositions within the drains and furthermore the choking phenomenon is also very obvious due to higher rates of solid waste depositions from the residential areas as well.

Fig. 4.10: Diversion of untreated effluent & effluent from treatment plant in June 2009

Fig. 4.11: Diversion of untreated effluent and treatment plant effluent in Dec 2009

Fig. 4.12: Drain 3 overflow situation observed in 2011 (Picture taken in April 2011)

Although Drain 4 (Drain Rohi) coming from the center of city is not carrying heavy pollution loads of tannery waste yet it carries effluent discharge from tanneries adjacent to Drain Rohi, which is mainly carrying municipal wastewater from the city. Another important feature of Drain 4 is that it is still unlined, however in the center of city this drain has recently been lined, which has not only increased its capacity within city but also provided safe embankment to the thickly populated residential area through which it passes. Drain 4 is also blocked at various places along its route, the prevailing situation can be observed in Fig. 13. Such high blockages results into immense overflow in the surrounding areas and affecting the agricultural crops badly.

Fig. 4.13: Drain 4 (Drain Rohi) passing through center of Kasur showing the blockage and end of the drain (picture taken in Nov 2008)

Due to improper solid waste management practices in the area most of the municipal solid waste gets stuck in the drains as it can be seen in Fig. 4.13, 4.14 & 4.15. Furthermore when these drains are cleaned for their sludge removal and solid waste disposals at the bed of the drains, the removed material is not properly disposed off rather it is dumped on the sides of the drains making a heap of waste in the surroundings of the drains.

Unlined Drain 4 (Drain Rohi), ends into a junction point with Drain 3 at Debalpur

Road (Fig. 4.14). This is a cement brick structured tank from where the effluent is carried for final disposal through the underground sewer, as shown in Fig. 4.15 and 4.16. Ultimately the wastewater collected from Drain 3 & 4 being carried by the underground sewer is thrown into the main drain "Drain 5", which is already carrying wastewater from a number of other industries which exist on its sides, outside the boundary of the city. The total length of underground sewer after the junction up to the final disposal point in Drain 5 is about 6 kilometers. From this drain the wastewater continues its path and finally opens into the River Sutlej.

Fig. 4.14: Junction of Drain 3 & 4 completely covered with waste disposal on the sides (picture taken in Nov 2008)

Fig.4.15: Endpoint of Drain 3 into a junction of Drain 3 & 4 (Dec 2009)

Fig. 4.16: Another view of junction showing the opening point of underground sewer for final disposal into Main Drain (picture taken in Dec 2009)

4.2.4 Local communities and Authorities involvement

After meetings with district authorities, DCO, District Coordinator Officer, and KTWMA officers, and based on the survey report it was finalized to conduct the research in the surrounding areas of Drain 3 and Drain 4.

4.3 Research Methodology

Surface contamination, which once was limited to tannery area, is heading beyond the drains and wastewater treatment plant, as obvious from the observations during field survey. Fig. 4.17 shows satellite image of nearby areas of drains and the adjacent agricultural fields which are potentially posed threat to human lives and environment.

Research methodology was divided into four phases, first two including preliminary and confirmatory site investigations respectively followed by Phase III and IV comprising of groundwater modeling to predict contaminant transport and health impact survey in the area regarding health conditions of the inhabitants. While in the end a framework to cope with the whole contamination scenario was proposed so as to conclude the research work.

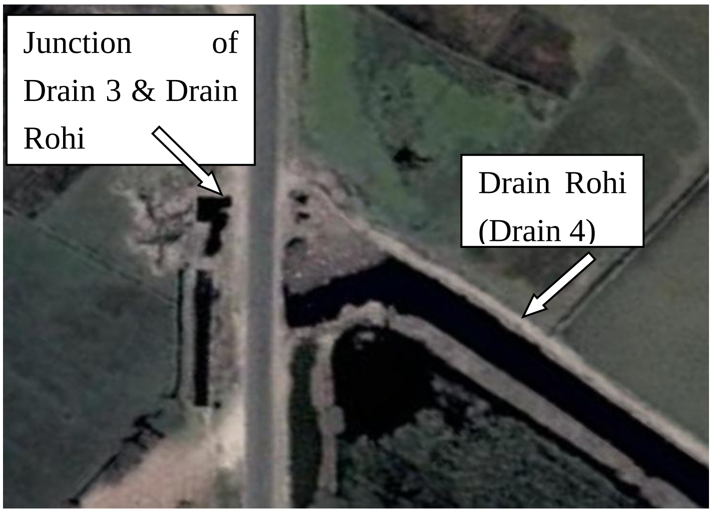


Fig. 4.17: Satellite image of junction of Drain Rohi and Drain 3 showing agricultural fields (Google earth)

4.3.1 PHASE I – Preliminary Site Investigations

Further rundown of the research conducted in this Phase is tabulated in Fig. 4.18. Initially overall sampling of soil, groundwater and wastewater was planned in order to understand the pattern of contamination in the study area. In this regard random sampling was preferred to be conducted on wide scale at important locations with reference to the contaminated sites. It would help to focus on critical areas which have significant role in transporting the contaminant from one medium to another i.e. from wastewater to soil and then groundwater. As most of the land was either agricultural land or owned properties of the residents along with industrial units, therefore the site selection for sampling was not possible in a symmetric manner. It mainly based on the availability of the site for sampling groundwater and soil. However it was ensured that each sampling point must have its significance regarding its location and should lead to logical comprehension of the contaminant transport mechanism.

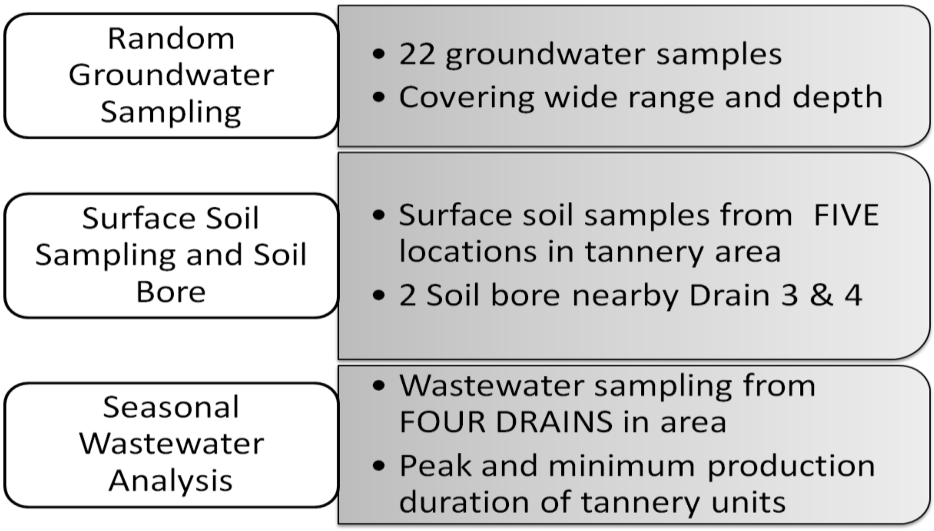


Fig. 4.18: Structure and sequence of Phase I methodology

4.3.1.1 Random Groundwater Sampling

Random groundwater samples from existing sources which include, tube wells, hand pumps and centrifuge pumps (motors), were collected from tannery area (Din Garrh), Basti Kambohan Wali, Kamal Chishti mazaar, Dole wala and Faqire wala. Initially 22 groundwater samples were collected, which were characterized on the basis of their source (hand pump, motor and tube well) and depth from where the water was drawn. These samples were analyzed for basic chemical parameters and total chromium concentration in the water samples. Location of sampling points were also observed using GPS meter. Table 4.1 described all the sampling details, including their coordinates, sampling source and nearest available source of contamination. The sampling locations of drinking water collected from different sources in the study area are shown in the site map in Fig. 4.19. While selecting the sampling location it was aimed to focus those areas which can guide the possible groundwater contamination flow trends. So that the results can be used to further extend the research in those areas.

Table 4.1: Groundwater sampling locations and their sources

No	**Location**	**Latitude Y**	**Longitude X**	**Sample**	**Possible depth**	**Possible Source**
1	Kamal Chishti Mazar	31°6'30.2"	74°28'6.5"	HP	< 30.5 meter	Drain 1 & 2
2	Kamal Chishti Chok	31°6'23.7"	74°28'11.7"	HP	< 30.5 meter	Drain 1 & 2
3	Kamal Chishti Chok (PCO)	31°6'21.4"	74°28'11.3"	HP	< 30.5 meter	Drain 1 & 2
4	Zameer ahmad BKW	31°6'23.5"	74°28'0"	HP	< 30.5 meter	Drain 1 & 2
5	Bashir ahmad BKW	31°6'20.8"	74°28'0.3"	HP	< 30.5 meter	Drain 1 & 2
6	Ramazan BKW	31°6'17.5"	74°27'58.8"	HP	< 30.5 meter	Drain 1 & 2
7	Ashar BKW	31°6'19.5"	74°28'0"	motor	30.5 to 122 m	Drain 1 & 2
8	Istakhar ahmad, BKW	31°6'21.2"	74°28'0.2"	HP	< 30.5 meter	Drain 1 & 2
9	Dr latif tann, DG	31°6'18.5"	74°27'24.7"	motor	30.5 to 122 m	Drain 1 & 2
10	Haji abbas tann, DG	31°6'21.2"	74°27'21.7"	motor	30.5 to 122 m	Drain 1 & 2
11	Bilal tann, DG	31°6'19"	74°27'23"	motor	30.5 to 122 m	Drain 1 & 2
12	Zeeshan ilahi tann, DG	31°6'21.9"	74°27'22.4"	motor	< 30.5 meter	Drain 1 & 2
13	Batala tann, DG	31°6'23.7"	74°27'23.9"	motor	30.5 to 122 m	Drain 1 & 2
14	Haji Naeem tann, DG	31°6'23.2"	74°27'22.3"	motor	30.5 to 122 m	Drain 1 & 2
15	Ghousia tann, DG	31°6'18"	74°27'19.5"	motor	30.5 to 122 m	Drain 1 & 2
16	Amanat tann, DG	31°6"19"	74°27'18.7"	motor	30.5 to 122 m	Drain 1 & 2
17	Haseeb tann, DG	31°6'20.7"	74°27'17.2"	motor	30.5 to 122 m	Drain 1 & 2
18	Dhera - DP road	31°5'24.2"	74°26'39"	TW	> 122 meters	Drain 4
19	tube well opp brick kiln	31°5'12.9"	74°26'19.5"	TW	> 122 meters	Drain 4
20	Dolewala adda	31°5'40.3"	74°27'8.8"	HP	< 30.5 meter	Drain 3
21	Mosque Dolewala adda	31°5'38.9"	74°27'7.7"	motor	30.5 to 122 m	Drain 3
22	Huts Dolewala adda	31°5'41.9"	74°27'11.7"	HP	< 30.5 meter	Drain 3

HP: Hand pump; DG: Din Garrh; DP Road: Debalpur Road; TW: Tube Well

The pH, TDS, EC and salinity were measured in field using EUTECH Instruments manufactured Multi Parameter PCSTestr 35 series (Fig. 4.20). The PET bottle used for sampling groundwater is shown in Fig. 20. In the laboratory, pH was measured by Electrode method, TDS by gravimetric method, hardness by titration, total chromium by spectro photometric method using AES - ICP. The groundwater samples were analyzed for the above described parameters by using the standard techniques at Environment Protection Department Punjab Lahore as described in standard methods for examination of water and wastewater (APHA, 1998). In field observations were used for comparison with laboratory observations obtained after experimentation.

4.3.1.2 Soil Sampling - Surface Soil Sampling

Surface soils were sampled from the areas adjacent to the tanneries for obtaining the maximum concentrations of chromium in the surface soil, and the samples from downstream side of the drains were also collected to find out the variation trend in chromium concentrations. Fig. 4.21 shows the surface soil sampling locations and their significance. Surface soil samples were also collected from city area where there were no tannery areas ever or which were on the upstream side of drains with no chances of surface overflow or soil contamination due to tannery waste. These values were used as the background values to compare with concentrations in the tannery waste affected soils.

4.3.1.3 Soil sampling - Soil Boring and Subsoil Sampling

In order to obtain basic information about the soil profile and concentration variation pattern of total and hexavalent chromium along the depth in the study area, initially two soil bores were conducted in the nearby vicinity of junction of Drain 3 and 4 as shown in Fig. 4.19 and Table 4.2 shows the coordinates of these soil bores. Subsurface soil strata were explored by conducting manual soil boring at two places up to the depth of 18.3 and 24 meters respectively. First bore was at a distance of 180 meters while the second bore was 350 meters from Drain Rohi.

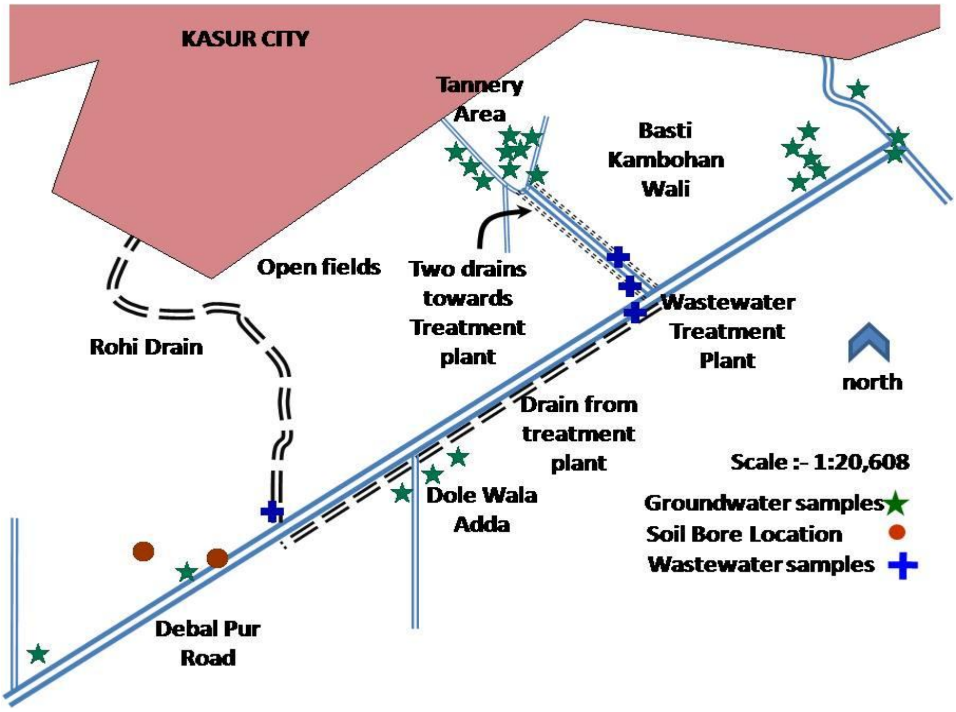
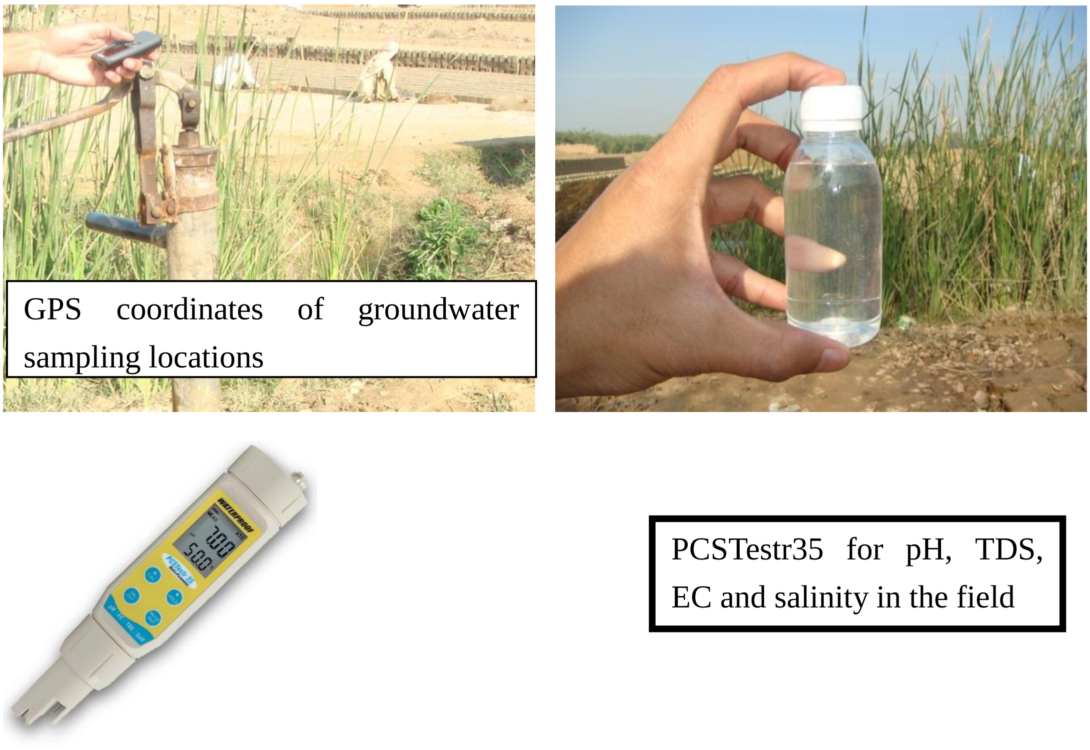


Fig. 4.19: Groundwater sampling, soil bore and wastewater sampling locations in Kasur study area


GPS coordinates of groundwater sampling locations

PCSTestr35 for pH, TDS, EC and salinity in the field

Fig. 4.20: In field determination using PCSTestr35 and sampling (June 2009)

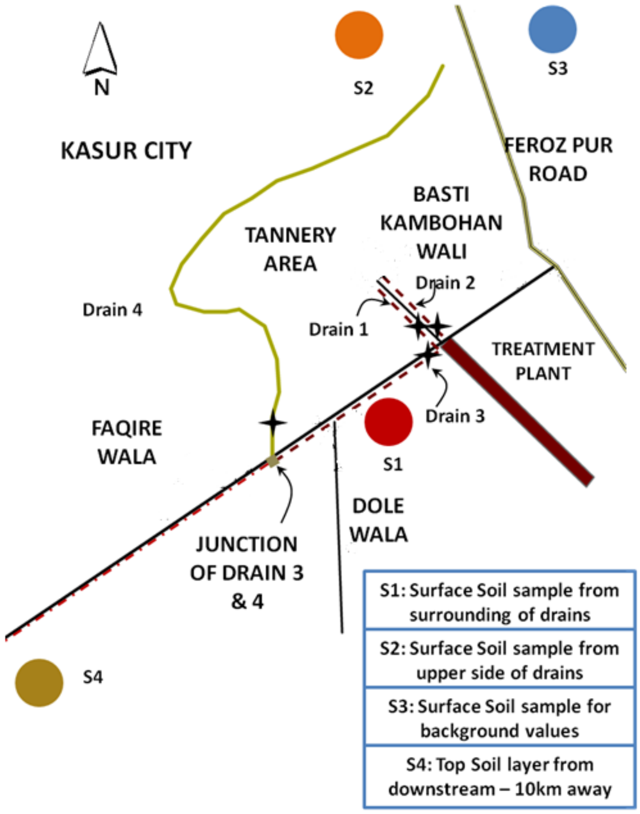


Fig. 4.21: Surface soil sampling locations in Kasur study area

For each soil bore, samples were collected at constant depth interval of 1.5 meters. For bore one thirteen (13), while for the second soil bore seventeen (17) soil samples were collected in total along the depth. Manual procedure for conducting soil bore was adopted which is also called agar method. Different steps while soil boring are shown in Fig. 4.22. While using manual bore method, immense amount of water was used for soil drilling, therefore it was not possible to take undisturbed soil sample. Physical soil texture observations were also noted at the field during the procedure. Variations in the soil textures observed were later on confirmed by conducting hydrometer analysis for particle size distribution analysis of the soil samples. Sometimes very hard clayey rock was observed as shown in Fig. 4.23 and sometimes all sand textured soil near groundwater aquifers.

Fig. 4.22: Different procedures, and tools and set up for manual soil bore (April 2011)

All the soil bores were manually conducted due to difficulty in mobilizing the heavy machinery for drill bore in remote study area. However it was best attempted to maintain the soil sampling and groundwater procedures so as to ensure precision in the results.

Fig. 4.23: Clayey layer present in the unsaturated zone in the study area (April 2011)

Fig. 4.24: Soil collection and sampling during soil boring (Picture taken in June 2009)

All the soil samples were collected and packed zipped polythene bags as shown in Fig. 4.24 for their safe carriage to the laboratories in Lahore and Tokyo Institute of Technology. . These soil samples were sun dried before conducting for further soil analysis for physical characteristics as well as for heavy metal determinations.

Initially these samples were tested for their particle size distribution in order to understand what type of soil profile does exist in the subsurface strata. These investigations also provided information about distribution of groundwater aquifers which could help in understanding the role of soil stratification in retaining or transporting the contaminant in subsurface layers.

TABLE 4.2: Two (2) soil bore locations for preliminary investigations (Phase I)

SOIL BORE	Latitude (N)	Longitude (E)	Distance from Drain 4
SB 1	31°05’25.5”	74°26’45.0”	180 meters
SB 2	31°05’24.4”	74°26’38.1”	350 meters

4.3.1.4 Analytical Methods and Chemical Analysis

Particle size distribution of the soil samples were obtained by using sieving and hydrometer methods. The soil samples were classified into Silt loam, Silty Clay loam, Sandy loam, Loamy sand, Loam and Sand on the basis of the percentage proportion of silt/clay/sand in the soil samples (Fig. 4.25). This type of analysis was conducted at Soil Survey Laboratory Lahore for all the soil samples collected from soil boreholes.

Fig. 4.25: Particle size distribution at laboratory of Soil Survey of Pakistan Lahore (June 2009)

Furthermore all the soil samples obtained from soil bores and from surface soil sampling were analyzed for leaching ability and total retention of total chromium and hexavalent chromium using TCLP (Toxicity Characteristics Leaching Procedure) and Aqua Regia Acid Digestion methods in Takemura Laboratory at Tokyo Institute of Technology.

Table 4.3: Wastewater sampling locations for seasonal variation analysis (June 2009 & Dec 2010)

DRAIN #	**CONDITION**	**Latitude (N)**	**Longitude (E)**
DRAIN 1	Untreated effluent to treatment plant	31°06’02.1”	74°27’38.8”
DRAIN 2	Untreated effluent to treatment plant	31°06’02.3”	74°27’39.3”
DRAIN 3	Diverted effluent & treatment plant effluent for final disposal	31°05’59.8”	74°27’38.8”
DRAIN 4	DRAIN ROHI – domestic and tannery waste	31°05’29.88”	74°26’49.86”

Fig. 4.26: Sample collection of wastewater from four drains in the study area during peak production duration in June 2009 and minimum duration in January 2010

4.3.1.5 Seasonal Wastewater Analysis

In order to incorporate the seasonal variation in the concentration of the chemical parameters in wastewater, the wastewater samples from the four drains in the study area were taken on seasonal basis for analysis. Firstly the wastewater samples were taken during the peak production season of the tannery industries, i.e. in the month of June 2009. The tanneries run at their peak capacity from May to September. During this duration peak discharge rates from the tanneries along with maximum concentrations of chemicals and other parameters is expected in wastewaters. Secondly the samples were taken in the month of January 2010, when most of the tanneries were out of production or closed and minimum discharge rates were expected. Sampling was not conducting during rainy season so as to avoid the impact of dilution of concentration of significant parameters of wastewater.

Four samples of wastewater were collected from the drains carrying effluent in the surrounding area of the tannery units as shown in Fig. 4.19 and the detailed sampling location along with coordinates is described in Table 4.3. First two samples were collected from the drains carrying untreated wastewater from the tannery area to the wastewater treatment plant, named as Drain 1 and Drain 2. At the time of sampling Drain 1 was flowing and Drain 2 was not. Third sample was taken from Drain 3, which carries the effluent from the wastewater treatment plant along with diverted untreated tanneries effluent. Fourth sample was collected from Drain 4 (Drain Rohi) near the junction of Drain 3 & 4 at Debal Pur Road. For peak duration sampling the samples was collected in June 2009 while for minimum duration the samples were collected in January 2010. But in both cases the sampling locations were not changed as described in Table 4.3.

The wastewater samples were collected in plastic bottles as shown in Fig. 4.26 and were kept in controlled temperature of 4°C and were delivered to EPD Punjab and PCSIR laboratories in Lahore within 30 minutes after collection so as not to disturb the original composition for accurate results of biochemical oxygen demand and other parameters. The wastewater samples were analyzed for the chemical parameters, pH, BOD_5, COD, TDS, TSS, chloride, sulphate, sulfide and total chromium by using the standard methods as described by USEPA.

4.3.2 PHASE II - Confirmatory Site Investigations

In order to further investigate the study area, confirmatory site investigation was conducted. Same approach was adopted as it was used in the first phase, but more detailed investigation of sub soil strata and groundwater was targeted in the second phase. Significant features of Phase II are described in Fig. 4.27, which constitute of further soil boring, installation of monitoring wells and extended seasonal wastewater analysis. The reason to conduct Phase I was to develop a baseline study and data collection which was planned to be used during Phase II. As it has been discussed earlier that there was severe lack of initial data, the results obtained in Phase I provided all the required information which was to necessary for development of methodology to conduct chromium transportation studies. Thus Phase II can be declared as extended part of previous phase so as to validate the findings.

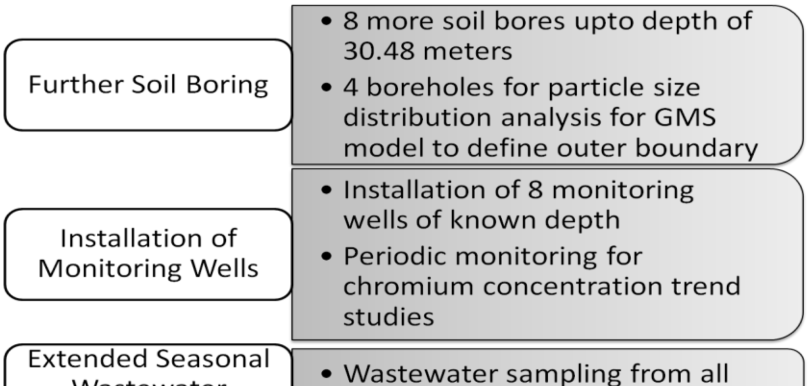


Fig. 4.27: Structure and sequence of methodology of Phase II – Confirmatory Phase

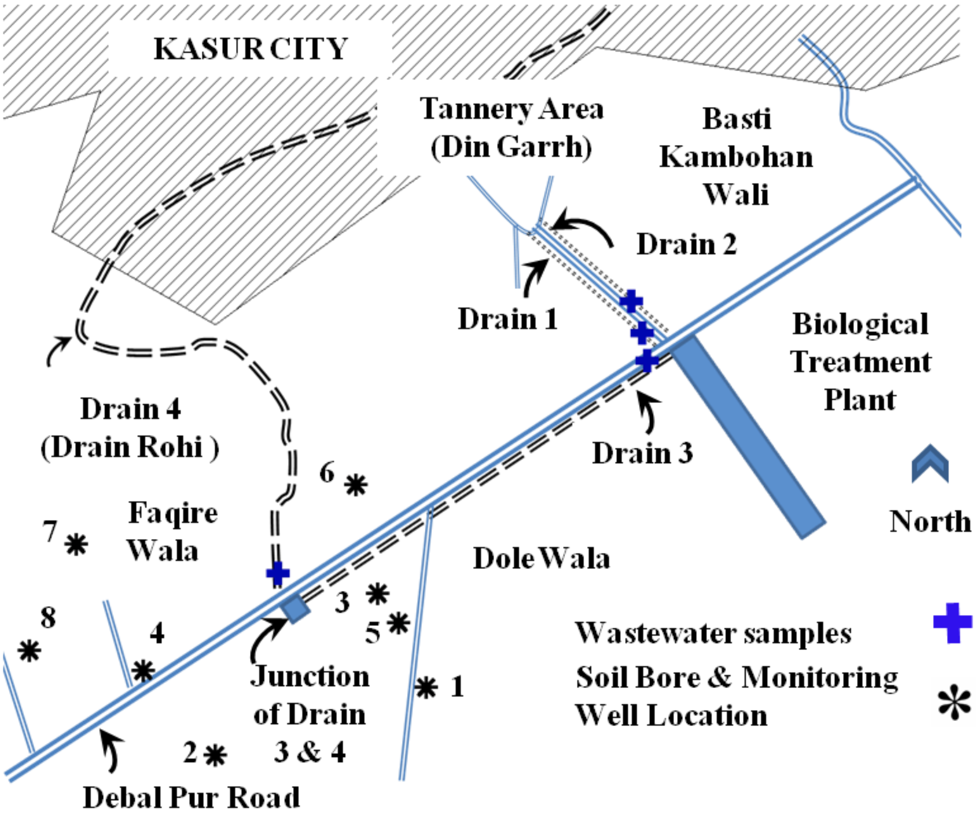


Fig. 4.28: Location of 8 soil bores and monitoring wells for Phase II

TABLE 4.4: Eight (8) soil bore and monitoring well locations for Phase (II)

Soil Bore & Monitoring Well	Latitude (N)	Longitude (E)	AREA
SB 1 & MW 1	31°05’26.7”	74°27’9.4”	DOLEWALA
SB 2 & MW 2	31°05’17.4”	74°26’44.2”	FAQIREWALA
SB 3 & MW 3	31°05’34.5”	74°27’5.7”	DOLEWALA
SB 4 & MW 4	31°05’21.8”	74°26’36.2”	FAQIRE WALA
SB 5 & MW 5	31°05’33.1”	74°27’7.2”	DOLEWALA
SB 6 & MW 6	31°05’40.2”	74°27’03.4”	DOLEWALA
SB 7 & MW 7	31°05’31”	74°26’27.2”	FAQIREWALA
SB 8 & MW 8	31°05’23.1”	74°26’23.6”	FAQIRE WALA

4.3.2.1 Soil Boring and Subsoil Sampling – For Confirmatory Phase

It was aimed to get maximum information about soil strata and in this regard as a continuation to the previous phase in which only two soil bores were analyzed, eight locations were selected in the same area but this time wider region was selected to maximum incorporate the study area. The location of eight (8) soil bores is presented in Fig. 4.28 and 4.29. The procedure adopted for conducting soil bores and soil sampling was same as in Phase I. However in Phase II the maximum depth was fixed upto 30.5 meters for every soil bore. In this regard 20 soil samples at every depth of 1.5 meters starting from the ground surface were collected. Thus in total 160 soil samples from all the eight (8) soil bores were taken and preserved for particle size distribution by Hydrometer method. Later on these samples were carried to Geo Environmental section, Takemura Laboratory, where these samples were further analyzed for leaching ability and total chromium retention for Total Cr and Hexavalent Cr by using Toxicity Characteristics Leaching Procedure (TCLP) and Aqua Regia Acid Digestion method respectively. For each soil bore water table levels were also measured which were repeated in December 2010 so as to find out the variation in water table level in aquifer during one year.

Four further soil bores were conducted whose locations are shown in Fig. 4.30. These soil bores are named Bore 9, Bore 10, Bore 11 and Bore 12. The objective to conduct these soil bores was to verify the soil strata and water table existing conditions along with the variation trend with time, describing the water table level fluctuations due to seasonal variations so as to help in obtaining physical characteristics which are all used for GMS – FEMWATER simulation in Chapter 6.

4.3.2.2 Monitoring Wells Installation

After conducting 8 soil bores at the constant depth of 30.5 meters, monitoring wells were installed in the same soil boreholes with known water table depths for each monitoring well as shown in Fig. 4.28 & 4.31. The purpose of the installation of these monitoring wells was to collect groundwater samples periodically once a month from all the wells so as to observe the variations in chromium concentrations at these monitoring wells. Later on these samples were carried to Environmental Quality Laboratories at Fatima Jinnah Women University Rawalpindi and Pakistan Council of Research in Water Resources (PCRWR) Islamabad for determination of total chromium concentrations. Thus groundwater was monitored periodically to understand the effect of particle size distribution and infiltration rate of chromium during different seasons.

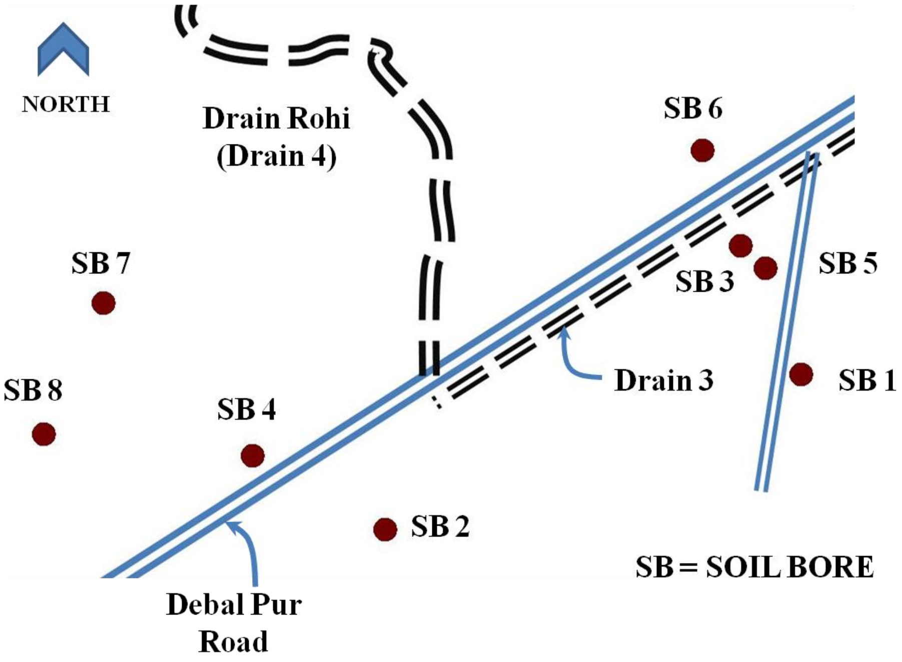


Fig. 4.29: Location of 8 soil bores conducted up to depth of 30.5 meters in surrounding area of Drain 3 and 4

It was targeted to have six (6) months of monitoring of groundwater at least so as to evaluate the seasonal impact on the changing trends of total chromium concentrations in groundwater aquifer.

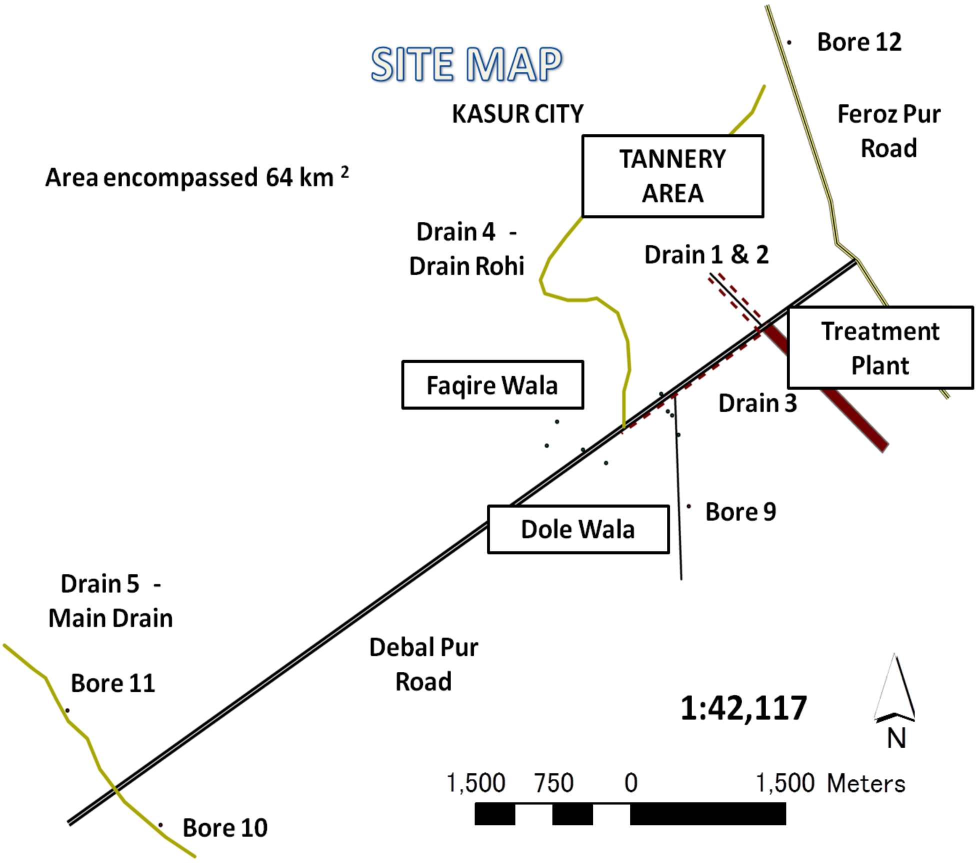


Fig. 4.30: Site map showing the location of additional boreholes to develop more accurate soil strata and water table depths for model calibration (GIS developed map)

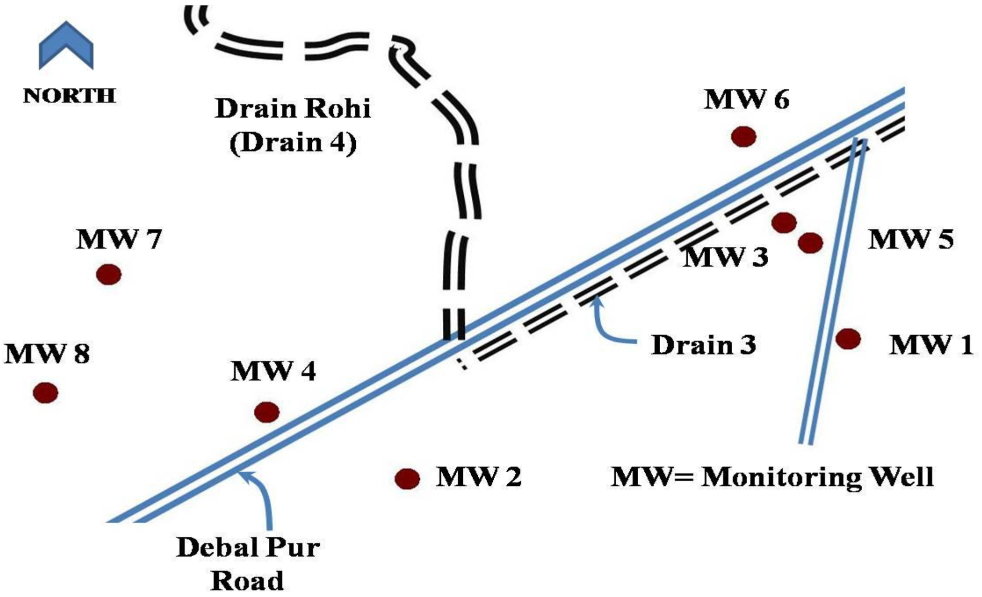


Fig. 4.31: Location of Eight (8) monitoring wells installed at the same place where 8 soil bore holes were conducted

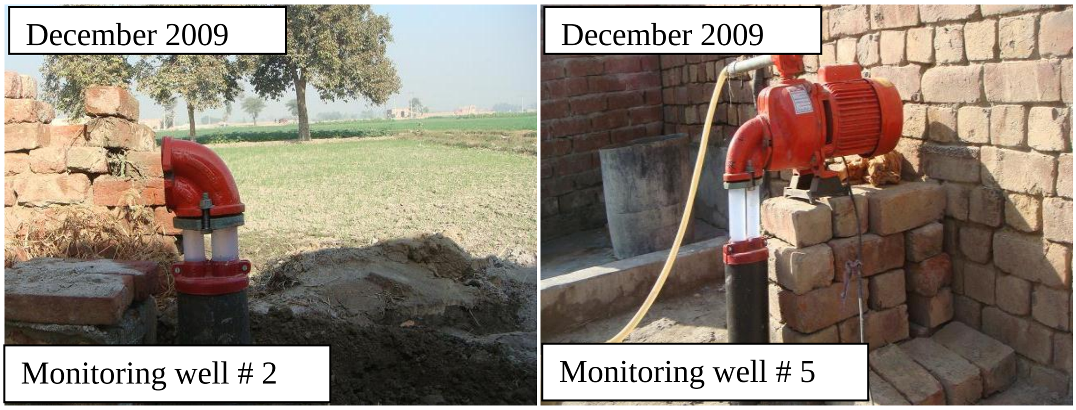


Fig.4.32: Eight (8) monitoring wells installed at different locations for periodic monitoring

4.3.2.3 Seasonal Wastewater Analysis – For Confirmatory Analysis

The fifth drain (Main Drain) was also included in Wastewater analysis and its seasonal variation was also investigated along with the other four drains in the area. The locations of all the drains from which samples were taken are shown in Table 4.5. Similar to Phase I, in this phase also the seasonal variation of soil samples were observed during minimum production duration and peak production duration in this regards the sampling was conducted in December 2010 and April 2011 respectively.

Table 4.5: Wastewater sampling locations for seasonal variation analysis (Dec 2010-April 2011)

DRAIN #	**CONDITION**	**Latitude (N)**	**Longitude (E)**
DRAIN 1	Untreated effluent to treatment plant	31°06’02.1”	74°27’38.8”
DRAIN 2	Untreated effluent to treatment plant	31°06’02.3”	74°27’39.3”
DRAIN 3	Diverted effluent & treatment plant effluent for final disposal	31°05’59.8”	74°27’38.8”
DRAIN 4	DRAIN ROHI – domestic and tannery waste	31°05’29.9”	74°26’49.86”
DRAIN 5	Groundwater Sewer opening in Drain 5 – final disposal of all wastes	31°03’29.8”	74°23’53.7”

4.4 Experimental Methodology

For all the soil samples collected from ten (10) soil boreholes and also from the surface soil sampling, analysis was conducted for total retention in soil and for leaching behaviour in soil by using Aqua Regia Acid Digestion and Toxicity Characteristics Leaching Procedure (TCLP) for both total chromium and hexavalent chromium respectively. Furthermore DR 2800 spectrophotometer was used to find out the concentration of total and hexavalent chromium in respective solutions.

4.4.1 Aqua Regia Acid Digestion

The amount of total chromium and hexavalent chromium retained in the soil existing in both liquid and solid phase in the soil was determined by extraction of chromium content from the soil by aqua regia acid digestion (Hindu, 2008)

In a 200 ml glass beaker, about 0.5 mg of the soil powder was mixed with 2 ml of nitric acid (HNO_3) and 4ml of hydrochloric acid (HCl). The beaker was then placed in a thermostatically controlled oven at a temperature of 95^oC for 45 minutes. The beaker was covered with a glass plate to reduce chances of evaporation. After digestion, the soil-solution was allowed to equilibrate with room temperature. Then, the soil-solution was diluted with 100 ml of 1% nitric acid solution. To separate soil and solution, the soil-solution was kept in the still condition for 30 minutes and then poured into 50 ml centrifuge tubes and centrifuged for 30 minutes at 4000 rpm by using the centrifuge. Then, the supernatant from the centrifuge tube was filtered by using a 0.26 mm thick filter with 1.2 µm openings and 47 mm diameter (GF/C Whatman). The filtered solution was stored in a 250 ml Erlenmeyer flask the flasks were then kept in a refrigerator with a temperature of 10^oC until the time when solution could be analyzed to obtain the total and hexavalent concentration retained in the unit mass of soil (C_{soil}).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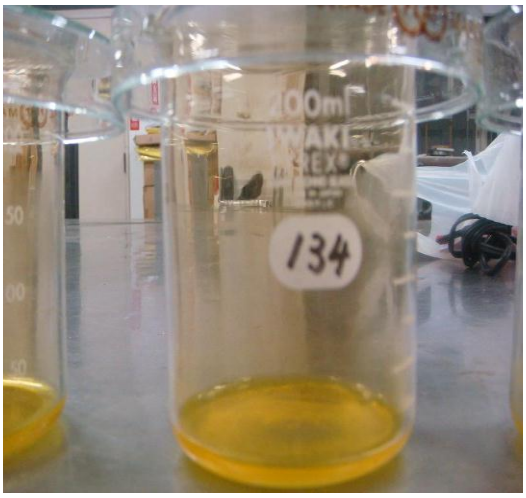
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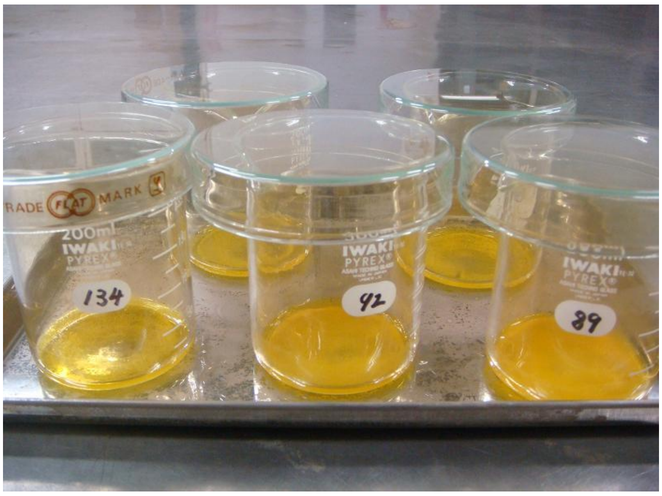
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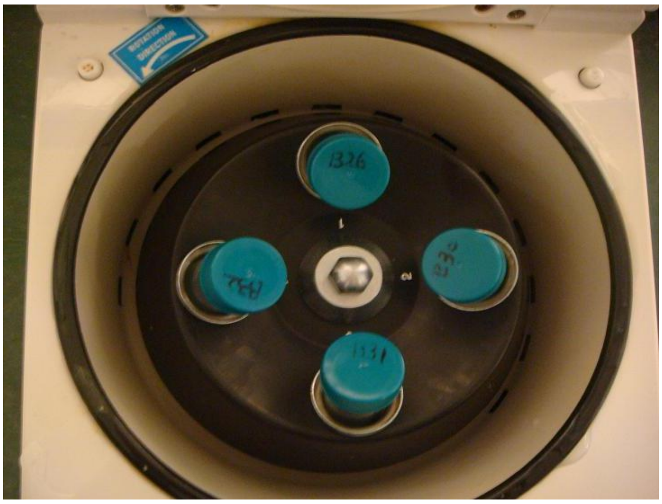
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Fig. 4.33: Different processes of aqua regia acid digestion method for chromium retention determination at Takemura Laboratory, Tokyo Institute of Technology

4.4.2 Toxicity Characteristic Leaching Procedure (TCLP)

The standard USEPA Test method 1311 for toxicity characteristics leaching procedure (USEPA TCLP, 1990) was adopted to understand leaching behaviour of hexavalent and total chromium in the soil samples collected from soil bore and surface in study area.

Toxicity Characteristic Leaching Procedure (TCLP) follows three steps to evaluate the samples; 1) determination of extraction fluid, 2) preparation of extraction fluid, and 3) extraction and filtration. All of these will be explained in detail below;

Equipment

Magnetic Stirrer+heater

pH meter

filtration equipment

Reagent

Distilled water

HCl 1 N

NaOH 1 N

Glacial acetic acid (CH_3CH_2OOH)

Nitric acid (HNO_3) 1 N

PROCEDURE

Determination of Extraction Fluid

1. Sample 5 g
2. Add Distilled water 96.5 ml
3. The samples are mixed using a magnetic stirrer for 5 minutes.
4. Determine pH of the sample

If the pH < 5 will be used extraction fluid 1

If the pH > 5, the sample will be added 4.5 ml of hydrochloric acid (1N HCl) then the slurry of the sample will be heated to 50 °C for 10 minutes. The mixture is allowed to cool to room temperature and the pH is measured.

If the pH < 5 will be used extraction fluid 1

If the pH > 5 will be used extraction fluid 2

Preparation of Extraction Fluid

Extraction fluid 1

1. Glacial acetic acid 5.7 ml will be added to 500 ml distilled water
2. Add sodium hydroxide (NaOH) 64.4 ml
3. Dilute the fluid to 1000 ml

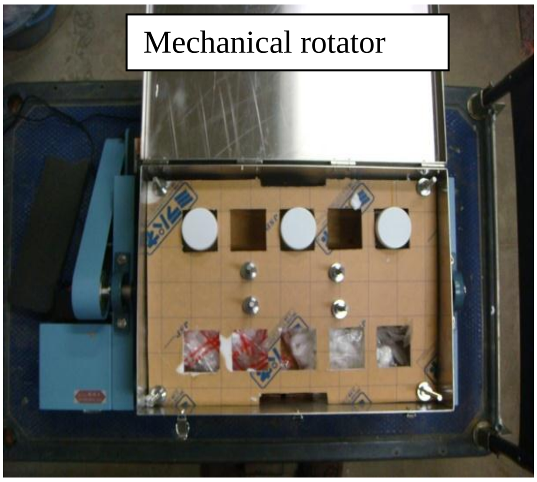
The pH of this solution is maintained around 4.94±0.05. If the pH does not fall between the ranges, the appropriate calibration is done by the addition of glacial acetic acid or 1 N sodium hydroxide.

Extraction fluid 2

1. Dilute 5.7 ml of glacial acetic acid with distilled water to 1000 ml.
2. The pH of this fluid must be within the range of 2.88±0.05. If the pH falls out of the range, it must be calibrated similar to that of extraction fluid 1.

Extraction and Filtration

After determining the appropriate extraction fluid for the sample, the extraction fluid was mixed to the soil mass with the volume of the extraction fluid in milliliters 20 times the mass of the sample in grams. The sample slurry was then subjected to a rotary extractor for 18±2 hours at a rate of 30 rpm. Subsequent to the extraction, the leachate was separated from the solid phase through decantation and pressure filtration. Prior to filtration, the filter paper was acid-washed so that the heavy metal contaminants would not adhere to the filter. The filtrate was placed in acid-washed PET bottles and the pH of the filtrate was calibrated to less than 2.0 by the addition of concentrated Nitric Acid.


Mechanical rotator


Prepared Soil Extract


Filter Assembly


Filtered Soil Extract

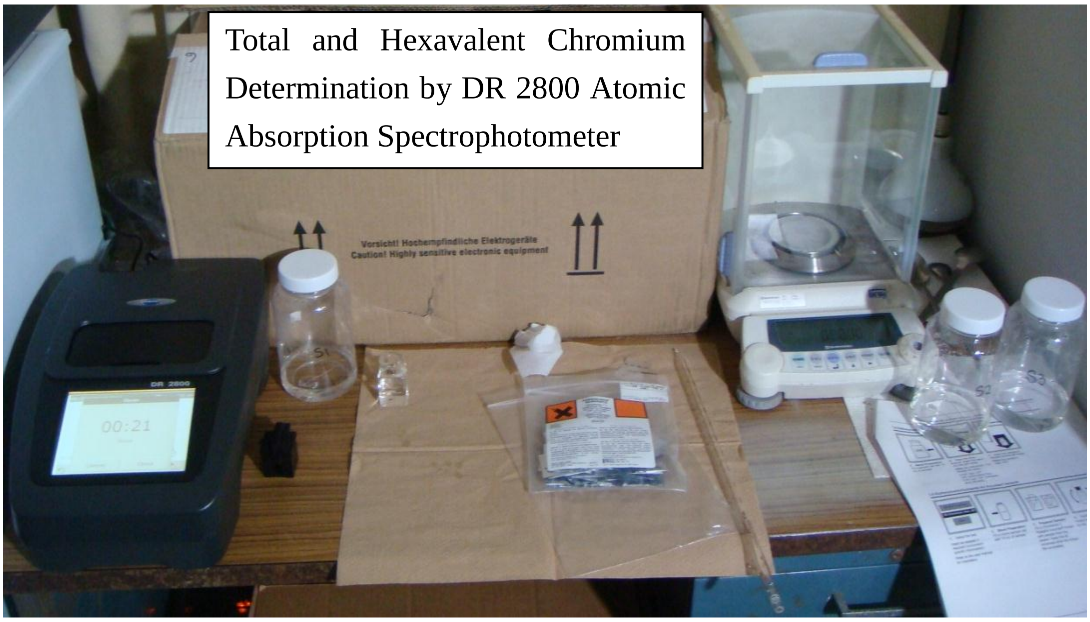


Fig. 4.34: Different processes for TCLP experimentation

4.4.3 Concentration of Total Chromium and Hexavalent Chromium Measurement Using DR 2800 Spectrophotometer

Following Chromium determination method as defined by standard procedure by Hach (Hach, 2008a; Hach, 2008b), total and hexavalent chromium was analyzed by using DR 2800 spectrophotometer. The items required for analysis of Total Chromium were Acid Reagent Powder Pillows, ChromaVer® 3 Chromium Reagent powder Pillows, Chromium 1 reagent Powder Pillow, Chromium 2 reagent Powder Pillows, Hot Plate, water Bath , finger cots and samples cells. First of all instrument was set for stored programs to chromium total. A sample cell of 25 mL was filled with sample. One chromium 1 reagent powder pillow was added swirled and mixed. Removing the cap the prepared sample was inserted in boiling bath. After five minutes time reaction, the prepared sample was taken out and capped and running water was used to cool the sample. Contents of one acid reagent powder pillow were added and swirled to mix. The contents of one ChromaVer®3 chromium reagent Powder pillow were added, swirled and mixed. Instrument timer was started. While the sample was reacting, 10 mL from the mixing bottle into a second sample cell. After the time expired another sample cell was filled with 10 mL of sample. This was the blank sample preparation. This blank sample was placed in the cell holder. The instrument was adjusted at ZERO reading showing the display as 0.00mg /L Cr. Then the prepared sample was placed in the cell holder and the reading as displayed was noted. This was the mg/L of the Cr concentration.

For hexavalent chromium determination, using DR 2800, first of all 90, Hexavalent chromium program was started. The sample was prepared by filling a sample cell with 10 mL of sample. The contents of ChromaVer®3 Reagent powder pillow were added to the sample cell. After swirling, purple color showed the presence of hexavalent chromium. Blank sample was prepared by adding 10 mL of sample. Then blank sample was placed into cell holder and ZERO was adjusted. Then the sample cell was placed in the cell holder and reading of hexavalent chromium in sample was obtained in mg/L Cr^{6+}.

4.4.4 Final Chromium Concentrations Determination

While conducting Toxicity Characteristics Leaching Procedure (TCLP) the values obtained for both total chromium and hexavalent chromium were depicting the leaching behavior in solution as concentration of total or hexavalent chromium in mg/L. But for aqua regia acid digestion method, the values are required to be obtained in mg/kg because the mass adsorbed with solid phase soil medium is required. Therefore the concentrations of total and hexavalent chromium obtained for solution in mg/L from DR 2800 results, required to be converted in mg/kg. The concentration that was measured ($C_{measured}$) from the spectrophotometer was converted to the mass of total chromium and hexavalent chromium in unit mass of the soil (C_{soil}) in mg/kg by using following equation

$$C_{soil} = \frac{C_{measured} \times Volume_{(liquid)}}{M_s} \qquad (1)$$

In this equation the $C_{measured,}$ is the concentration obtained from the analysis of the extraction, by using the spectrophotometer. $Volume_{(Liquid)}$ is the volume of the solution used for the extraction and M_s is the amount of the soil sample in grams. Finally C_{soil} is the amount of total chromium or hexavalent chromium retained in unit mass of the soil.

4.5 Impact Evaluation Approaches

4.5.1 Voxler Software for geospatial distribution

Voxler ® 3 D geologic and scientific modeling software was used in order to understand the spatial distribution of total and hexavalent chromium in the study region. Main purpose of its application was not only to work out the pattern of contaminant concentration in three dimensional domains of the area but also to determine the contaminant load at each sampling location along with the prediction of future trends of concentration gradients based on the nature of groundwater flow mechanisms. 3 Dimensional graphical presentations were developed by using Voxler software for depth wise concentration variations as obtained for all the Eight (8) soil boreholes. Results for mobility of total chromium and hexavalent chromium as determined by TCLP through soil layers and retention of total and hexavalent chromium in the soil medium were graphed for Voxler 3 D presentation. With Voxler's extensive 3D modeling tools, it is easy to visualize multi-component data for geologic and geophysical models, contamination plumes, LiDAR point cloud, borehole models, or ore body deposit models. Distinguish areas of interest, highlight important information, and easily communicate knowledge to stakeholders in three dimensions.

The purpose of using Voxler ® was particularly to incorporate field collected data directly in simulation so as to demonstrate 3 dimensional behavior of contaminant transport with the research area. GMS modeling with the help of FEMWATER however is very much specific to contaminant concentration variation with respect to time. Therefore in order to only develop the scenario of existing situation, how the contaminant exhibits its existence in its particular location, i.e. soil layers and varied soil contents, Voxler software was used.

4.5.2 GMS – FEMWATER

Stratification and groundwater modeling based on the real time scenarios were conducted by using GMS – FEMWATER. It was applied in order to find out the concentration gradient with reference to specific time variations. Its application differentiates from that Voxler in terms of model development with reference to time and space simultaneously. It helped in demonstrating the subsurface geological conditions and its stratification. The data obtained from soil texture analysis was used to define different layers which ultimately developed the three (3) dimensional soil profiles within the domain of the model. Furthermore the research site maps were geo referenced to exactly correlate with the existing global positioning system.

Studies on subsurface lithology by applying 3 dimensional geological modeling with the help of GMS modeling software have gained significant focus by most of the groundwater modelers and geological researchers. (Touch, 2014)

Different industrial pollution scenarios were developed in order to express the empirical mode of contamination transport which was presented based on the existing contamination loads and mass flux, so that future prediction may be demonstrated for the simulation of tannery pollutants at father distances.

Geological data obtained from the field, which consist of soil texture and particle size distribution, along with other soil data pertaining to hydraulic conductivity, bulk density and soil moisture contents were used as input data in order to develop the FEMWATER model simulation. The earlier developed scenarios were converted to conceptual models based on their specific input parameters. Standard procedures required to develop the model were adopted as described in GMS FEMWATER manuals (GMS, 2016). Defining of the boundary conditions and initial conditions were according to the previously available literature and GMS manuals.

4.5.3 Health impact evaluation

In order to conduct health impact evaluation, previously conducted field survey and interview data was used and analyzed in order to describe the toxicology of the chromium concentration in groundwater and soil medium. The most important fact required in this regard was the total intake dosage of chromium into the human body. It was evaluated based on the fact that the availability of chromium concentration in water was compared to the total population which is consuming this contaminated groundwater. Then total intake dosage was estimated and thus health impact of chromium on residents in the area were determined.

4.6 Research limitations

During conducting field survey and laboratory investigations following limitation were observed in obtaining accurate data. A few of the mentionable limitations are described briefly as follows.

There is no research studies conducted so far which may explain the subsoil strata information of soil and its behavior with heavy metals present in the leachate from the tannery waste. No such research work has been found in the area which may depict groundwater on wide range showing the flow pattern of groundwater contamination.

No detail about the hydrologic details of all the drains in the area is available. There is also no mechanism of determining discharge rate in these drains for frequent observations.

The surroundings of the drains are mostly agricultural lands or residential areas. Therefore a great difficulty was faced in obtaining the permission to conduct soil boring on such large scale as done in this research. It was even more difficult to install monitoring wells under the ownership who may is supposed to be responsible for bearing the running cost of these monitoring wells. As the research area lies in suburbs therefore there are no proper modes of communication and utilities in the area. Therefore to arrange for electric power supply to monitoring wells was very challenging especially when the samples had to be taken on periodic basis.

Soil, groundwater and wastewater samples had to be transferred to big cities like Lahore, Rawalpindi and Islamabad for chemical analysis. Therefore it was not easy to carry these samples with precise time margin after collection. Therefore chances of discrepancies in results are quite high and accuracy in data obtained could be questionable.

Kasur being just 10 kilometers from the border with India, lies in high security zone. Therefore SPARCO and Geological Survey of Pakistan could not provide detailed map sheets for topographic, geological and hydrogeological maps of the area. Unavailability of so crucial information and maps was really a major shortcoming faced throughout the research.

Undisturbed soil sampling for core sampling at deeper depths could not be obtained due to difficulty in mobilization of heavy machinery in remote areas.

CHAPTER 5

RESULTS OF SITE INVESTIGATIONS AND DISCUSSION

5.1 Introduction

Based on the site investigations and sampling procedures in Phase I and II as explained in the previous chapter, the results of the groundwater, wastewater and soil boring and surface soil sampling are described and discussed in detail in this chapter.

5.2 Phase I (Preliminary Site Investigations)

Results of groundwater samples, initial soil bores, wastewater samples collected in Phase I are described and discussed as follows.

5.2.1 Random groundwater sampling

Twenty two (22) groundwater samples from the existing sources were collected for random groundwater analysis in the study area. These samples were obtained from different sources which include hand pump, motors and tube wells and represent shallow, middle and deep sampling depths with possible depth ranges of $\leq$ 30.5 meters, 30.5 to 122 meters and > 122 meters respectively. The results of groundwater samples analysis for basic chemical properties and total chromium concentrations, along with sampling distance from the nearest line source of contamination are shown in Table 5.1.

From the results as shown, it can be observed that pH for all the samples, as ranging from 6.9 to 7.6, was found to be within permissible limit of 6.5 to 8.5 set by USEPA secondary standards (USEPA, 1992).

For all the samples, total dissolved solids were observed to range from 1,060 to 6,770 mg/L having all values higher than the permissible limit of 500 mg/L according to secondary standards set by USEPA (USEPA, 1992). Fig. 1 shows TDS values plotted against the possible distance of sampling points from the nearest source. As TDS is a measure of the dissolved solids in water, it can be observed that the values of TDS are extremely higher for sampling points which are nearer to the source. Furthermore samples collected from motor source in tannery area are showing relatively higher values than those samples collected from other areas.

A correlation existed between electrical conductivity and TDS, describing that TDS is 0.55 to 0.9 times the electrical conductivity (Hoko, 2005). Taking the average of the range of 0.55 to 0.9, i.e. 0.725, and dividing the TDS permissible limit of 500 mg/L by this value, EC became approximately equal to 690 µS/cm. This limit for electrical conductivity is used as standard limit as reference. It can be observed from Table 1 that all the values for electrical conductivity are higher than 690 µS/cm as the values are ranging from 1,690 to 10,750 µS/cm. Fig. 2 shows the electrical conductivity values of twenty two (22) groundwater samples plotted against the distance from the nearest source of contamination. Similar pattern can be observed for electrical conductivity as it was observed for TDS. It is mainly due to the fact that electrical conductivity is actually presenting the measure of ion activity while TDS is measure of the total ions present.

Hardness does not pose any health risk however it can be a nuisance regarding taste and aesthetic point of view. Depending upon the interaction of other factors, such as pH and alkalinity, water with hardness above approximately 200 mg/L may cause scale deposition in treatment works, distribution system and pipe work and tanks within buildings (WHO, 2012) As far as results of hardness, measured as $CaCO_3$, are concerned, three samples in Basti Kambohan Wali from the hand pump source and three samples from tannery area from motor source have shown relatively lesser values than the others. Fig. 3 describes variation of hardness for all the twenty two thirty (22) samples with the distance from the nearest source. Hardness values are not only higher in the samples from the nearer locations to the source but also in a few samples which are at farther distance from the source. Hardness is also due to dissolved minerals in the water like TDS and EC. Showing almost the same pattern of variation as that of TDS and EC, hardness is found in excess in the samples taken from the hand pump and motor pump sources as well.

For results of total chromium in groundwater, it can be observed that samples from the northeastern sides including the locations of Kamal Chishti Mazar, Kamal Chishti Chok and Basti Kambohan Wali have not evidenced presence of total chromium either from samples taken from hand pump or motor pump source. However for tannery area (Din Garrh) sample number 12, taken from motor pump source has shown extremely high concentration up to 90 mg/L while other samples from the motor pump sources in the same area were below maximum contaminant level of 0.1 mg/L for total chromium as set by USEPA (USEPA, 1992). Such a high concentration is most probably due to the undefined parameter of the sampling depth and may be due to potential source of contamination e.g. stagnant ponds. Likewise one hand pump sample (sample number 20) on the southwestern side in Dole Wala, on the downstream of Drain 3, has shown alarmingly higher concentration of total chromium of 10 mg/L just at a distance of 6 meters from line source of contamination i.e. Drain 3. There is great possibility of direct interference of wastewater with the groundwater aquifer for this point.

The results are plotted in Fig. 5.4 for total chromium concentration against the distance of the sampling locations from the nearest source. No specific trend could be observed from the graph as only two samples showed existence of chromium in groundwater samples. But the values obtained for those two samples reveal the contamination level for total chromium far more than the maximum contaminant level of 0.1 mg/L as defined by National Primary Drinking Water Regulations (USEPA, 2009) are extremely high, of 90 mg/L and 10 mg/L concentrations. Such alarming values are not only clear indication of presence of chromium contamination in groundwater aquifer. It indicated the severity of the chromium contamination in the groundwater in the areas of Dole Wala and Faqire Wala, which are at the downstream of Drain 3 and 4.

Table 5.2 provides relevant statistical distribution parameters. The comparison of average and median values shows that there exists a lesser variation for electrical conductivity and hardness with reference to mean values. Large standard deviation values for total chromium indicate a large fluctuation of the concentration in the groundwater while TDS, EC and hardness has not shown much deviation. The higher kurtosis values in the case of chromium indicate that most of the variance is due to infrequent extreme deviations. The skewness results depict that the higher the values from zero the higher is the deviation from mean values, showing positive skewness. In this case the chromium has the highest positive skewness value with the highest deviation referenced to the mean value of it. It depicts unsymmetrical data distribution.

Table 5.3 presents the correlation coefficient matrix for the basic parameters and total chromium. The data is evaluated on the basis of correlation between the different parameters in terms of the significant positive correlation coefficient i.e. $r \geq 0.361$, at $p \leq 0.05$, where p value is the 5 % estimated probability of the rejection of hypothesis. Strong positive correlation was observed between TDS-EC, TDS-hardness, EC-hardness. Heavy metal total chromium has not shown any significance correlation with any of the other chemical parameter.

Even all the basic parameters were found to be in excess and existed in significant concentrations, the major contaminant; chromium released from the tanneries has not shown any particular trend across the research area. At some particular locations the alarmingly high values of total chromium are indication of alarming situation in groundwater but no trend can specifically be described based on this chromium speciation results of chromium in saturated aquifers. It is due to source dependent origin of chromium contamination in surface and subsurface in the form of clusters.

Table 5.1: Groundwater samples collected from existing sources

Sample No	**Sample Area**	**Nearest Source**	**Source Distance (m)**	**Sampling Source**	**TDS (mg/L)**	**EC µS/cm**	**Hardness as $CaCO_3$ (mg/L)**	**Total Cr (mg/L)**
1	Kamal chishti mazar	Drain 1 & 2	1,120	Hand Pump	1,070	1,690	220	< 0.01
2	Kamal chishti chok	Drain 1 & 2	1,085	Hand Pump	1,090	1,710	200	< 0.01
3	Kamal chishti chok	Drain 1 & 2	1,025	Hand Pump	1,110	1,760	220	< 0.01
4	Basti Kambohan Wali	Drain 1 & 2	850	Hand Pump	1,120	1,795	90	< 0.01
5	Basti Kambohan Wali	Drain 1 & 2	800	Hand Pump	1,150	1,825	105	< 0.01
6	Basti Kambohan Wali	Drain 1 & 2	700	Hand Pump	3,670	5,750	345	< 0.01
7	Basti Kambohan Wali	Drain 1 & 2	765	Motor	1,240	1,940	500	< 0.01
8	Basti Kambohan Wali	Drain 1 & 2	810	Hand Pump	1,150	1,820	120	< 0.01
9	Tannery area (Din Garrh)	Drain 1 & 2	52	Motor	3,540	5,640	135	< 0.01
10	Tannery area (Din Garrh)	Drain 1 & 2	68	Motor	5,310	8,350	500	< 0.01
11	Tannery area (Din Garrh)	Drain 1 & 2	35	Motor	3,820	6,000	470	< 0.01
12	Tannery area (Din Garrh)	Drain 1 & 2	100	Motor	3,200	5,040	495	90
13	Tannery area (Din Garrh)	Drain 1 & 2	165	Motor	1,090	1,740	100	< 0.01
14	Tannery area (Din Garrh)	Drain 1 & 2	125	Motor	1,060	1,690	95	< 0.01
15	Tannery area (Din Garrh)	Drain 1 & 2	22	Motor	6,770	10,750	810	< 0.01
16	Tannery area (Din Garrh)	Drain 1 & 2	33	Motor	3,910	6,080	530	< 0.01
17	Tannery area (Din Garrh)	Drain 1 & 2	24	Motor	3,950	6,240	450	< 0.01
18	Debal Pur Road	Drain 4	320	Tube Well	1,590	2,490	220	< 0.01
19	Debal Pur Road	Drain 4	940	Tube Well	1,620	2,570	460	< 0.01
20	Dole Wala	Drain 3	6	Hand Pump	1,670	2,620	455	10
21	Dole Wala	Drain 3	21	Motor	1,910	3,000	420	< 0.01
22	Dole Wala	Drain 3	13	Hand Pump	3,590	5,620	400	< 0.01
	USEPA Permissible Limits (USEPA, 1990, 1992)				500**	690*	No guidelines	0.1**
	WHO Guideline Values (WHO, 2008)						No guidelines	0.05

MW – monitoring well installed at the depth of 30.5 meters; 0.01 is the detection limit for total chromium; *derived limit; ** 0.1is Max. Contaminant level for drinking water

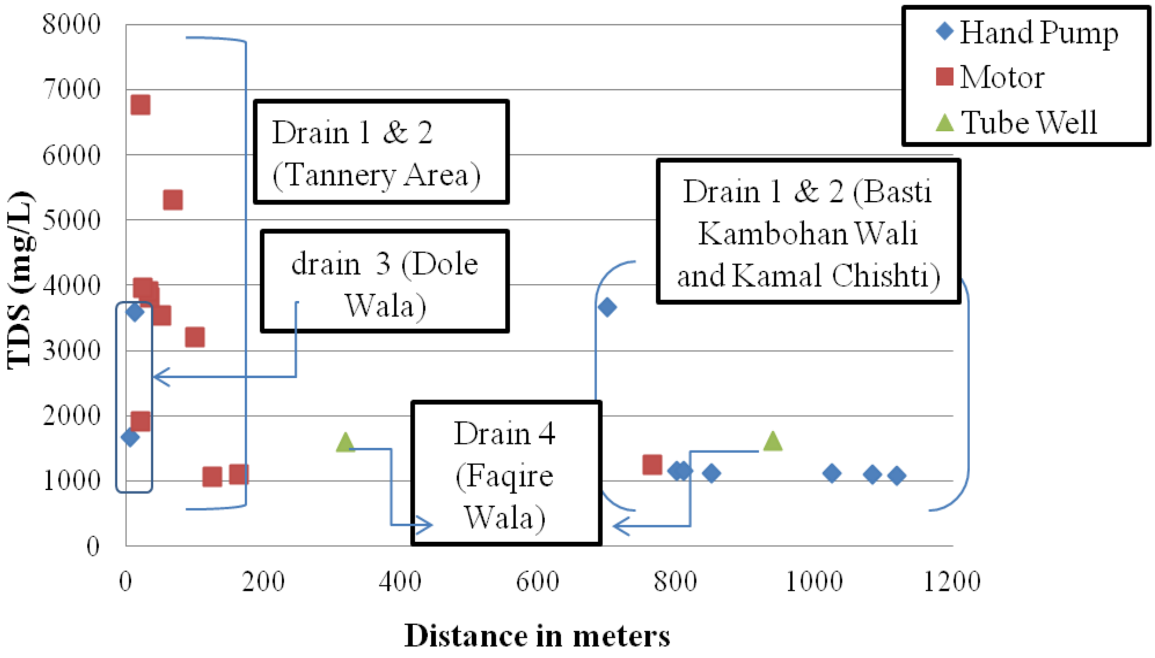


Fig. 5.1: Graph presenting TDS results for random groundwater samples

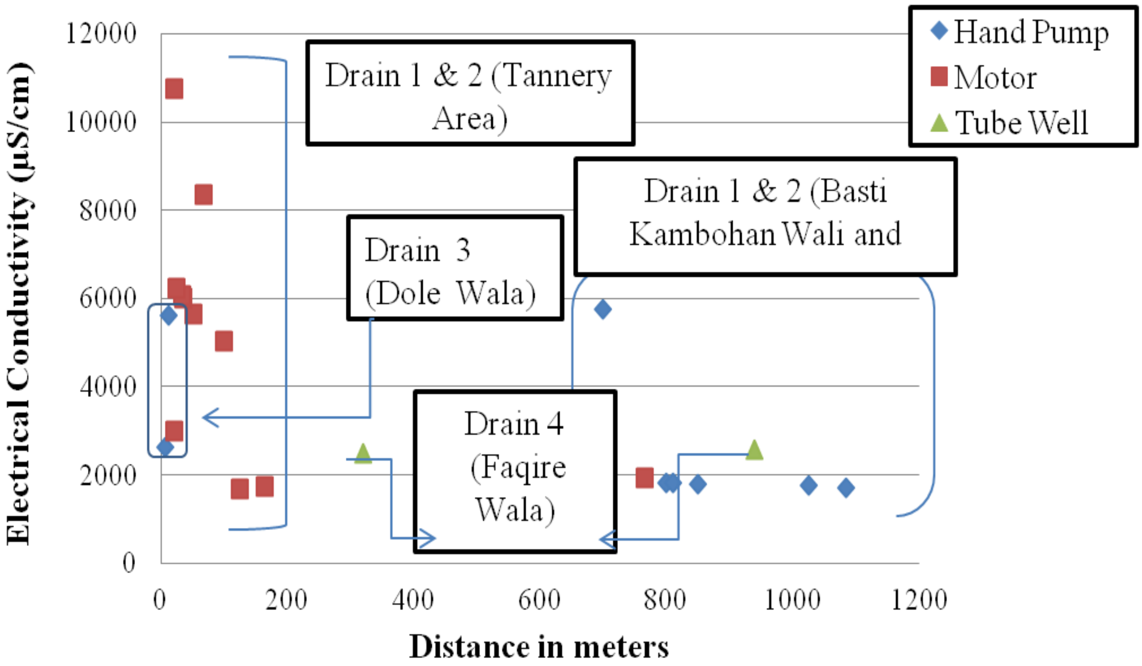


Fig. 5.2: Graph presenting electrical conductivity of random groundwater samples

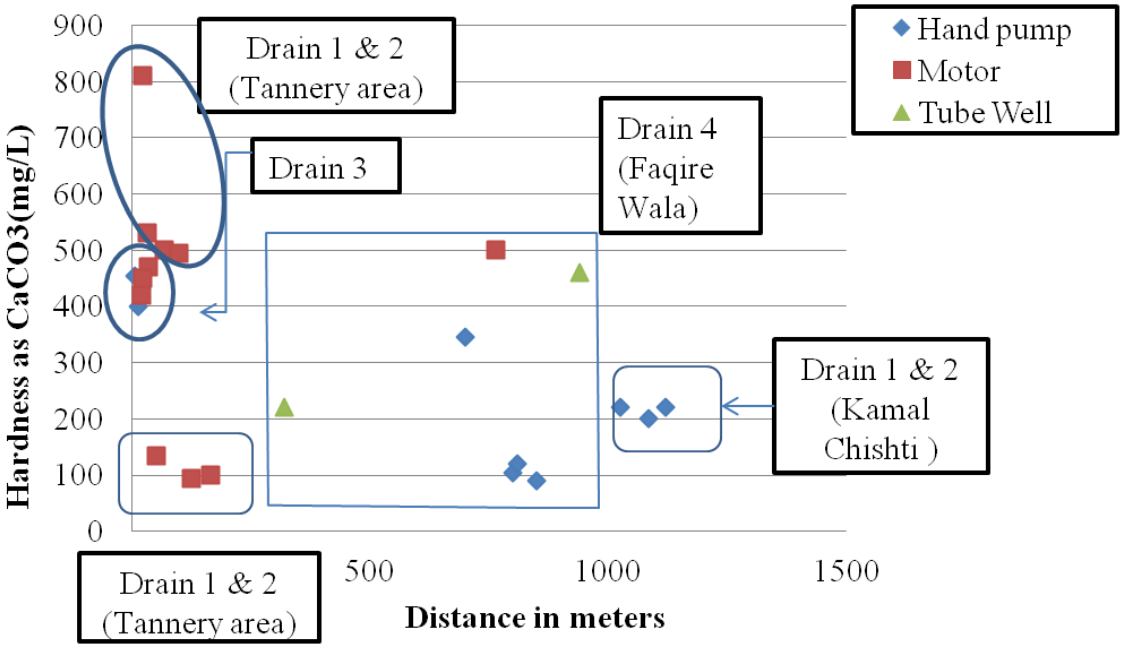


Fig. 5.3: Graph presenting hardness of random groundwater samples

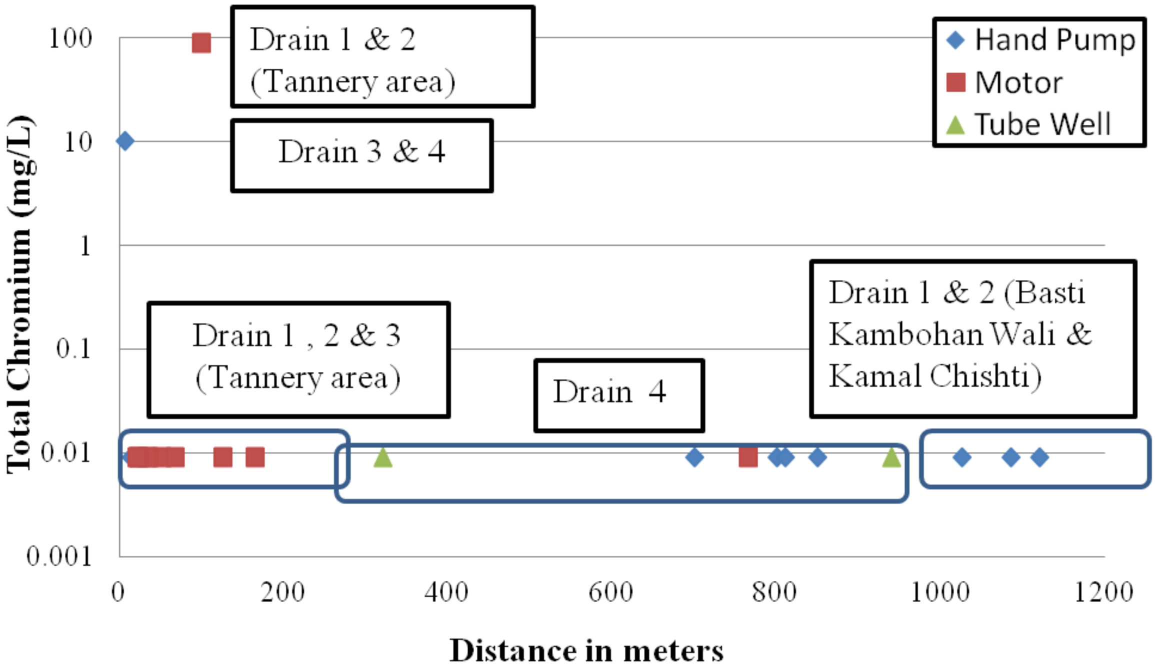


Fig. 5.4: Graph presenting total chromium of random groundwater samples

Table 5.2: Basic statistical parameters (μS/cm for EC & mg/L where applicable) for basic chemical parameters in groundwater samples from Kasur (n=22)

	Minimum	**Maximum**	**Average**	**Median**	**SD**	**Kurtosis**	**Skewness**
TDS	1,060	6,770	2,483	1,645	1,631	0.56	1.08
EC	1,690	10,750	3,914	2,595	2,572	0.67	1.10
Hardness	90	810	333	372	1,93.5	-0.17	0.44
Total Cr	0.009	90	4.5	0.009	19.2	21.4	4.6

Table 5.3: Correlation coefficient matrix for the basic chemical parameters and total chromium in groundwater samples from Kasur (n=22)

	TDS	EC	Hardness
EC	**0.99**		
Hardness	**0.73**	**0.73**	
Total Cr	0.086	0.085	0.20

Bold values are significant at $p \leq 0.05$ *for* $r \geq 0.361$

5.2.2 Surface soil sampling

Regarding soil analysis, samples were analyzed for both soil retention and soil mobility as determined by TCLP (toxicity Characteristics Leaching Procedure Test). Samples were collected from significant location from surface as well as depth in order to properly understand overall variation trends of examined parameter, i.e. Total chromium and hexavalent chromium. Soil retention tests were conducted by using Aqua Regia acid digestion method for determining total and hexavalent chromium in soil

The purpose of these surface sampling and analysis was to understand the areas of higher risk and their association with the potential source of contamination, which might be drains itself or contaminated soils in the form of stagnant ponds. As far as surface soil sampling was considered, it was important first to select the most appropriate sampling location. Therefore, four sampling points were finalized for this purpose, which has been explained in detail in the previous chapter. Following is the detail of results of these surface soil samples.

In order to compare the results with standard permissible values International standards were used furthermore background soil samples were also taken so as to obtain rational data based on the naturally existing concentrations of the contaminants under study.

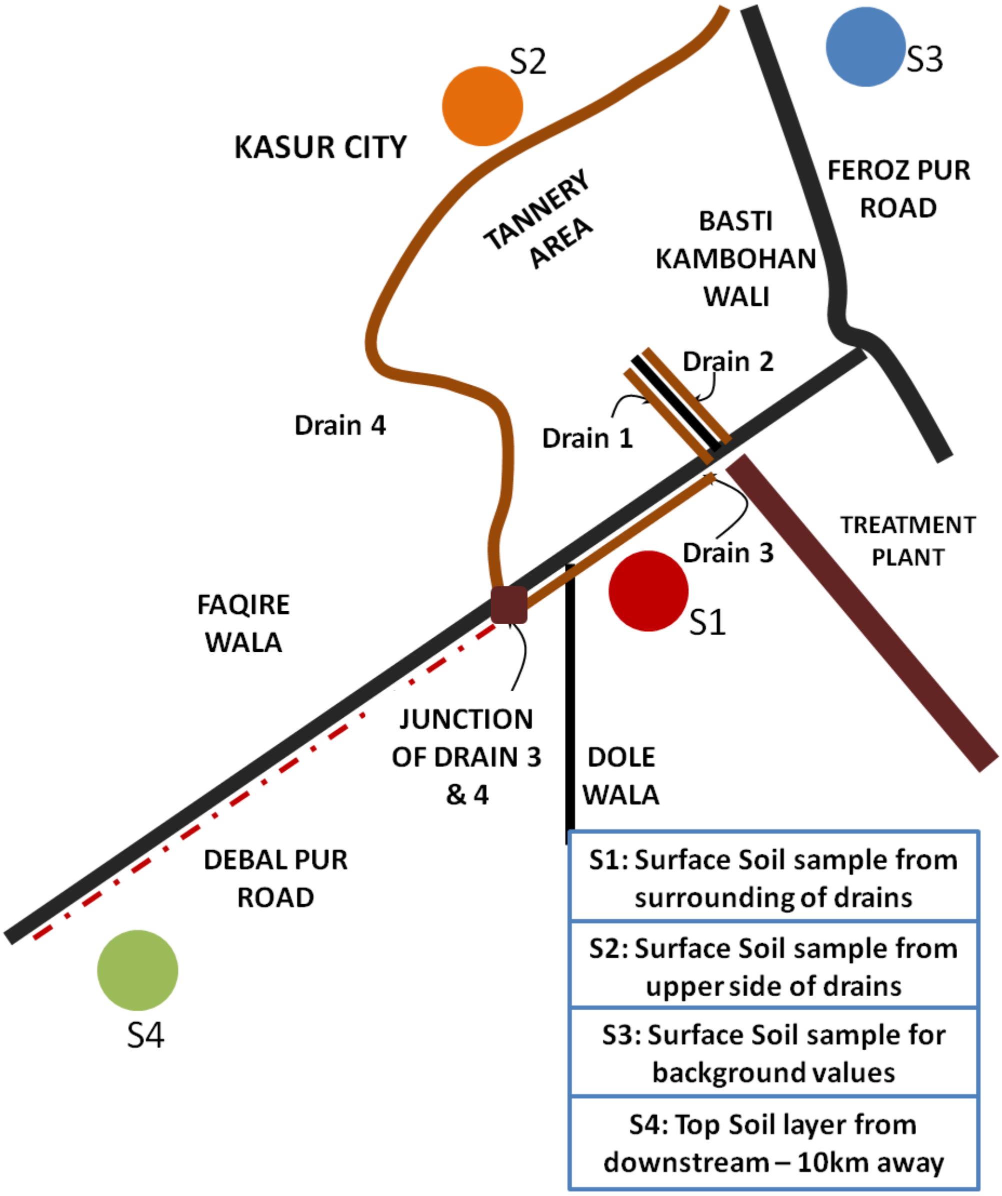


Fig. 5.5: Wide range surface soil sampling locations in the study area near the treatment plant and at farther distances.

5.2.2.1 Soil Sampling in the Surrounding Areas of Drains – S1

Five samples were collected from the surrounding areas of drains so as to determine the maximum concentrations of chromium existing in top layers due to overflowing wastewater. The samples are marked as S1. The results are shown in Table 5.4, explaining the aqua regia acid digestion results showing the total retention in soil for total and hexavalent chromium. From the table, results shows all the values for total chromium retention not exceeding the Japanese standard limit set my MOE Japan (MOE, 2003) i.e. 250 mg/kg. The values obtained are from 180 to 127 mg/kg for total chromium and between 34 to 20 mg/kg for hexavalent chromium.

5.2.2.2 Soil Sampling from Areas Adjacent to Tanneries – Upper Side of Drains – S2

These five samples were collected from areas on the upper side of Drains, marked as S2 adjacent to tanneries as shown in Fig 5. The results are shown in Table 5 describing the results of total and hexavalent chromium analysis by aqua regia acid digestion for total retention in soil medium. Very low values of both total and hexavalent chromium can be observed ranging between 25 to 17 mg/kg for total chromium and 9.1 to 5.3 mg/kg for hexavalent chromium.

5.2.2.3 Soil Sampling from Kasur City for Background Values – S3

Two samples were collected to determine the background values in the research area which were used as reference for uncontaminated soil conditions particularly related to that area. This location was marked as S3 and is shown in Fig. 5. The values obtained are far less than other values obtained in S1 and S2 as these are presented in Table 6. The range obtained for total chromium is between 8.5 to 6.4 mg/kg and that for hexavalent chromium is 4.2 to 6.4 mg/kg.

5.2.2.4 Top Soil Layer from Down Stream – 10 Kilometers from Tannery area (S4)

Three samples which were collected from top layer at a distance of 10 kilometers from tanneries near Drain 5 were also analyzed for total chromium and hexavalent chromium in order to determine the extent of contaminant in top layer at farther distance of 10 kilometers from Tannery area. The location is marked as S4 and is shown in Fig. 5.5. Top layer was explored up to 4.5 meters. The concentration of total chromium was found to be in between 38 and 23 mg/kg while hexavalent chromium varied in between 13 and 5.7 mg/kg. The results of soil analysis for total and hexavalent chromium in top layer at a distance of 10 kilometers from the tannery area are shown in Table 7. It must also be considered that the site S4 was selected at downstream side of the drains carrying the major share of tannery effluents as obvious from Fig. 5.5.

These wide spread sampling was to obtain concentrations of total and hexavalent chromium at wider range of the area so as to analyze the impact of different sources of contamination. It has been observed that the sources of contamination are not specifically a single point but widely spread out. It is because the sources are in the form of clusters. It is also justified by the results of groundwater when the concentrations of chromium are varying along the study area with no specific trend. Thus cluster like formation of the existence of the chromium can be observed. Regions with frequent exposure to tannery effluent have relatively higher concentrations of chromium as compared to background values or upstream values. This depicts higher potential of carrying the contaminant from one medium to other. As the top soil layers in the adjacent areas to the drains have the maximum concentrations of chromium, therefore the agricultural fields are a potential source of carrying the contamination from the wastewater to soil and then to the crops and vegetables, which highlight alarming conditions.

Table 5.4: Soil sampling from surrounding areas of drains – S1

Sample	Total Chromium (mg/kg)	Hexavalent Chromium (mg/kg)
1	180	28
2	174	34
3	131	26
4	123	27
5	127	20

Table 5.5: Soil sampling from areas adjacent to tanneries (upper stream) – S2

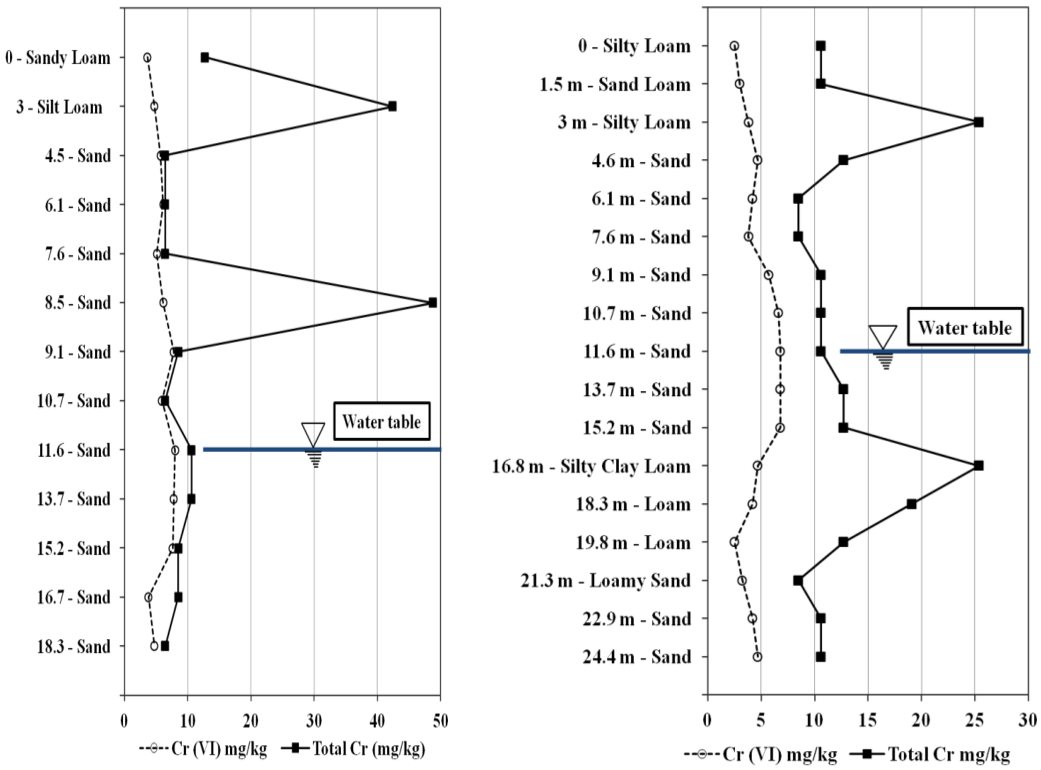
Sample	Total Chromium (mg/kg)	Hexavalent Chromium (mg/kg)
1	21	5.3
2	23	7.8
3	25	5.7
4	17	9.1
5	23	6.6

Table 5.6: Soil sampling from Kasur city for background values – S3

Sample	Total Chromium (mg/kg)	Hexavalent Chromium (mg/kg)
1	6.4	4.2
2	8.5	6.4

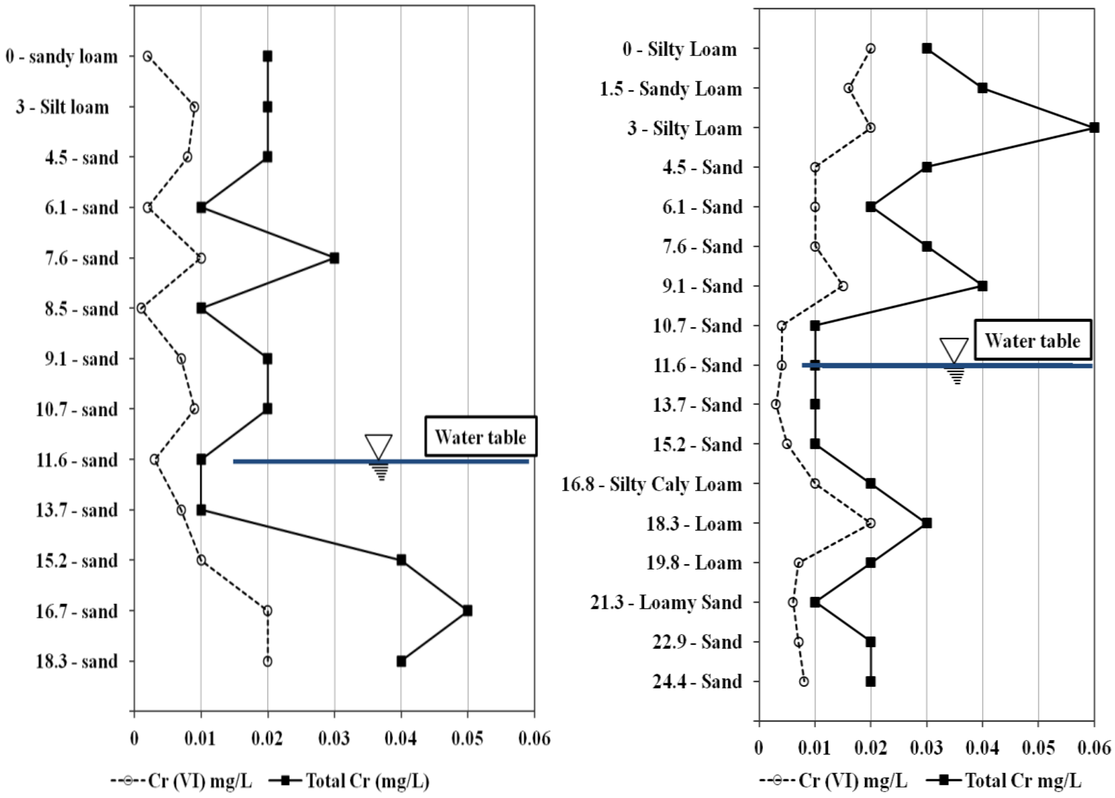
Table 5.7: Soil sampling from top layer at downstream 10 Km from tanneries – S4

Sample	Total Chromium (mg/kg)	Hexavalent Chromium (mg/kg)
1.5 m	29	6
3 m	38	5.7
4.5 m	23	13



Initial Bore 1 **Initial Bore 2**

Fig. 5.6: Initial Bore 1 & 2 depth profile and analysis by Aqua Regia Acid Digestion



Initial Bore 1 **Initial Bore 2**

Fig. 5.7: Initial Bore 1 & 2 depth profile and analysis by TCLP

5.2.3 Soil Analysis for Initial Bore 1 & 2

As described in previous chapter two initial soil bores were conducted to analyze for particle size distribution to investigate the soil texture of substrata along with retention and percolation of total and hexavalent chromium for depth wise sample analysis.

For initial soil bore 1 total number of soil samples was 13 up to the depth 18.3 meters while for initial soil bore 2 the sampling depth was 24.4 meters The results of particle size distribution are described in detail in Appendix and are also incorporated in the graphs plotted for aqua regia acid digestion and TCLP for both bores as shown in Fig. 5.6 and Fig. 5.7. The particle size distribution analysis shows that for Bore 1 that the top soil layer consists of sandy loam and silt loam up to the depth of 3 meters. From there onwards texture of soil is constantly that of soil up to 18.3 meters. For Bore 2 the soil texture is more variant starting with same sandy loam and silt loam up to 3 meters like Bore 1 but the sand layer is interrupted by silty clay loam and loamy soil at the depth of 16.8.

All the samples collected were analyzed for total chromium and hexavalent chromium retention in soil by Aqua regia acid digestion (Hindu, 2008) and possible percolation ability by TCLP i.e. toxicity characteristic leaching procedure. (USEPA, 1994). The variation trend for both aqua regia acid digestion and TCLP analysis is quite obvious along the depth from the graphs in Fig.5.6 & Fig. 5.7.

TCLP analysis is used in order to find out the mobility of hexavalent chromium and total chromium into the soil. Results of TCLP analysis of samples for Bore 1 are presented in Fig. 5.7. The observed concentrations of hexavalent chromium and total chromium are quite small ranging from 0.002 to 0.018 mg/L and 0.01 to 0.05 mg/L respectively, which are all less than the standard leaching value shown in Table 5.5. The nature of soil is mostly sandy except above 3.0 meters depth, where the soil has finer content i.e. silt loam. However, the concentrations of hexavalent chromium and total chromium are both higher in the deeper portions of the bore as shown in Fig. 5.7. The graphs give the content of hexavalent chromium and total chromium retained in the soil, which was measured by aqua regia digestion for the soil samples from Bore 1 & 2. The contents of hexavalent chromium and total chromium of the soil ranged from 3.6 to 8.1 mg/kg and 6.4 to 48.8 mg/kg respectively, which are all within the standard soil contents. The relatively high values of hexavalent chromium were obtained at the depths near groundwater table (z = 11.6 meter). There are two peak contents of total chromium having values 42.4 and 48.8 mg/kg at the depths of 3.0 and 8.5 meters respectively. Results of aqua regia digestion results for the soils of Bore 2 are shown in Fig. 5.6. Hexavalent chromium content varied from 2.5 to 6.8 mg/kg and total chromium content retained in soil varied from 8.5 to 25.4 mg/kg, all less than the relevant standard i.e. <-250 mg/kg for total chromium. Similar to Bore 1, the retention of hexavalent chromium was found to be relatively higher at the depths near the water table level. There are also two peak contents of total chromium with the same value of 25.4 mg/kg at the depths of 3.0 meters and 16.8 meters. At the two depths the highest silt & clay contents i.e. 82 and 81% were obtained respectively. The results at these two depths of Bore 2 and 3.0 meter depth of Bore 1 indicate that the higher the silt and clay proportion, the higher the retention of total chromium in the soil.

Results of TCLP analysis for the samples collected from Bore 2 are shown in Fig. 5.7. Hexavalent chromium concentration varied from 0.003 to 0.021 mg/L while that of total chromium ranged from 0.01 to 0.06 mg/L. Similar to Bore 1 these values are all within the standard given in Table 7. However, the depth profiles of the observed concentrations are different between the two bores. For Bore 2, the concentrations are relatively higher at the shallower depth than the deeper depth in the bore.

The low TCLP concentrations and retention values of hexavalent and total chromium indicate that soil in the research area is not significantly contaminated with the tannery effluent and might not be a serious threat to the groundwater environment in the future. Although the level of the soil contamination is not so high, it supports the concept of the occurrence of the direct interference of tannery effluent with the groundwater, which is most likely to be due to direct percolation from unlined drains or cracking in the lined channels especially at the junction.

There are some variations in the results of soil analysis obtained from the two bore. To have more clear view about the soil contamination at the investigated site, additional soil bores and testing was suggested in the second phase.

5.2.4 Seasonal Wastewater Analysis

Wastewater characterization was one of the major components of research as it would not only explain the potential source of contaminant seepage into subsurface but also it will explain the overall scenario of wastewater production and its discharge. For the wastewater analysis during the peak production season, four samples were taken from all the four drains from specific locations. The parameters analyzed were pH, BOD_5, COD, TDS, TSS, chloride, sulphate, sulfide, and chromium. The basic chemical parameters are given in Table 5.8 with the maximum and minimum values along with the respective effluent standard limits according to the national environmental quality standards (NEQS) developed by the government of Pakistan to regulate the industrial effluent and municipal wastewater (GOP, 2000).The results of the chemical analysis of wastewater samples from the four drains are compared to these effluent standards in Fig. 5.8.

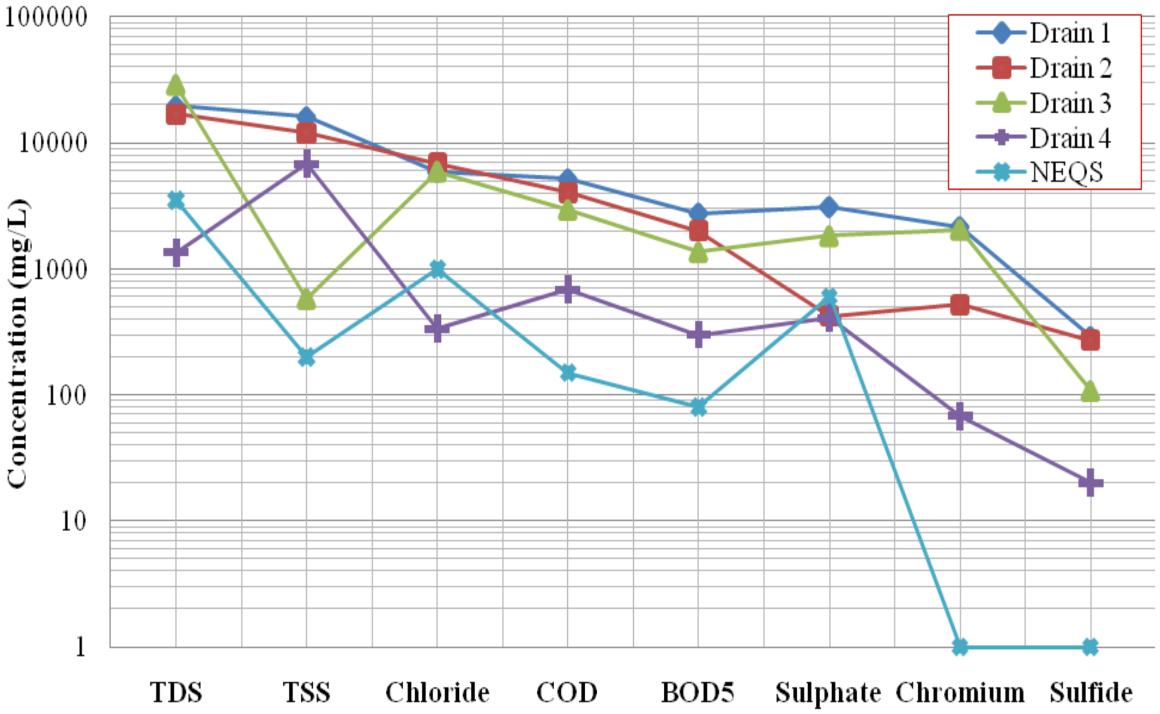


Fig. 5.8: Basic chemical properties and total chromium level in the four drains of research area during Peak production duration

Table 5.8: Basic chemical parameters (mg/L) of the wastewater from four drains for peak production season (n=4)

	Minimum	**Maximum**	**NEQS (GOP, 2000)**
pH	7.1	7.7	6-9
BOD_5	300	2,760	80
COD	680	5,152	150
TDS	1,340	28,740	3,500
TSS	580	16,020	200
Chloride	335	6,808	1,000
Sulphate	407	3,106	600
Sulfide	20	288	01
Chromium	68	2,150	01

Drain 1, which was in flowing condition at the time of sampling, showed all the values extremely high for the analyzed parameters. At the time of sampling Drain 2, which is parallel to Drain 1, was not in flow but it carried the same untreated effluent from the tannery units. All the parameters, except chlorides, have relatively lower values when compared with the values of parameter obtained for Drain 1. It is considered due to the sedimentation of the suspended organic matters and other chemicals present in the effluent. Drain 3, which contains the treatment plant effluent (treated wastewater) as well as diverted untreated effluent from Drain 1, showed the maximum TDS i.e. 28,740 mg/L. However this sample from Drain 3 is considered to have relatively lower organic matters in the form of BOD_5 and COD and also had lower remaining parameter values as compared to Drain 1 and Drain 2. It might be due to the dilution by treatment plant effluent. The level of chromium concentration is Drain 3 is 2,050 mg/L which falls very near to that in Drain 1 where it is 2,150 mg/L. It is mainly due to carriage of Drain 1 wastewater into Drain 3 due to diversion. Drain 4, which is carrying the municipal wastewater along with the tannery effluent from a few industries, showed the minimum values of all the parameters among the four drains, in general. Fig. 5.8 clearly indicates most of the parameters in extremely high concentrations in comparison to effluent standards. The most mentionable is the concentration of chromium reaching up to the level of 2,150 mg/L in Drain 1. Even concentration level of 68 mg/L is found in Drain 4 which is mainly carrying municipal wastewater. Minimum production season wastewater analysis was conducted in January 2010 and the only parameter investigated was total chromium. The results are compared with those of the maximum production season in Fig. 5.9. The total chromium concentrations for the minimum production season are 20 to 60 times smaller than those for the maximum production season. However, the concentrations of minimum production were yet higher than the standard limits. It is interesting to note that the concentrations at these four drains exhibited similar relative difference for the two seasons.

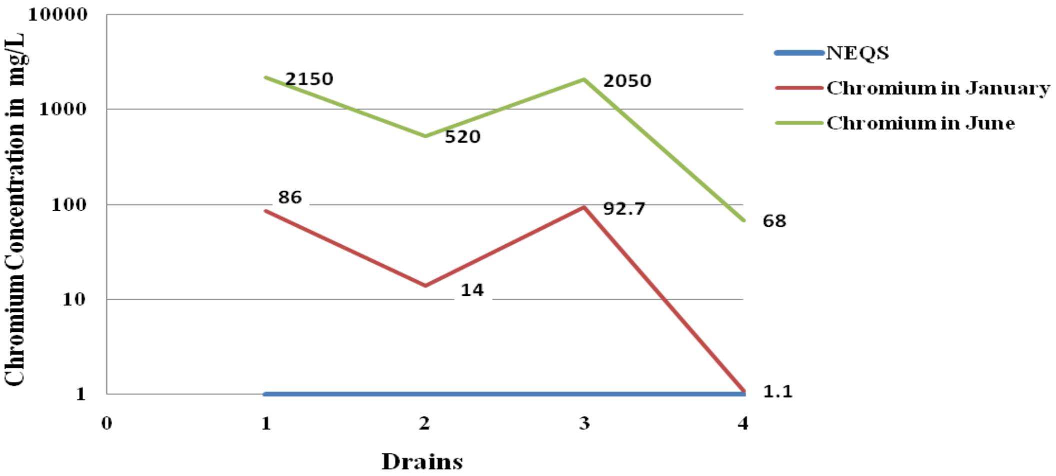


Fig. 5.9: Seasonal variation of total chromium in four drains of research area

It reflects presence of high concentrations of chromium in the wastewaters of all the drains in the study area throughout the year, especially in the peak production season. It also depicts higher possibility of leakage of chromium along with other pollutants from the drains and mixing with the groundwater as evidenced by the higher chromium concentrations in the groundwater at the downstream of Drain 3 and 4 in the areas of Dole Wala and Faqire Wala.

5.3 Phase II (Confirmatory Site Investigation)

After the initial phase of investigation conducted so as to find out general contamination trend in groundwater, wastewater and soil, second phase was planned for detailed investigation to study the behavior and fate of contaminant in the research area. Taking as high concentration as 10 mg/L of total chromium in Dole Wala into consideration, further spreading of contaminant was aimed to be investigated in this downstream area. For this purpose eight (8) new borehole locations were finalized for digging bore upto specific depth and then it was also planned to install monitoring wells at same places for periodic groundwater sampling in the areas of Dole Wala and Faqire Wala. These locations fall in the surrounding vicinity of Drain 3 and Drain 4, near the junction. The main components of confirmatory Phase include soil boring, groundwater monitoring and seasonal wastewater analysis. Furthermore four (4) new soil bores at the same depth of 30.5 meters were conducted for particle size distribution analysis only so as to gather maximum subsoil strata information for the development of GMS model on wider area. Further confirmation of the interaction of the major components of the research which include Drains, wastewater, groundwater and soil was determined and confirmed by using Voxler ® software. It was used to understand the varying trends of concentrations of total and hexavalent chromium both in horizontal and vertical directions, also explaining the significance of the soil texture and groundwater table level particularly in monitoring wells area. While GMS model was applied to explain the different scenarios pertaining to adverse environmental conditions prevailing in the study area since the tannery units has started polluting the rest of the area. Following is the detailed findings of the second phase.

5.3.1 Soil Boring in Research Area for installation of Monitoring Wells

Based on the outcome of initial investigations, specifically groundwater analysis and wastewater analysis, the surrounding area of Drain 3 and 4 were selected for detailed investigations. It was mainly due to extremely high value of total chromium found in groundwater up to 10 mg/L and very high values of total chromium n wastewater up to 2,050 mg/L in Drain 3.

Eight (8) soil bores were conducted as described in detail in the previous chapter and were analyzed for total chromium and hexavalent chromium retention in soil and its leaking possibility in soil by aqua regia acid digestion and TCLP respectively. The details are described as follows.

A wide range of soil texture was obtained from particle size distribution analysis from all the soil bore samples. Bore 1 has top 3 meter layer of silt loam with more than 50 % of silt followed by almost 100 % sand layer up to the depth of 30.5 meters. Bore 2 has most varied soil texture starting with loamy soil and sandy loam up to 3 meters. Then there is silt loam layer up to 6 meters, there is a bigger layer of sand up to 12 meters. After that there is silty clay loam up to 15 meters followed by clay loam and silt loam up to 20 meters. Further deep exist sandy loam and loamy sand up to 24 meters and then sand layer continues up to 30.5 meters hence forming a very complex structure underneath. Bore 3 starts with sandy loam and continues with sandy layer up to the end. Bore 4 soil textures is loam and clay loam at the beginning then sand layer prolongs up to 16 meters and is interrupted by clay loam, silt loam, loam and loamy sand, up to 26 meters from where onwards sand layer continues. The depth profile of Bore 5 is mostly sandy throughout the fixed bore depth of 30.5 meters. Soil of Bore 6 is also sandy except a silty and loamy sand layer portion in the middle of the Bore depth. Bore 7 and 8 have similar soil textures starting with silt loam and loam and then comes a big layer of sand up to the middle of soil bore, followed by another layer of loamy sand.

A flat water table was observed throughout the research area. At first a thin layer of wet soil was observed at the depth of 10.7 meters. Though it was in sand layer zone yet it was not extractable due to very small quantity of water. At the depth of 27.4 meters another water table was observed which was sufficient enough to be extracted and relied upon for water usage.

5.3.1.1 Aqua Regia Acid Digestion

Aqua regia acid digestion analysis results for Bore 1 to Bore 8 are presented in Fig. 5.11. The soil analysis showed similar trend for total and hexavalent chromium retention in soil as it showed for initial two soil bores. No significant values were observed in any soil bore samples. All the values were within the permissible limits for total retention of total chromium in soil .However increased values are observed for particular soil texture in some soil samples.

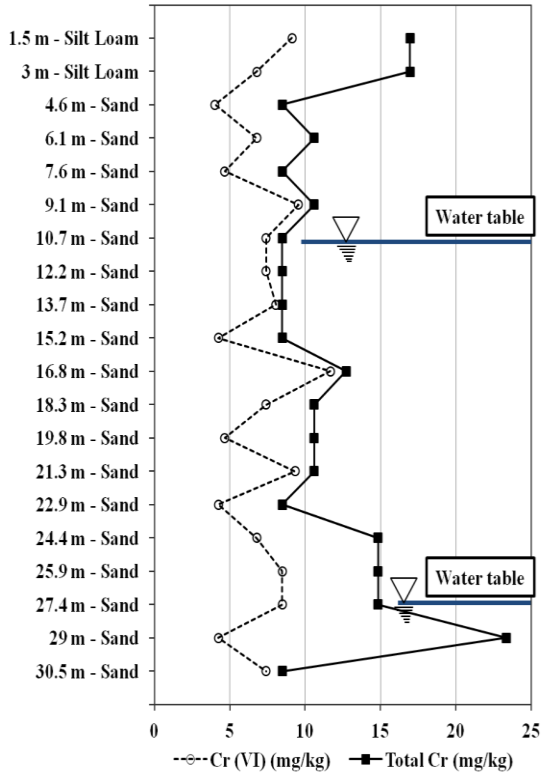
For Bore 1 soil samples the values of total chromium and hexavalent chromium could not present any specific trend and maximum values are observed at groundwater aquifer in sand layer portion. The values of total chromium varied in between 8.5 and 23.3 mg/kg and hexavalent chromium in between 4.0 and 11.7 mg/kg. Bore 2 soil samples showed a wide range of soil texture with varied clay, silt and sand proportions. Every layer of loam, sandy loam, silt loam, silty clay loam, sandy loam and sand shows different behavior regarding retention of total chromium and hexavalent chromium depending upon metal retaining capacity of soil. For example highest chromium retention of 70 and 44.5 mg/kg is observed in the layer of silty clay loam at depth of 13.7 meters with silt and clay proportions to be 87 and 85 % respectively. In this bore throughout the depth very low values of hexavalent chromium are observed with maximum value of 9.5mg/kg in top layers of silt loam at 6 meters. It indicates least interference of fresh waters or wastewater possessing chromium due to complex soil nature. Soil texture for Bore 3 throughout the depth is mostly uniform and Sandy thus very low values of retention of total chromium and hexavalent chromium i.e. 14.8 and 10.0 mg/kg respectively are observed in the top layers upto 3 to 5 meters of depth. It may be due to overflow of wastewater from the drains because Bore 3 exists at a nearer distance of 150 meters from Drain 3. Bore 4 showed maximum retention of total and hexavalent chromium at the depth of 18.3 meters i.e. 50.9 mg/kg and 11.4 mg/kg respectively for clay loam soil texture. Bore 5 presented uniform sandy soil texture throughout the depth. Therefore very low retention levels of total chromium and hexavalent chromium are observed. The maximum retained values of total and hexavalent chromium found are 29.7 mg/kg and 7.6 mg/kg respectively. The texture of Bore 6 is also very uniform and mostly sandy with thin layer of silt loam in the middle. The results of aqua regia acid digestion showed maximum values of 57.4 mg/kg in the middle while the maximum retention of hexavalent chromium is observed at the bottom level in groundwater aquifer.

Soil texture is constantly varying with top layer of silt loam and loam showing higher retention values of total chromium of 53.0 mg/kg and that of hexavalent chromium is 11.2 mg/kg. But with increase in depth the retention level of both total and hexavalent chromium decreases. It generally depicts results of overflow from Drain 4 because Bore 7 is 300 meters from the drain and is included in the flooded plain. Bore 8 exists in the downstream of Drain 3 & 4. Although the soil texture is mostly sandy, sandy loam, loam or silt loam yet sand layer dominates throughout the depth. Comparatively higher retention levels are observed with maximum total chromium and hexavalent chromium to be 91.1 mg/kg and 16.1 mg/kg respectively at the depth of 16.8 meters in silt loam layer. These are the highest values been observed so far regarding retention at this much depth among all the soil bores indicating chronic retention of total chromium and presence of hexavalent chromium in groundwater, even in not that higher values to be alarming.

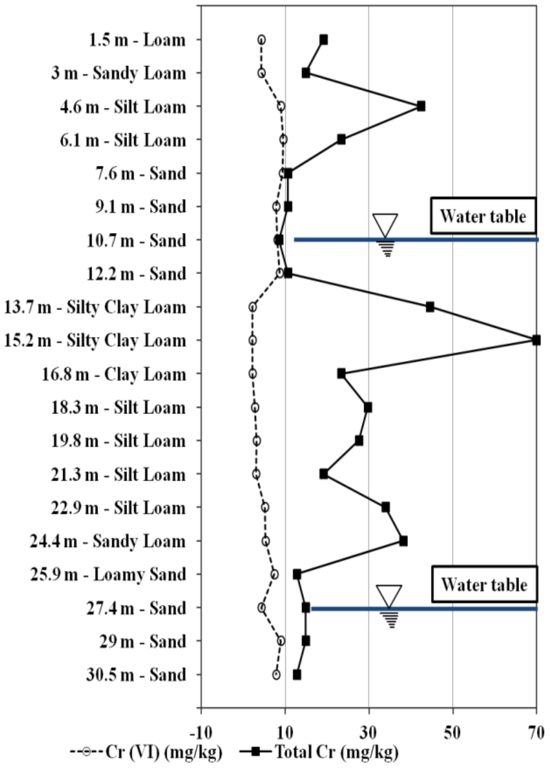
5.3.1.2 Summary and Findings of Aqua Regia Acid Digestion Analysis

The most significant observation regarding these eight soil explorations is the same level of water table for both first and second aquifers for each bore hole. The first water table was observed at depth of 10.7 meters and second water table was observed at 27.4 meters.

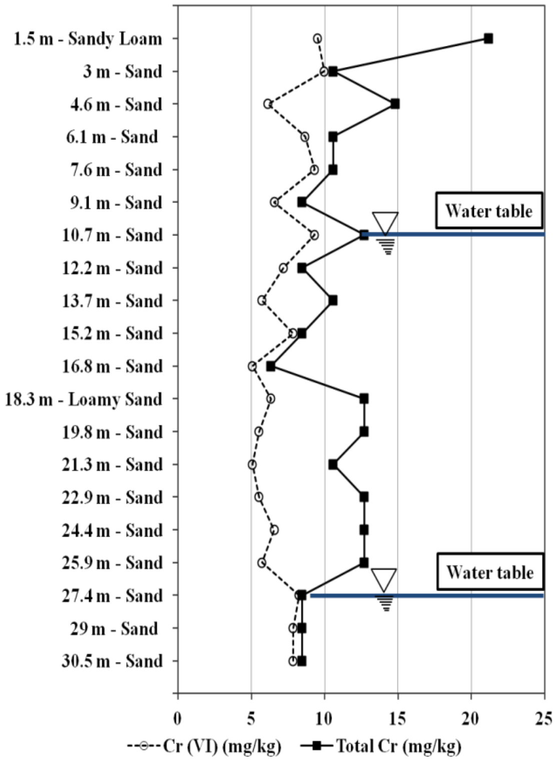
For all the boreholes a similar variation trend of hexavalent and total chromium concentration can be observed in comparison with the soil texture. In the top layers, with more silt and clay proportions higher concentrations can be observed. While at the bottom depths more the sandy texture lesser the chromium content retained. At the water table depths, most of the chromium is in the form of hexavalent chromium as the difference between the total chromium and hexavalent chromium is smaller than other depths. In saturated zone hexavalent chromium distributes preferentially in the water phase soil (Armienta and Quere, 1995). The concentrations of hexavalent and total chromium at water table depths and adjacent soils are having increased values of hexavalent chromium, dominating its presence in saturated zone. It is an evidence of transport of chromium in the form of hexavalent chromium along with direct interference of contamination source with groundwater. Although all the values obtained for hexavalent and total chromium are not significantly high enough to pose any serious environmental impact still a symmetric pattern among the values can be observed. The highest values obtained for hexavalent and total chromium are for soil bore 8 in which the maximum value of hexavalent chromium is 16.11 mg/kg and that of total chromium is 91.16 mg/kg obtained at the same depth of 16.8 meters. The soil texture at this depth is silt loam which has the maximum capacity of retention as compared to other soil textures. Thus the higher the silt and clay proportion, the higher will be the retention in the soil (Armienta and Quere, 1995).Most of the soils for all the eight bore holes are sandy or loamy sand that's why not high retention has been observed. But still among all the eight bore holes, bore 2 has the deepest silty clay loam layer of total depth of 10.7 meters which exhibits a zone of maximum retention on average basis. It ranges from 19.1 to 70.0 mg/kg for total chromium with average of 35.8 mg/kg. It is also interesting to observe that in comparison to total chromium values hexavalent chromium values are extremely small depicting most of the chromium in the form of trivalent form. Trivalent chromium is retained preferentially in the superficial soil layers (Armienta et al., 1996). It indicates longer duration of chromium existence in this area. Furthermore all the values obtained for hexavalent and total chromium are far less than the standard concentration as defined by ministry of environment Japan (MOE Japan, 2003) and interim soil criterion guideline by Canadian soil quality guidelines (CSQG, 1999). The standard limit defined by ministry of environment Japan for hexavalent chromium is $\leq$ 250 mg/kg (MOE Japan, 2003) and Canadian soil quality guideline for hexavalent chromium is 8.0 mg/kg and for total chromium it is 250 mg/kg. (CSQG, 1999)



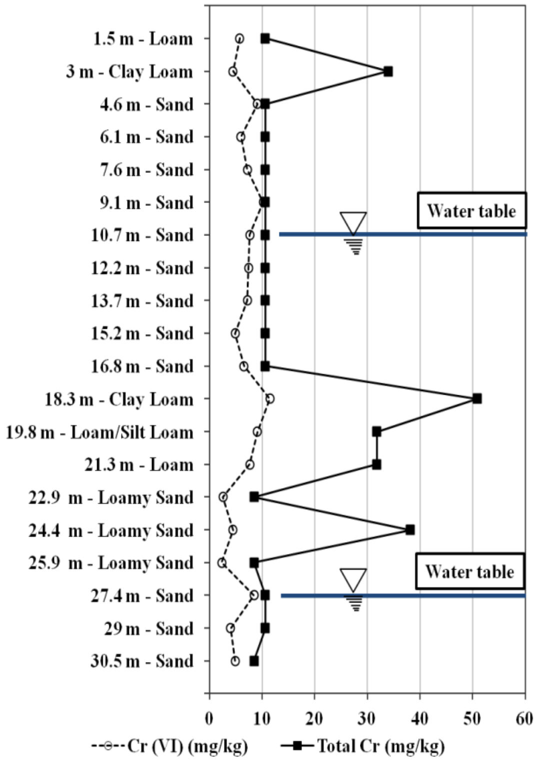
(SOIL BORE 1)



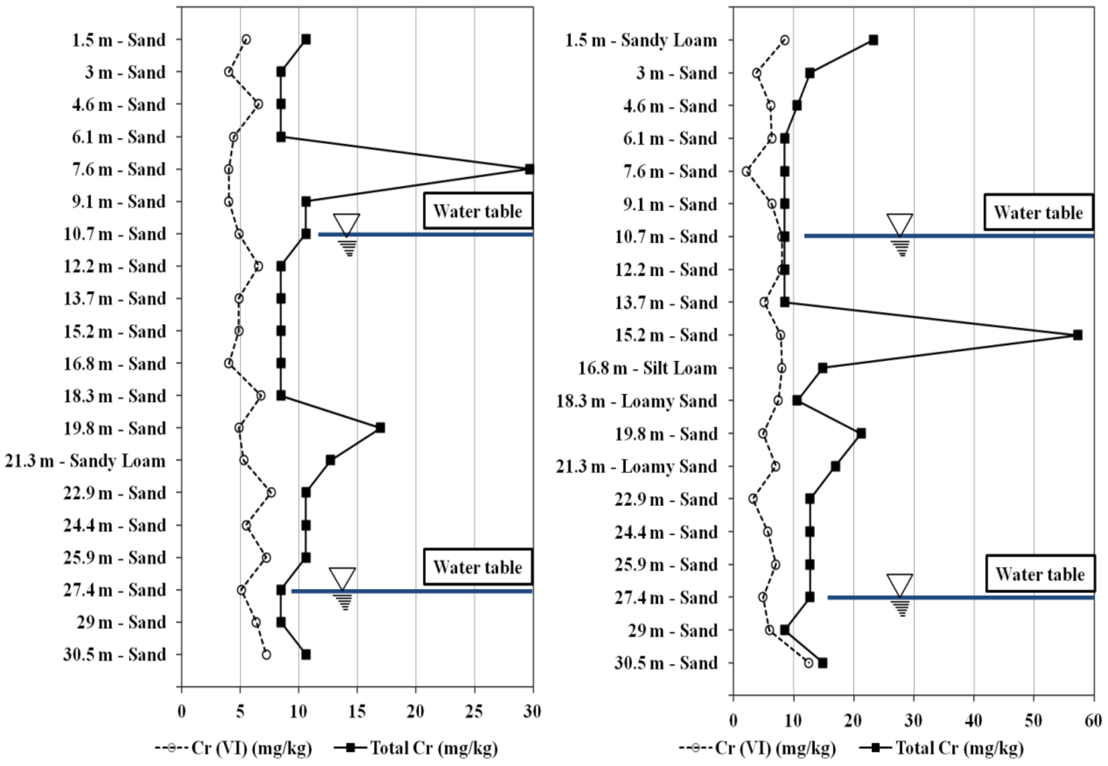
(SOIL BORE 2)



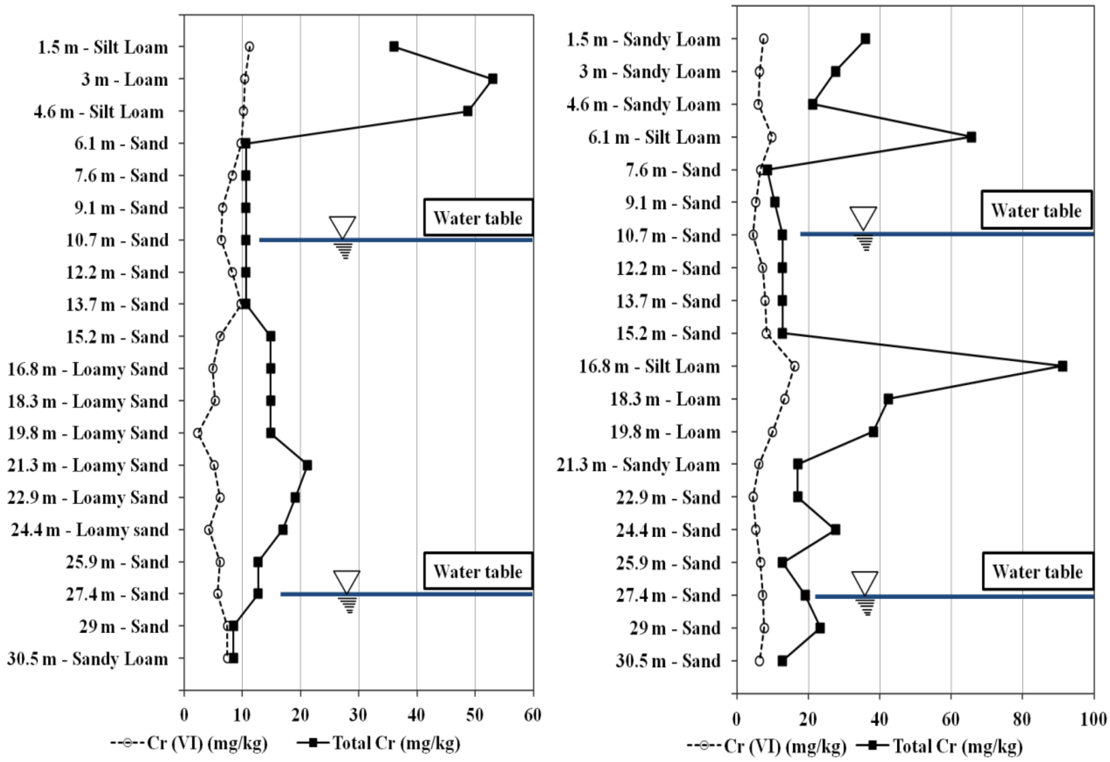
(SOIL BORE 3)



(SOIL BORE 4)



(SOIL BORE 5) **(SOIL BORE 6)**



(SOIL BORE 7) **(SOIL BORE 8)**

Fig. 5.10: Aqua Regia Acid Digestion analysis for Bore 1 to 8

5.3.1.3 Toxicity Characteristics Leaching Procedure (TCLP)

Main objective was to study leaching ability of total and hexavalent chromium through specific soil media. Trace metal mobile fractions are more significant rather than total contents in environmental matrices so as to evaluate risk assessment of contaminated sites. With the objective to determine mobility of total and hexavalent chromium in soil leaching test analysis by using TCLP for all the soil bore samples was conducted. The results of all the boreholes for TCLP analysis is shown in Fig. 5.11.

For the results of Bore 1, the higher concentrations of total and hexavalent chromium are observed in top layers upto 3 meters for silt loam soil texture. It depicts fresh intrusion of chromium in aquous phase. The maximum concentrations of total chromium and hexavalent chromium observed by leaching tests analysis provides the values of 0.05 mg/L and 0.035 mg/L respectively at top layer up to 3 meters from the surface. Most of the values of hexavalent chromium tend to increase along the depth especially nearer to water table and varies between 0.02 to 0.03 mg/L.

For Bore 2, maximum value of total chromium in aqueous form is obtained in silt loam layer at depth of 4.5 meters and i.e. 0.3 mg/L and at depth of 18 meters. No significant values were obtained for total and hexavalent chromium as there is no homogeneity or a specific pattern observed in all the values along the depth.

Bore 3 samples are also showing non uniform trend for total and hexavalent chromium concentration in aqueous solution. Values of chromium range between 0.01 to 0.03 while that of hexavalent chromium is in between 0.005 to 0.019 mg/L. Maximum values are obtained at the depth of 23 meters for sand layer.

Bore 4 samples showed higher mobility at top layer and middle layer along the depth of bore. However no significant concentrations were obtained with maximum value of 0.02 for total and 0.015 mg/L for hexavalent chromium. Higher values were obtained in top layers of loam and clay loam texture and in the middle of bore in layers of clay loam and loam.

Bore 5, with mostly sandy textured soil throughout the depth also did not show any significant values of total and hexavalent chromium concentrations for leaching test. The values of total chromium range between 0.01 and 0.02, while that of hexavalent chromium range in between 0.006 to 0.018mg/L.

In Bore 6 higher concentrations of total chromium of 0.05 mg/L was observed at water table level at depth of 27.4 meters and that of hexavalent chromium equal to 0.027 mg/L for same depth. At other depths no significant values were obtained. Most probably these higher values of total chromium depict direct intrusion of contamination through groundwater flow. It is also important to mention that Bore 6 is at a distance of 200 meters from Drain 4. Therefore high chances of percolation of total chromium from drains are there to mix with groundwater.

Leaching test for Bore 7 samples showed varied pattern of concentration of total chromium and hexavalent chromium along the depth. But all these values are insignificant and far less to depict any impact of soil texture on leaching behavior. Concentrations of total chromium vary in between 0.01 and 0.02 mg/L while that of hexavalent chromium range in between 0.004 and 0.016 mg/L.

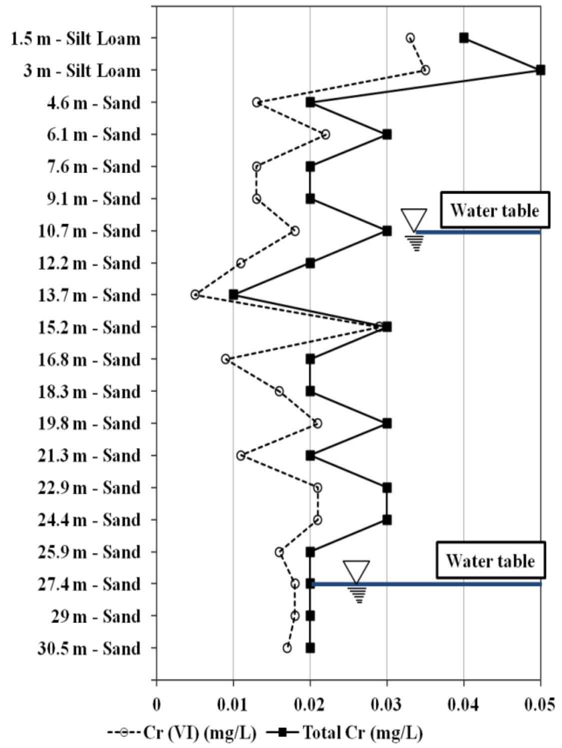
Similarly for Bore 8 samples no particular trend could be observed along the depth with varying soil texture. The values of total chromium range between 0 and 0.02 mg/L and that of hexavalent chromium in between 0 and 0.018 mg/L.

5.3.1.4 Summary and Findings of TCLP

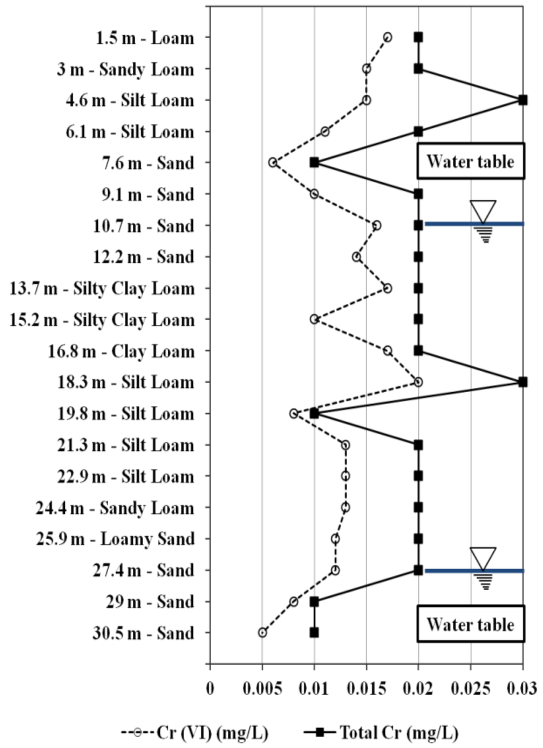
The maximum values are observed at groundwater level or at top layers for mobility of total and hexavalent chromium up to 0.06 and 0.027 mg/L respectively. It gives clear indication of intrusion of contaminant into groundwater as high values exist at water table level or near the surface. It can also be observed that total and hexavalent chromium presented identical pattern of concentration variation throughout the depth. Values of total and hexavalent chromium increase or decrease simultaneously.

Otherwise no special trend could be interpreted for total or hexavalent chromium variation based on specific soil texture regarding their mobility along the bore depth. However on the downstream side where there is higher level of chromium retention, at water table level there is higher potential of contaminant mobility into the deeper layers. On the upstream side the soil texture is also showing symmetric trends and thus the dominating sandy layers in the upstream side has shown relatively higher concentrations.

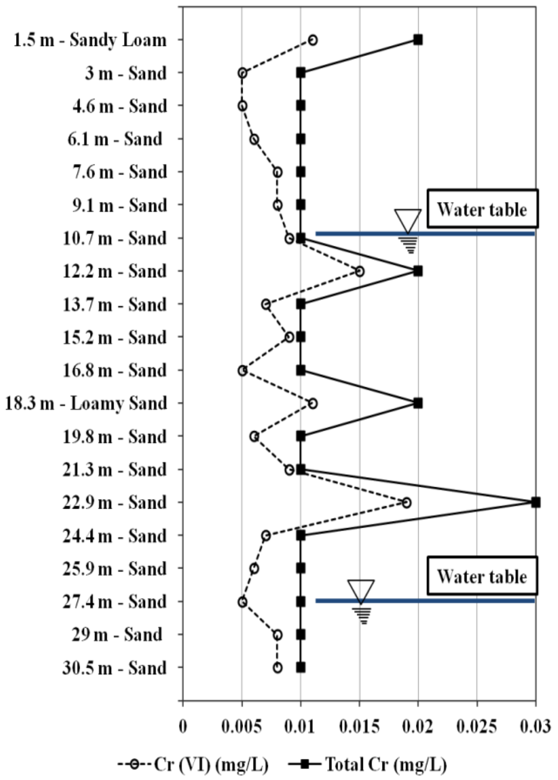
This can be observed in values of leaching concentrations of total and hexavalent chromium in Bore 3 and Bore 6. These two (2) bores are at a nearer distance from the Drain 4 and the junction point of Drain 3 and Drain 4. Thus the location is very significant in terms of mobility of contaminant. At second water levels the chromium concentrations have reached the maximum level of 0.06 mg/L which provides an evidence of direct interference from the drains into the soil layers and due to facilitation by soil texture in terms of sand layers the contaminant approached deeper aquifers.



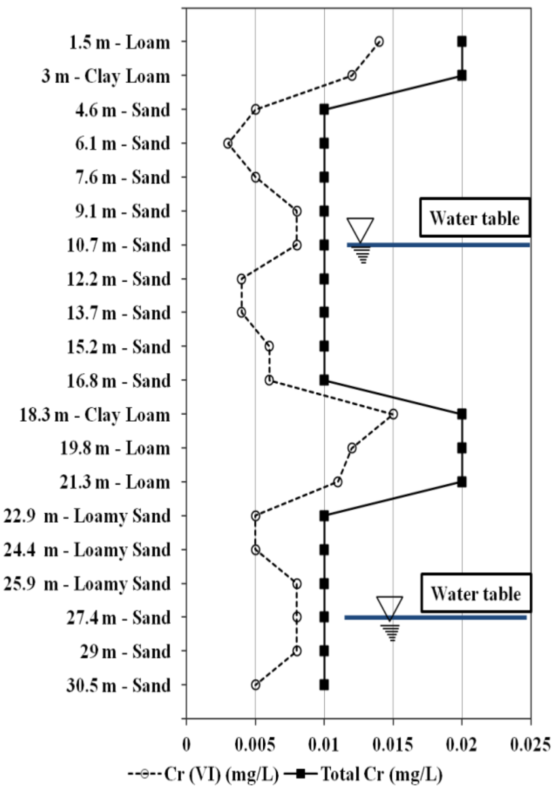
SOIL BORE 1



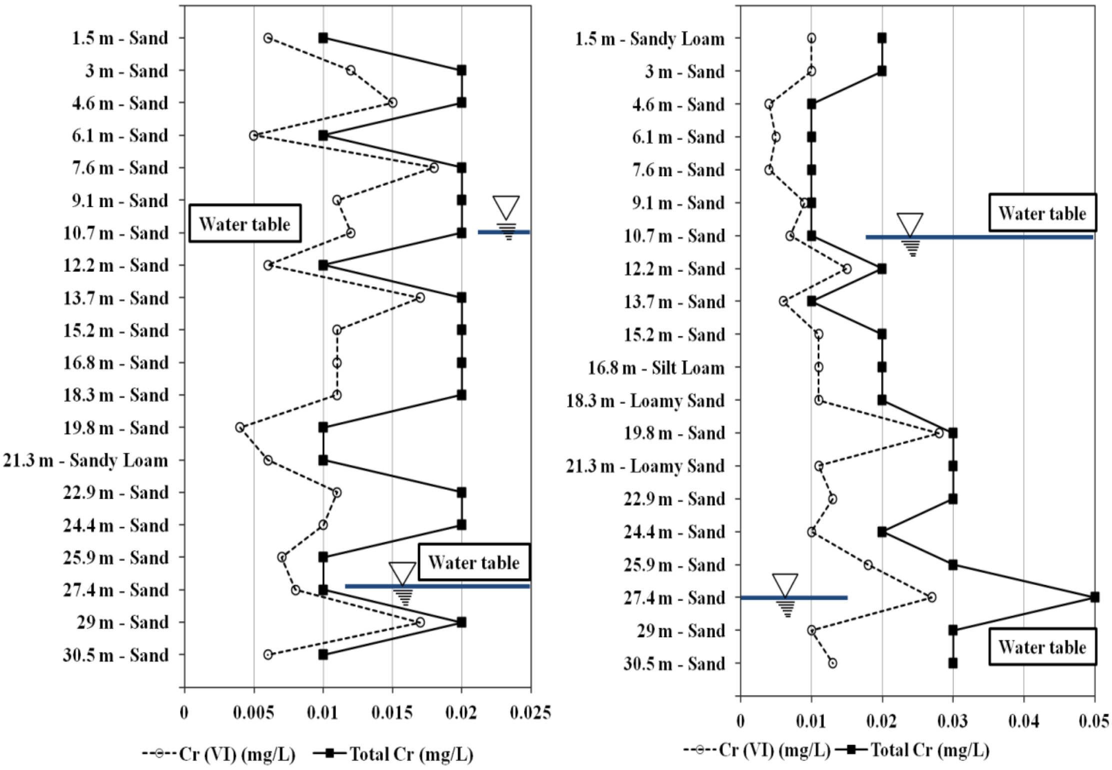
SOIL BORE 2



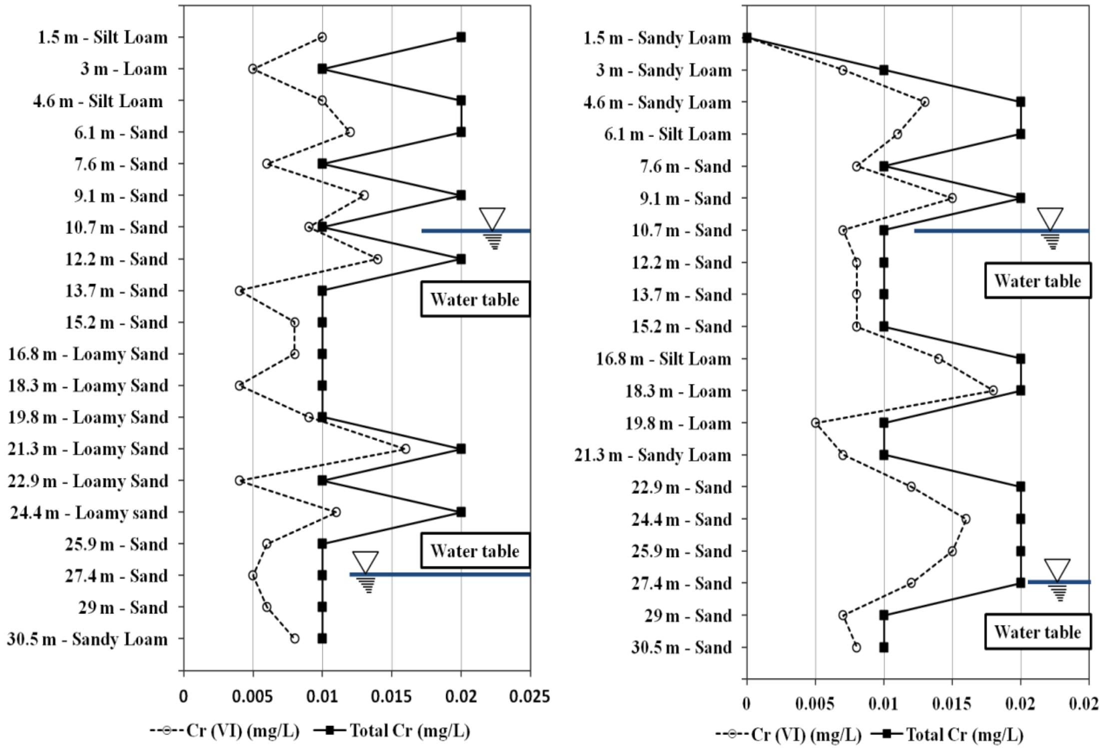
SOIL BORE 3



SOL BORE 4



SOIL BORE 5 **SOIL BORE 6**



SOIL BORE 7 **SOIL BORE 8**

Fig. 5.11: Toxicity Characteristics Leaching Procedure (TCLP) analysis for Bore 1 to 8

5.3.1.5 Concentration variations with Silt and Clay Proportion for Aqua Regia Acid Digestion

All the results obtained from aqua regia acid digestion for total chromium and hexavalent were plotted against their specific silt and clay proportions.

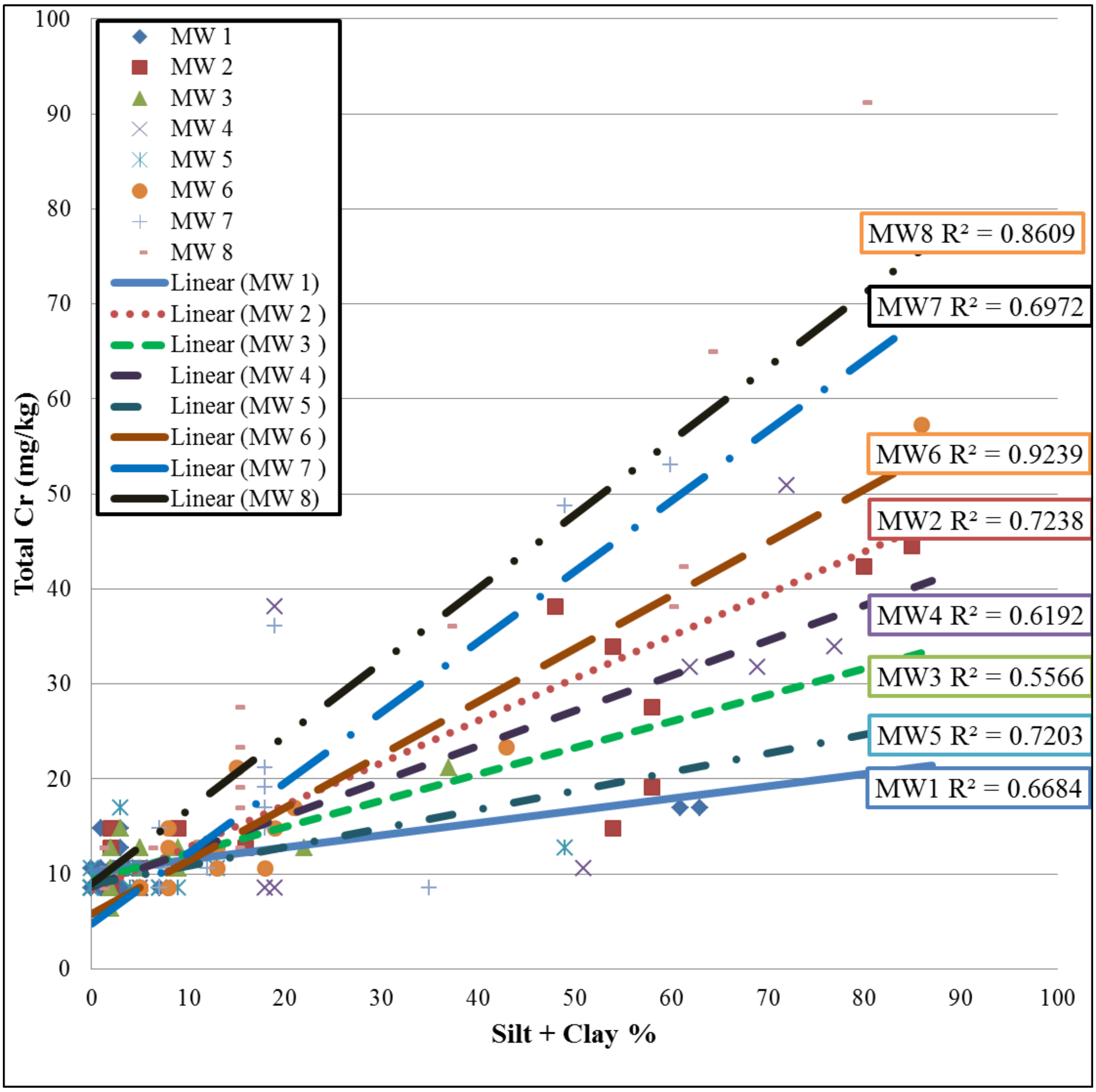


Fig. 5.12: Total chromium vs silt & clay proportion for aqua regia acid digestion analysis

Results of total chromium are plotted against silt and clay proportion of relative sample and are shown in Fig. 5.12. From the graph it can be seen that with the increase in silt and clay proportion the value of total chromium retention has shown significant increasing trend. Although the increasing pattern is not so symmetric due to other crucial factors like depth of sample and location of sample however the increasing trend is quite obvious. For lesser percentage of silt and clay the adsorption is also in a decreasing pattern as obvious from Fig. 5.12. It is mainly due to higher adsorption capacities of Silt and clay. Silt constitutes of secondary minerals components and clay itself being negatively charged have adsorption capacity for the cations. Hexavalent chromium being unstable, got dissolved in water, thus it indicated fresh chromium contamination. The result of hexavalent chromium, plotted against silt and clay proportions is presented in Fig. 5.13. Trend for hexavalent chromium is not as specific as the retention in soil is mainly due to trivalent chromium, once hexavalent chromium has been reduced to trivalent chromium. Therefore trend for total chromium has been more prominent and is more for total chromium due to inclusion of trivalent chromium component in it. It may be due to presence of trivalent chromium as a major part of total chromium which is more stable and have more retaining capacity as compared to hexavalent chromium which is unstable and have lesser capability to retain in silt and clay medium. Another important factor which can cause unsymmetrical trend could be the more or less equal distribution of hexavalent chromium along the depth. That's why total chromium has better correlation as compared to hexavalent chromium with the silt and clay proportion.

In order to predict the trend of variation of total chromium retention with changing silt and clay proportion, linear regression analysis was used. It was used to show the association of observed points with the ideal values thus generating a trend line. R square values obtained from the regression equation were used to define the co relation between the independent variable (Silt and clay in this case) and dependent variable (Total Chromium retention in this case). Higher the R – square value indicated stronger association between the variables. For MW1, the regression equation developed was $y = 1292x + 10.196$ with $R^2 = 0.6684$. As value of R – square is found higher than 0.5 therefore it depicts significant association between the variables. Values of R – square greater than 0.5 are considered to be more acceptable. For MW2, the regression equation developed was $y = 0.4449x + 8.3755$ with $R^2 = 0.7238$. In this case the relationship between the total chromium retention and percentage of silt and clay were found to be stronger as compared to first monitoring well. Similarly for MW 3, the regression equation developed was $y = 0.2772x + 9.431$having $R^2 = 0.5566$. For MW 4 the regression equation is $y = 0.3704x + 8.6822$ while $R^2 = 0.6192$. For MW 5 the regression equation is $y = 0.1969x + 8.929$ while $R^2 = 0.7203$. For MW 6 regression equation is $y = 0.5586x + 5.83$ while $R^2 = 0.9239$. Similarly for MW 7 the regression equation developed is $y = 0.7411x + 4.8279$ while $R^2 = 0.6972$. For MW 8 the regression equation is $y = 0.7763x + 9.006$ with $R^2 = 0.8609$. Regression is used to predict the value of one variable based on the value of a different variable. Correlation is a measure of the strength of a relationship between variables. The variables under consideration are the total chromium retention and proportion of silt and clay in soil. Thus based on the correlation factor as presented by R – square the strongest association between these variables was observed for MW 6 with R^2 value equal to 0.9239 and MW 8 with R^2 value equal to 0.861.

5.3.1.6 Concentration variation with Silt and Clay Proportion for TCLP

All the TCLP values for total and hexavalent chromium were plotted against silt and clay proportion to investigate any relation of ion capacity of soil with the mobility of metal in soil. Fig. 5.14 and Fig. 5.15 represent the relationship between TCLP concentration of total chromium and hexavalent chromium vs silt and sand proportions respectively. Both the graphs represent non uniform trend of leaching concentration variation with increasing silt and clay proportions.

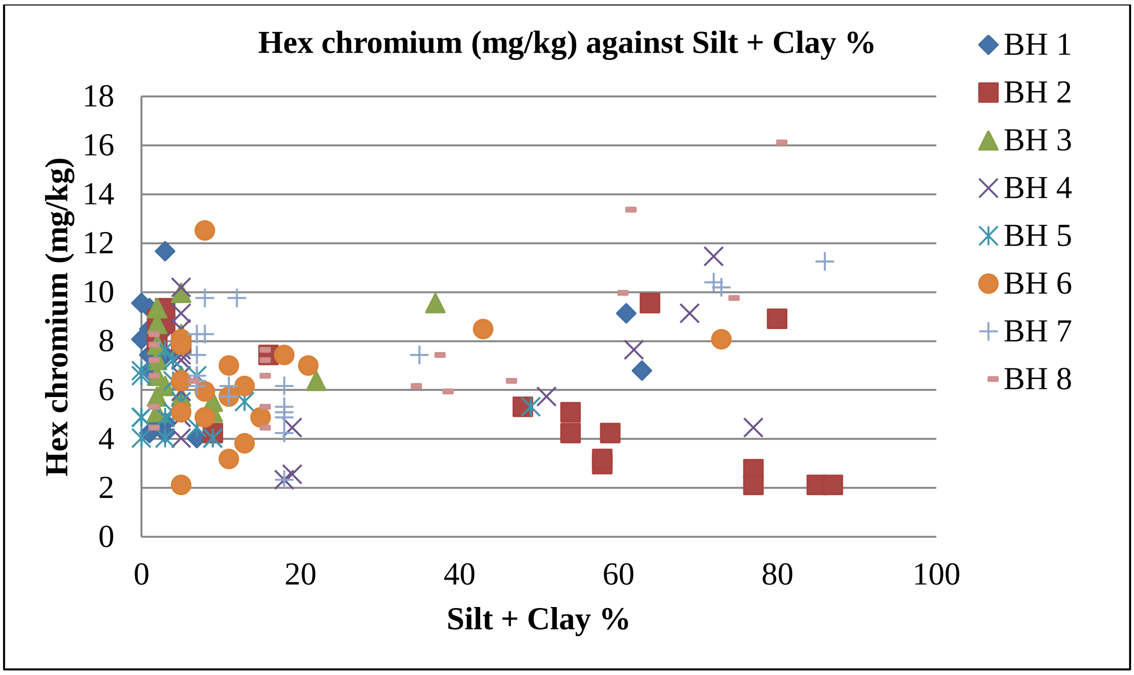


Fig. 5.13: Hexavalent chromium vs silt & clay proportion for aqua regia acid digestion analysis

TCLP gives the value of total chromium and hexavalent chromium in pore volume. While retention is the mass of total and hexavalent chromium adsorbed on soil particle. This could be main reason that no specific trend could be observed regarding TCLP analysis vs silt and clay proportions. It is because silt and clay has higher retention and adsorption capacity than sand. Aqueous solution carrying total and hexavalent chromium is mainly a source for metal adsorption on solid particles which is expressed in terms of retention of metal in solid part of the soil matrices. For both hexavalent chromium and total chromium no specific trend could be predicted regarding the leaching behavior through silt and clay layers.

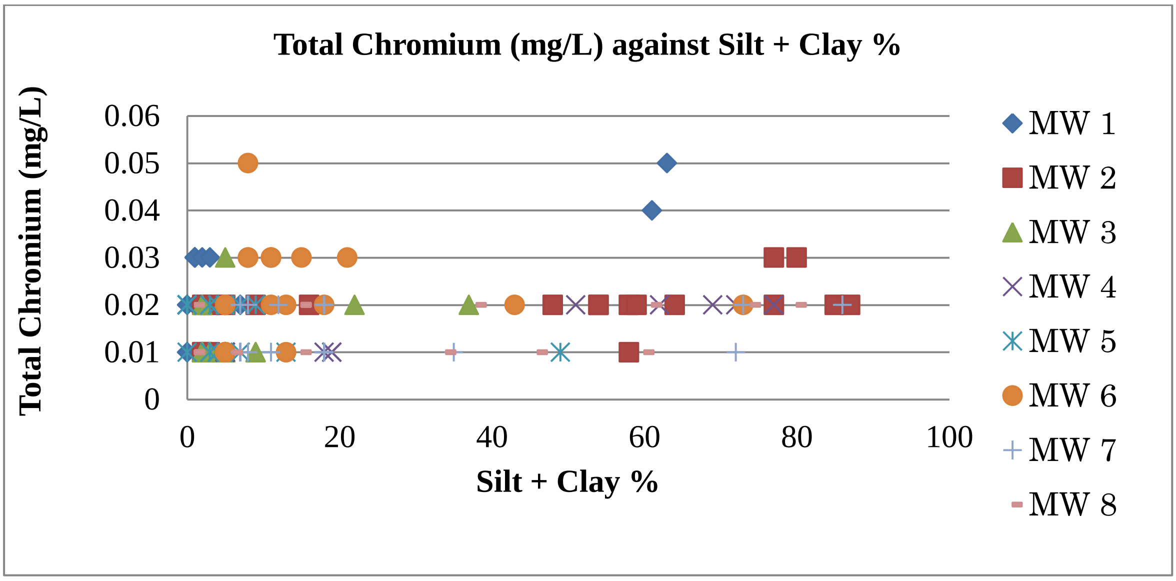


Fig. 5.14: Total chromium vs silt & clay proportion for TCLP analysis

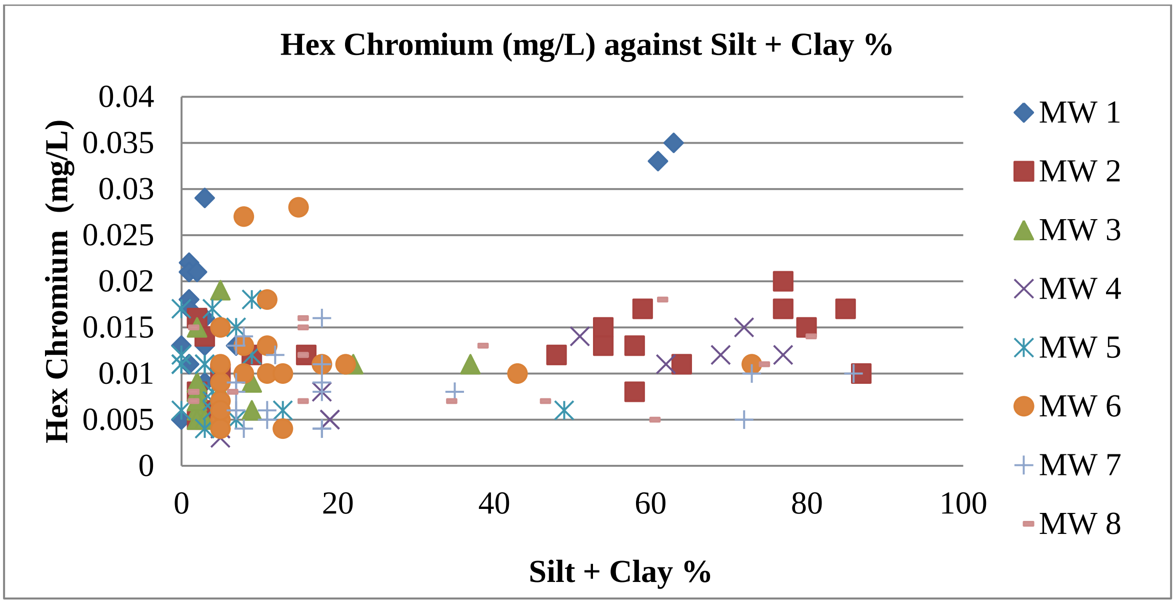


Fig. 5.15: Hexavalent chromium vs silt & clay proportion for TCLP analysis

Behavior of contaminants in soil medium and their geochemistry has a vital role in determining their fate in soil and its leaching properties. The mobility of different states of chromium in aqueous phase can help in restoration process of the environment. The important factors involved in the mobility and fate were soil texture in terms of proportion of the soil and secondly the nature chromium species. These factors were determined on large scale covering a wide area to explain the leaching and retention phenomena in subsurface.

The leaching test, TCLP, was conducted with the purpose to understand the mobility of contaminant i.e. chromium through the soil layers in aqueous form. While tracing the contaminant from tannery effluent through the soil layers, two species of Chromium were found to be significant in describing the behavior of chromium released from tannery units, which are trivalent chromium and hexavalent chromium. Trivalent chromium is the difference between total chromium and hexavalent chromium. It was observed during field investigations that actual ground conditions in the form of geological formations, soil textures and groundwater availability played an important role in speciation of chromium in the study area.

Most of Cr (VI) remaining in soil was found in the water soluble or exchangeable fraction, especially in the batch of basic soil. Cr (III) is less soluble and remains adsorbed or precipitated in soils, meanwhile Cr(VI) is soluble and also a high toxic specie for living organisms (Banksa et al., 2006). While Retention of Chromium in the soils was correlated to Cr (III) content, the hexavalent chromium related to aqueous form in the pores. Hexavalent chromium determines the mobility and leaching behavior of chromium released from tanneries and its movement through the soil layers to mix with groundwater. As hexavalent chromium is soluble in aqueous form therefore its retention with the silt clay has not been found significant as its characteristic of trivalent chromium to get adsorbed on silt and clay fraction of soil medium.

Bartlett (1991) showed that Cr (VI) is capable of moving towards groundwater due to its extreme mobility, and it is in thermodynamic equilibrium with the atmosphere. Cr (VI) is the product of oxidation of Cr (III) with atmospheric oxygen and its presence is greater into the earth crust. Since the natural oxidation of Cr (III) is extremely low, most of the Cr (VI) found in soil and groundwater results from anthropogenic source of contamination.

As it can be observed from the chemical analysis of soil for Toxicity Characteristics Leaching Procedure (TCLP), there is inconsistent pattern of total and hexavalent chromium concentrations along the depth describing the mobility of the contaminants through various soil layers. There is a wide range of soil texture variation as the contaminant leach down into the soil layers which has shown impact on the leaching and mobility patterns of chromium.

5.3.1.7 Cross Section of Soil Profile

All the eight (8) soil bores and monitoring wells were divided into two portions upstream side and downstream side. It was mainly due to the flow direction in Drains 3 & 4. Soil bores and monitoring wells on upstream side included Bore 1, 3, 5 & 6 while on downstream side the soil bores and monitoring well were Bore 2, 4, 7 and 8. These upstream and downstream side bores can be observed from Fig. 5.16. It was aimed to understand the impact of natural flow of the drains on the spreading of the contaminant in soil and groundwater. It was also used to understand how naturally existing site conditions are significantly influencing the movement of contaminant to farther areas adjacent to the drains and agricultural fields.

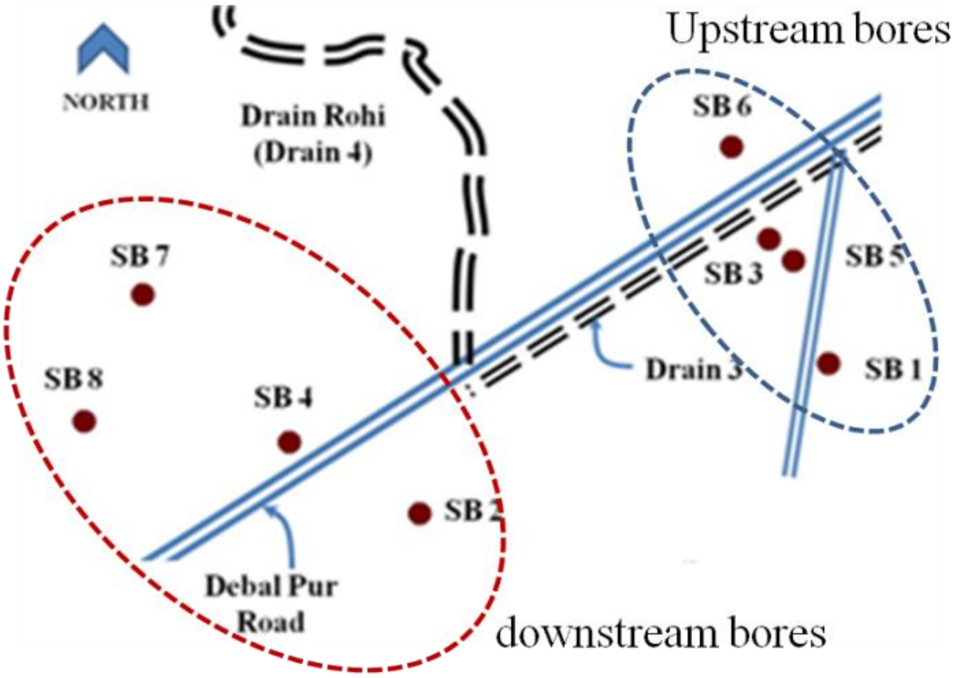


Fig. 5.16: Upstream and downstream of drains for cross section of soil profile

Particle size distribution analysis for every bore was used in order to develop soil profile for two cross sections A A’ and B B’ for upstream and downstream sides respectively. The outcome of both cross sectional soil bores, upstream side and downstream side, are shown in Fig. 5.17 and Fig. 5.18. The depth wise particle size distribution was expressed in terms of elevation from sea level and shown graphically along with water table levels which were almost flat showing a minor deflection or slope. This slope was mainly due to localized impact of nearby passing drains due to the infiltration of effluent into to the soil. Furthermore the rainy season also showed comparatively higher accumulation of water in sandy layers at shallow depths of subsurface profile.

These soil profiles for both sections represent the general trend of soil texture existing in the research area. The variations in the soil texture along the depth can be observed from these plotted graphs.

Section A A’ showed more variation along the depth in soil texture as compared to section B B’ which is mostly sandy. As far as groundwater flow direction is concerned a very minor deflection in water table can be observed from the soil profile along the direction of bores but mostly water table is static and flat.

High rate of correlation do exist in between the soil texture and the level of contaminant retained in the soil or leaching down to groundwater aquifers. Previously described explanation in terms of TCLP and aqua regia acid digestion results clearly exhibited the strong impact of subsurface soil strata with the chromium concentrations.

Upstream side has higher bands of sandy loam or sand throughout the depth of soil profile under observation while on the downstream silty clay strands are also found in significant concentrations.

5.3.2 Groundwater Monitoring and Analysis

As described earlier eight (8) monitoring wells were installed at the place of eight (8) soil bores and groundwater samples were monitored on monthly basis repeatedly for six months. Total chromium being the prime contaminant under investigation was thoroughly Although the observed values of total chromium were not increasingly alarming however a specific trend can be observed which defines the contaminant flow behavior. Concentrations of total chromium observed during the monitoring period are tabulated in Table 5.9.

Table 5.9: Six months groundwater monitoring for total chromium concentration

	MW 1	**MW 2**	**MW 3**	**MW 4**	**MW 5**	**MW 6**	**MW 7**	**MW 8**
Jan 2010	0.022	0.015	0.026	0.03	0.015	0.026	0.025	0.019
Feb 2010	0.025	0.035	0.038	0.041	0.022	0.037	0.038	0.04
Oct 2010	0.02	0.02	0.026	0.038	0.02	0.033	0.04	0.035
Nov 2010	0.01	0.024	0.014	0.02	0.015	0.03	0.033	0.03
Dec 2010	0.01	0.02	0.015	0.011	0.012	0.02	0.029	0.015
Jan 2011	0.01	0.02	0.012	0.011	0.01	0.02	0.021	0.022
Average	0.016	0.022	0.022	0.025	0.016	0.028	0.031	0.027

Samples were collected in the months of January 2010, February 2010, October 2010, November 2010, December 2010 and January 2011. The sample analysis can be explained in terms of dry season and rainy season and peak production duration and minimum production duration. The samples were collected in rainy season during January, for post rainy season during February and October 2010 while dry season samples in November and December 2010. The samples are checked for the total chromium content in groundwater on regular basis and are drawn in Fig. 5.18. There are two important parameters which must be observed while considering the trends of total chromium over the given span of time of six (6) months. First of all it's the seasonal variation and secondly it is the peak and minimum working durations of the tannery industries which are directly associated with the release of tannery effluent into the drains, leading to acute interference with the soil and groundwater aquifer.

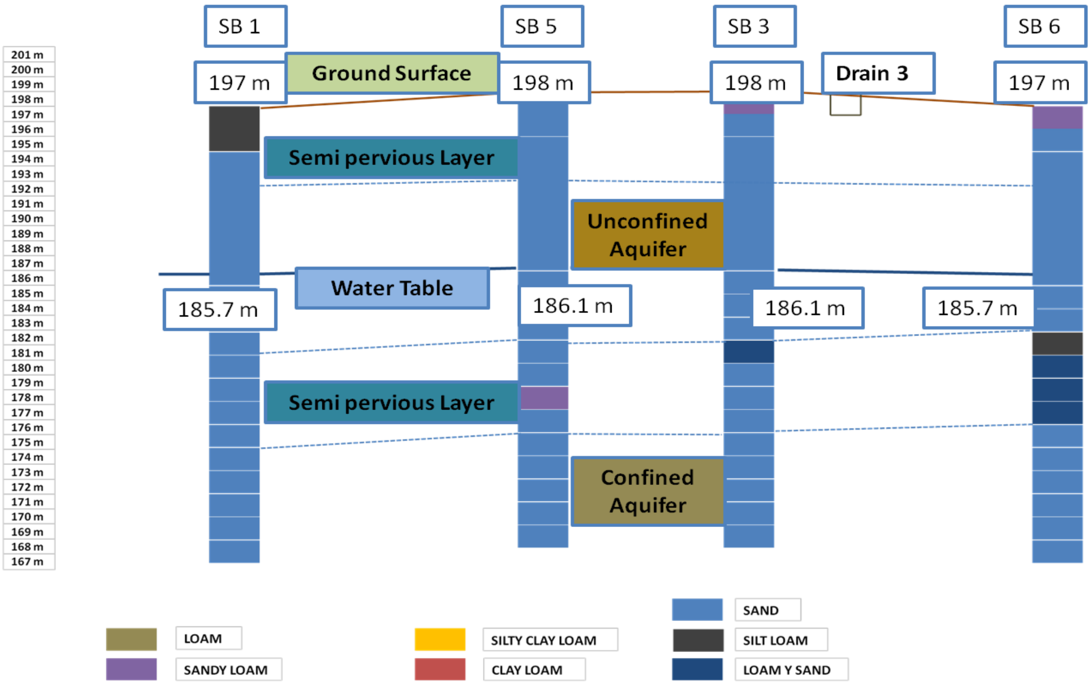


Fig. 5.17: A – A' cross sectional soil profile

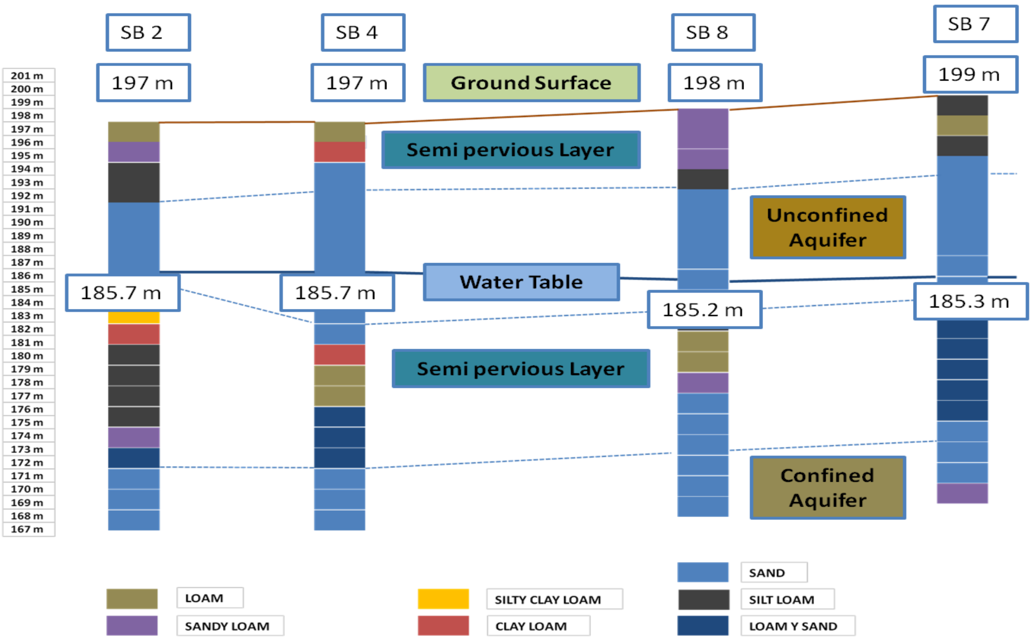


Fig. 5.18: B – B' cross sectional soil profile

A varying trend can be observed throughout the sampling period depending upon a number of factors including location and soil nature ruling the movement of groundwater flow and chromium content absorption capacity. From Fig. 5.19 the variation trend can be observed for different seasons and upstream and downstream monitoring wells. Generally the monitoring wells on downstream have higher values as compared to upstream monitoring wells but the variation trend are same throughout, average values are also higher for downstream monitoring wells. In rainy season overall concentration of total chromium in all monitoring wells is observed to be less.

It may be due to dilution of chromium in groundwater. During post rainy season maximum values of total chromium are observed in all the monitoring wells. There is no more increased recharge due to rainwater but the contaminant has already moved into subsurface and mixing with groundwater. During dry season the tanneries are also working at their minimum therefore there are already lesser quantities of total chromium in wastewater and therefore the seepage of total chromium also not so influential to exhibit higher values of total chromium in groundwater.

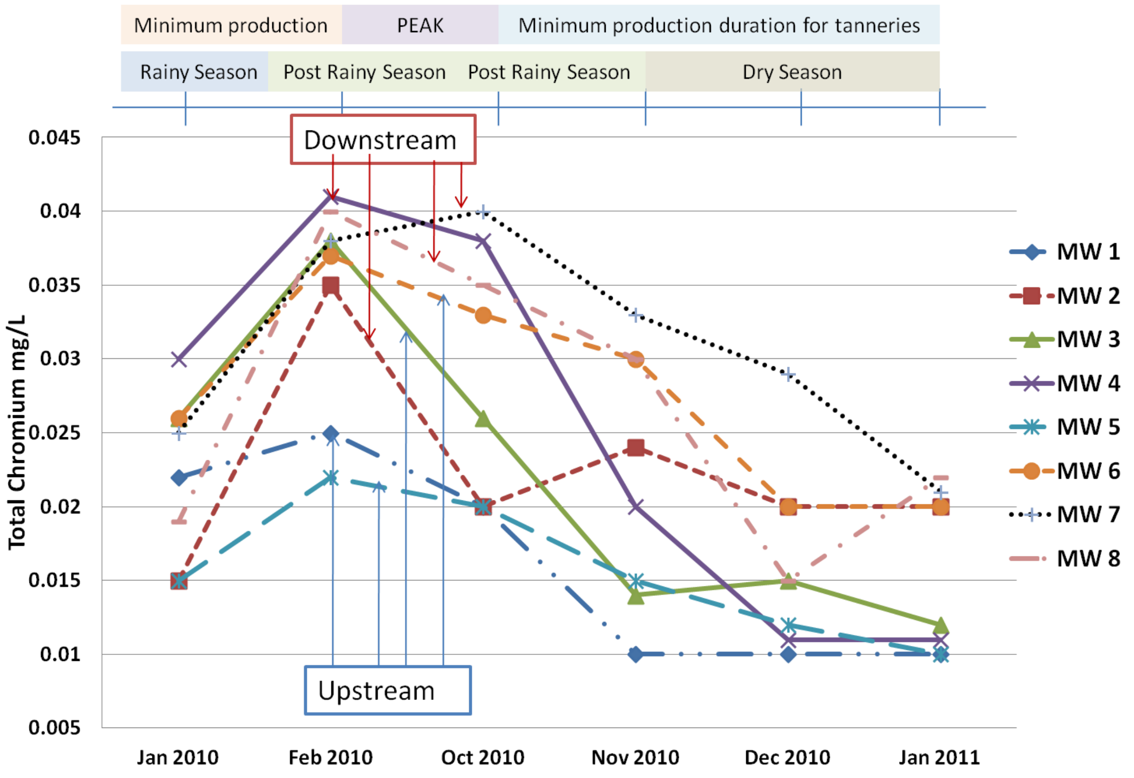


Fig. 5.19: Periodic groundwater monitoring results for total chromium for six months during 2010 and 2011

5.3.3 Seasonal Wastewater Analysis

Similar to previous phase seasonal wastewater analysis was continued in the second phase as well with one addition of the sample from Drain 5, Main Drain. The reason to include this drain was to find out the final quality of the wastewater before it is discharged into Drain 5. The comparative analysis of the results during Peak production duration and minimum production duration are shown in Fig. 5.20.

The observed values for all the drains is not that high as it were previous year in 2010 but still these values are extremely high and far more than National Environmental Quality Standards limitation for wastewater in drains for Total chromium i.e. 1.0 mg/L, except one value and that is for minimum production duration season in Drain 5, which is equal to 0.55 mg/L.

Consistency can be observed in the total chromium concentration variation pattern for both peak production duration and minimum production duration as symmetric trend is found for all the five drains.

For both the sampling season the concentrations are in excess of National Environmental Quality Standards (GOP, 2000) for total chromium i.e. 1.0 mg/L except one value i.e. for Drain 5 during minimum production duration. When the results of second phase are compared with that of first phase seasonal wastewater analysis, a decreasing trend is quite obvious in concentrations of total chromium during one year period. But still these values are alarmingly high and have great tendency to contaminate subsurface.

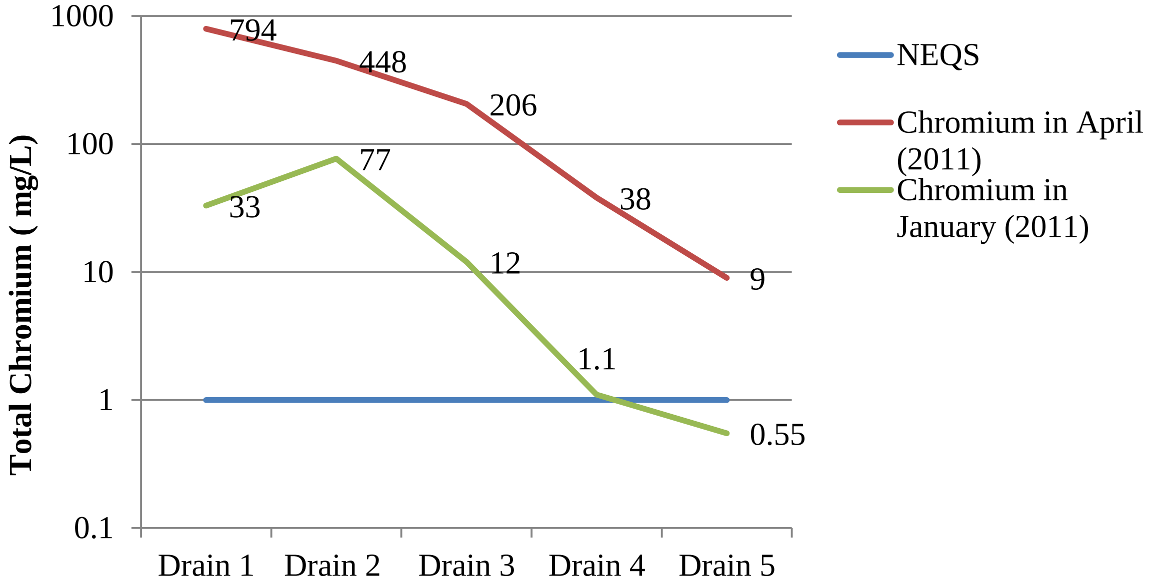


Fig. 5.20: Seasonal wastewater analysis comparison for five drains in research area 2010 and 2011

5.4. Impact Evaluation by Geospatial variation of total and hexavalent chromium in Soil and Groundwater

In order to understand combined effect of tannery effluent contamination in soil and groundwater medium VOXLER ® 4 version was used so as to work out three (3) dimensional geospatial contamination existence in the study area in terms of total and hexavalent chromium concentration variations throughout the soil and water table level. Objective to use the above mentioned software was to obtain 3 dimensional geological impacts of parameters under investigation and its behavior in horizontal as well as in vertical direction i.e. along the depth simultaneously.

Groundwater flow pattern and extended chromium concentrations were estimated using the graphical presentations of water table level in all the eight (8) monitoring wells. The field layout of all the sampling points is shown in Fig. 5.21. Application of VOXLER further helped in evaluating the contamination load along the depth at one point in terms of overall weightage of the total and hexavalent concentrations.

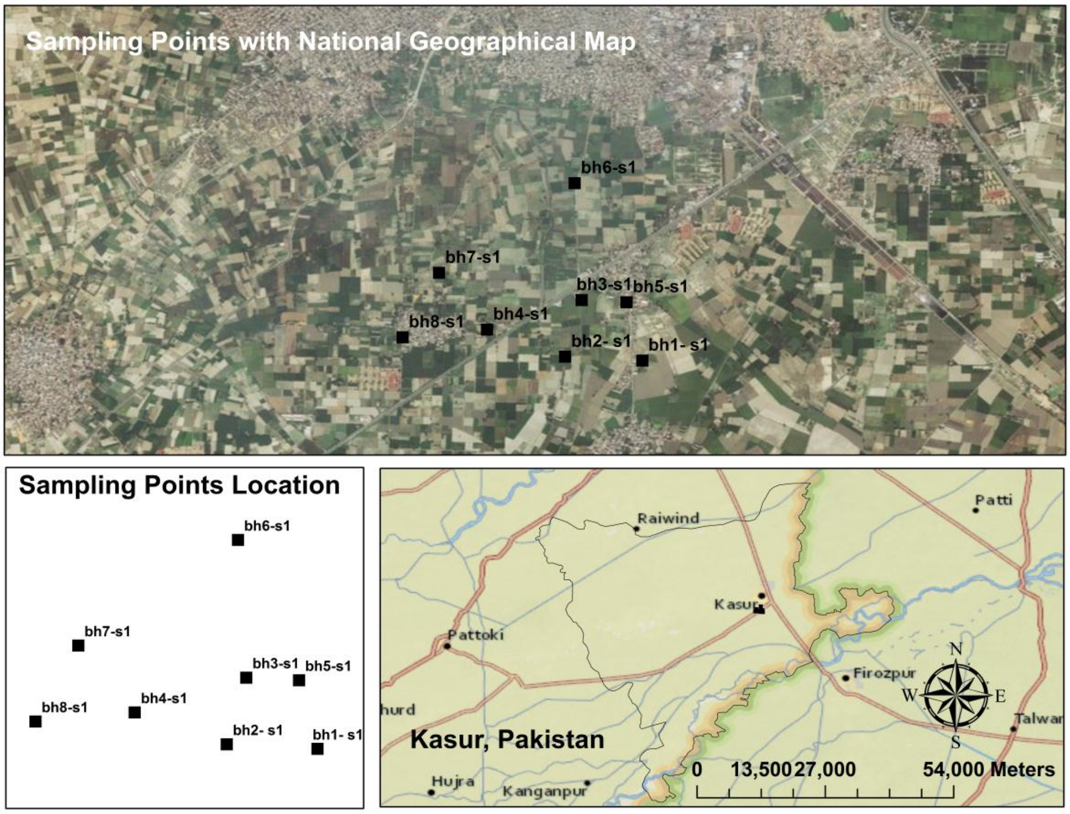


Fig. 5.21: Site map of the study area including tannery area as well as soil bore and monitoring well locations.

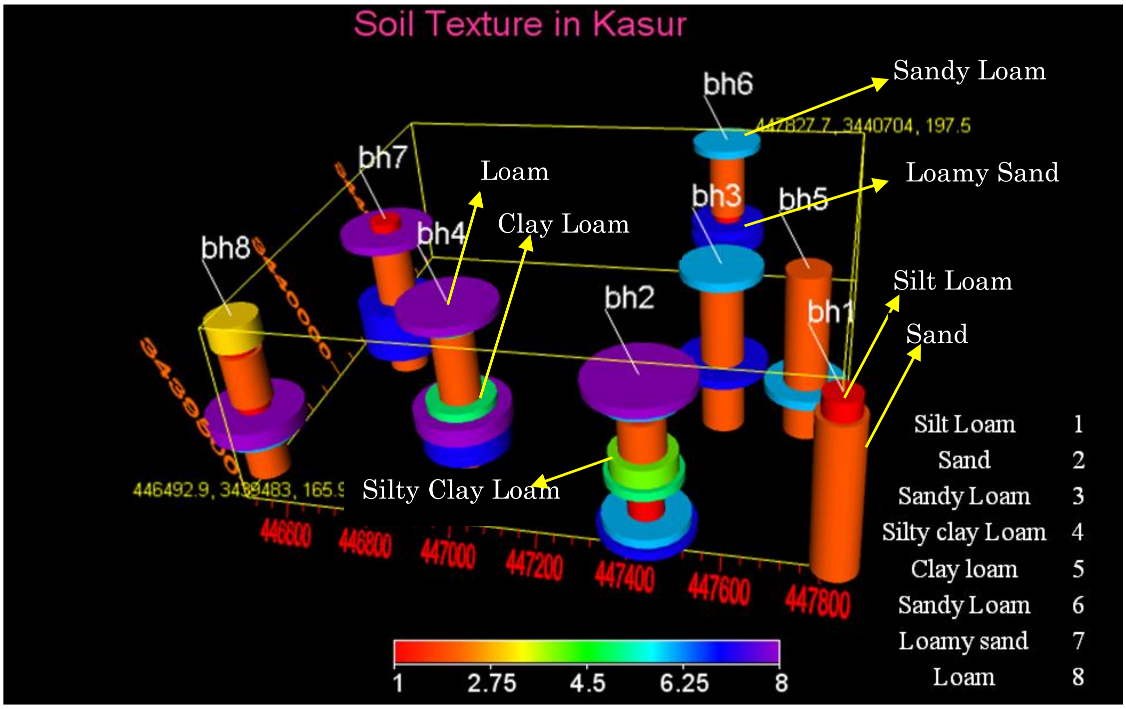


Fig. 5.22: Eight (8) Soil bores and soil texture variations along the depth

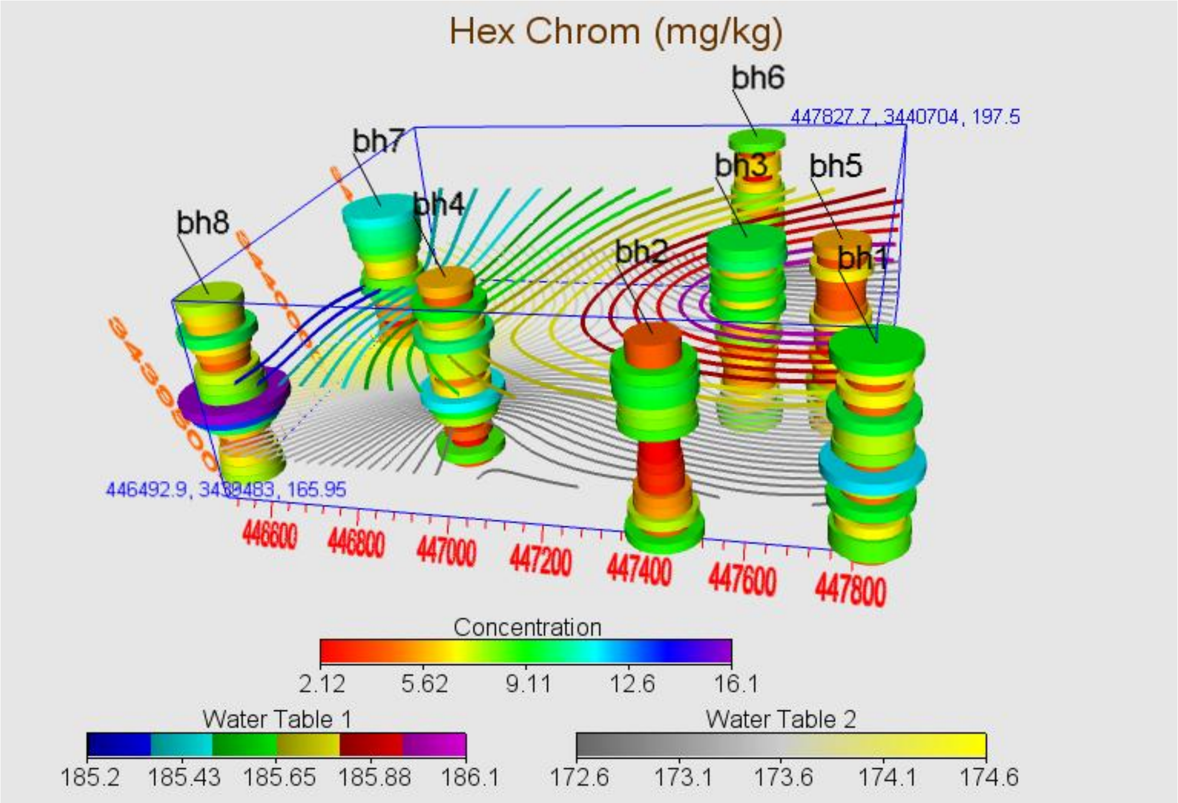


Fig. 5.23: Hexavalent chromium retention demonstration in eight (8) soil bores along with water table movement patterns

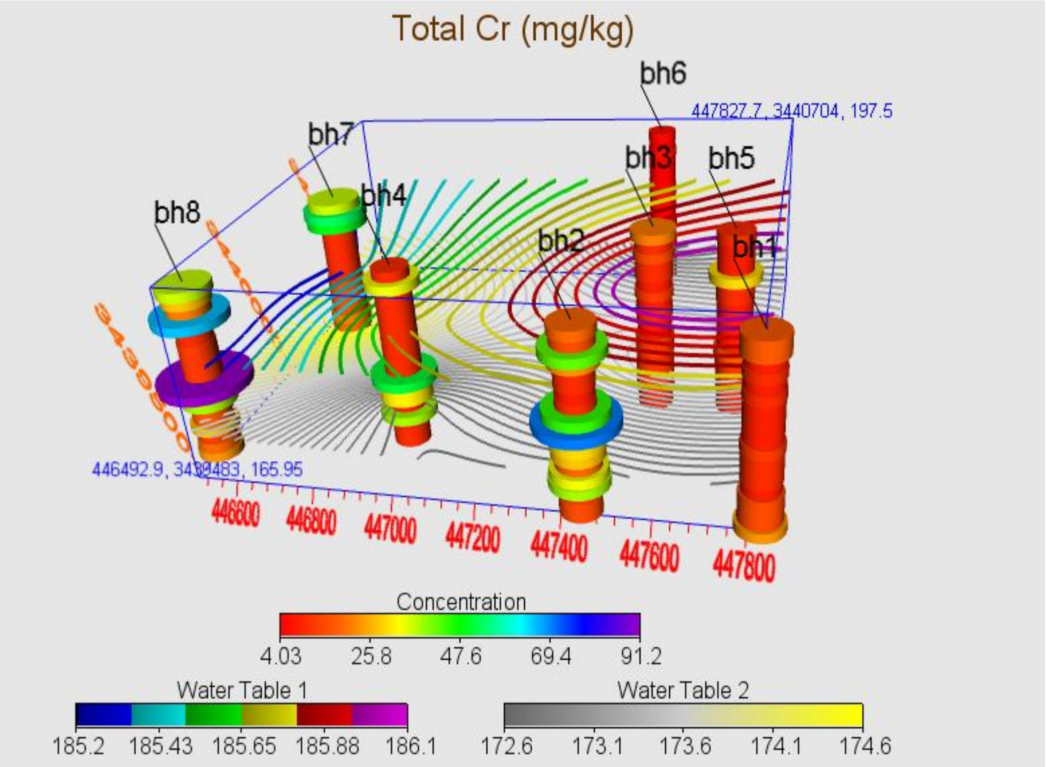


Fig. 5.24: Total chromium retention demonstration in eight (8) soil bores along with water table movement patterns

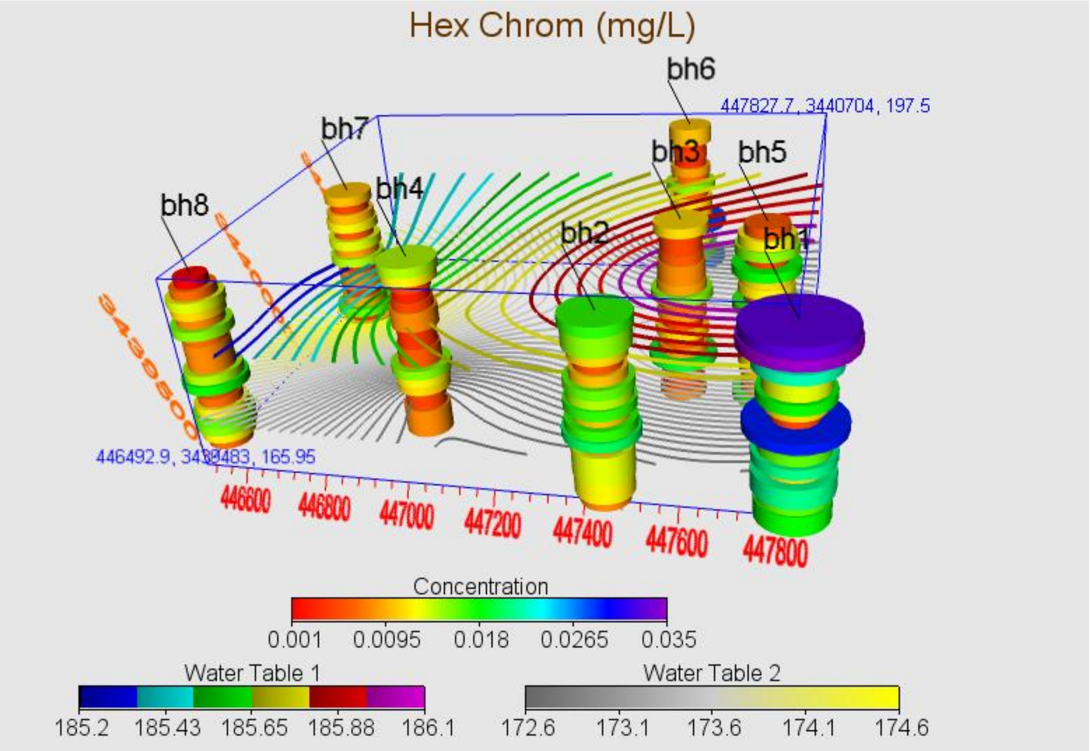


Fig. 5.25: Hexavalent chromium leaching concentration by TCLP demonstration in eight (8) soil bores along with water table movement patterns

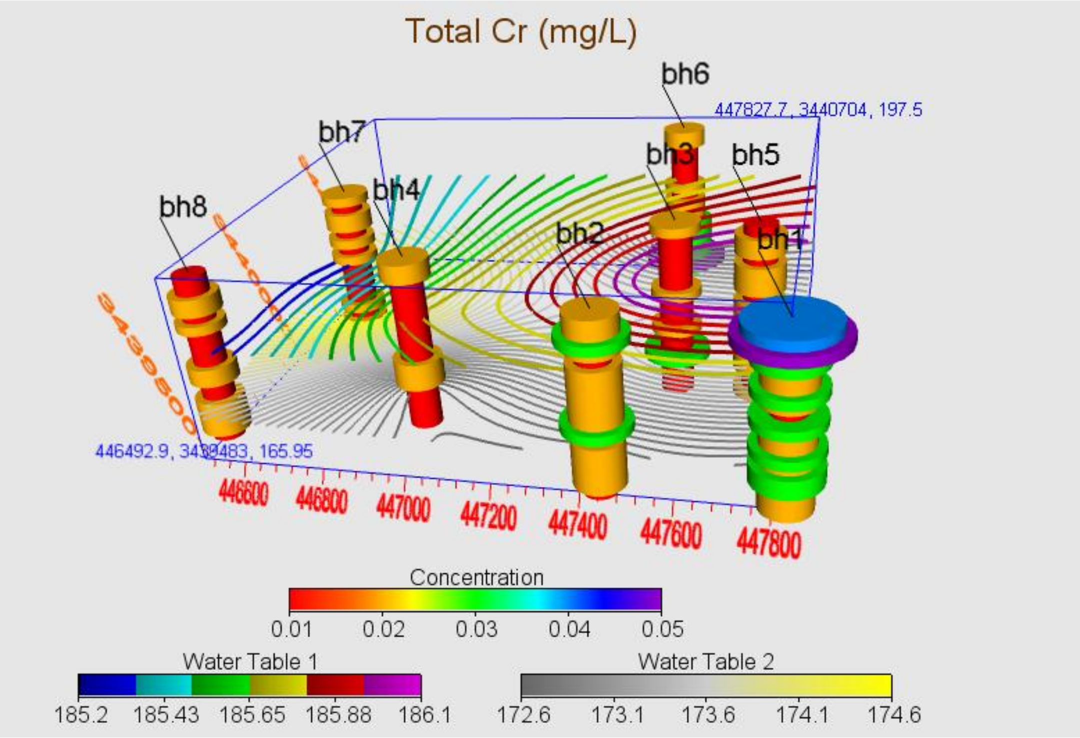


Fig. 5.26: Total chromium leaching concentration by TCLP demonstration in eight (8) soil bores along with water table movement patterns

As VOXLER ® software can be used to interpret the concentration gradient as well as the groundwater movement in the form of contours; the outcome of the software described the total mass content i.e. total chromium and hexavalent chromium along the depth and geo spatial variation with reference to other soil bores and monitoring wells. Furthermore as the water table level is almost flat and horizontal still a slight localized movement of groundwater can be interpreted.

Soil texture variations, as graded from 1 to 8 describing the respective level of soil complexity have been described in Fig. 5.22. It is obvious that soil is generally characterized as loamy sand to sand with prominent patches of silty clay loam as well. These soil texture bands are directly related to behavior of sub soil strata in terms of its capacity to retain soil or mobility of contaminant through soil layers.

Effect of soil characteristics, with specific contaminant existence and transport behavior, on the retention of hexavalent and total chromium can be observed in Fig. 5.23 and Fig. 5.24. Usually presence of high concentrations of hexavalent chromium depicts fresh interference of sources of contamination into subsurface strata. While hexavalent chromium got reduced to trivalent chromium so as to get retained to negatively charged clay particles within the soil. Not only the distribution of hexavalent and total chromium along the soil profile is significant in understanding the behavior of contaminant transport but also total quantity of retained contaminant is also very important to describe the movement of contaminant accompanied by the groundwater flow patterns. Groundwater flow contours as developed in these graphs has shown a very stagnant conditions as no proper flow directions can be interpreted by these contours. However as the sources of groundwater infiltration is not so specific in the form of hydrological units therefore smooth flow of groundwater cannot be expected at this site. Only major source of infiltration is the effluent carrying drains, thus the direct interference of contaminated water into the soil layers is supposed to be the major source of groundwater movement, no matter what the concentrations of hexavalent and total chromium may be in these drains. This effect has also been observed in Chapter Six (6) while developing the groundwater flow model and contaminant spread out pattern. It has also been well interpreted due to lack of groundwater slope which restricted the movement of contaminant in specific areas only and hindered the path of contaminant transport to farther regions. Nevertheless soil layers with high silt and clay content has shown higher retention values as in Fig. 5.24 Soil bore 2 shows overall high volume of mass retained as compared to other soil bores. While in Soil Bore 8 again very high concentrations of contaminant has been observed in deeper layers, which is justified with the flow patterns of groundwater and particular silty clay soil textures.

Similarly for hexavalent chromium and total chromium mobility patterns in soil as shown in Fig. 5.25 and 5.26, higher values can be observed in the range of two water tables as demonstrated. The first water table level seems consistently unvaried throughout and occupied significant share in moving the contaminant from upstream to downstream side. It is obvious from the larger disk sizes for each soil bore at the elevation of first water table level. Concentrations of hexavalent and total chromium are relatively high in the second water table as well along the flow directions of groundwater. This flow trends are in accordance with that obtained from FEMWATER outcome and more or less confirms the similar groundwater movement as well contaminant flow trends as described in CHAPTER 6.

5.5 Summary of Chapter 5

From the findings of first phase random groundwater sampling depict varied contamination distribution pattern in two areas of main concern, first is tannery area and second one is near junction of Drain 3 and 4. Clusters of contamination rather than consistent existence of Total chromium concentrations of 90 mg/L in the middle of tanneries and up to 10 mg/L on the downstream of Drain 3 and 4, at Dole Wala and Faqire Wala, in the groundwater samples from shallow depths present an alarming situation of subsurface contamination in not only tanneries area but also in residential area on the downstream side the research area. Extremely high concentration of chromium in wastewater, reaching upto 2,150 mg/L along with other pollutants in excess, is a potential risk of subsurface contamination, especially groundwater contamination, due to the percolation of the effluent into the soil.

The soil analysis of the two soil bores which were conducted in the research area, indicate that the retention of chromium in the soil is dependent upon the nature of soil. The higher the clay and silt proportion in the soil is, the higher the retention of the chromium. TCLP analysis for all the 30 soil samples taken from two bores showed no significant probability of the leaching of hexavalent chromium and total chromium. However, the relatively low concentrations of both hexavalent and total chromium in the deeper sandy layer also illustrate that the soil was contaminated by the chromium transported by the groundwater. There must be some direct interference of wastewater with groundwater via line sources of contamination i.e. the drains, through which the contaminant is spreading farther areas from the tannery area.

The current soil contamination might not be a serious source of the groundwater contamination in the future. Therefore by focusing on the chemical treatment of the tannery effluent and on the seepage prevention of the untreated effluent from the drains or leakages from the concrete made sewers, further spreading of the groundwater contamination could be controlled up to large extent. Once the source of contamination has been stopped and controlled, the groundwater contamination might reduce by exhibiting natural attenuation.

The data of ground water is limited to one season and the data about the soil shows some variations at the two bores. To study about the seasonal variation of the groundwater quality and to have a more clear view of the soil contamination at the investigated site, periodical monitoring of ground water and additional soil bores and testing are needed.

As far as summary of Phase II is concerned detailed soil analysis of soil samples up to the depth of 30.5 meters has shown no significant concentrations of total or hexavalent chromium at any level of depth indicating no direct percolation of chromium carrying wastewater.

However at some depths presence of chromium in relatively higher concentrations especially in comparison with back ground values depict chronic percolation of chromium contamination.

High levels of chromium in groundwater in some monitoring wells indicate direct intrusion of wastewater with groundwater. Especially from the results of groundwater monitoring it is quite obvious from the abrupt changes in chromium concentrations in groundwater with the change in concentration of source.

Wastewater analysis also depicted consistent source of contamination as high concentrations of total chromium are present throughout the year. No measures have been taken to reduce the influx from the drains into the soil layers therefore the untreated wastewater flowing in the drains poses a severe environmental hazard in the study area.

CHAPTER 6

CONTAMINANT TRANSPORT MODEL DEVELOPMENT

6.1 Background

From the previous chapter the soil and groundwater contamination have been confirmed on the basis of existence of total chromium in soil samples, collected from top soil layer in tannery area and from depth wise soil sampling and from groundwater samples collected from tannery area and from other parts of the research area.

Purpose of the research was to determine contaminated site assessment approaches in the study area. It include, site characterization, understanding the contaminant mobility and retention so as to describe the behavior of the contaminant in different media and effect of the contaminant on the health of the inhabitants. After characterizing the site in terms of contaminant availability and its behavior in soil and groundwater, it was required to simulate the chromium for its mobility in groundwater. The basic purpose of this objective was to predict the movement of contaminant (Total chromium) in groundwater so that its potential impact on quality of groundwater followed by its impact on human health could be evaluated. Furthermore it was also aimed to work out the contaminant (total chromium) movement considering different possible scenarios based on the available facts and figures.

Therefore it is aimed to model the whole contamination scenario with the objective to understand subsurface hydrology regarding groundwater flow and solute transport mechanism in different soil layers. In this regard FEMWATER Model of GMS groundwater modeling software package was used to conduct a coupled flow and transport in unsaturated and saturated zones in the study area.

6.2 Site Characterization and Identification of Sources and their Possible Effect

In order to understand the sources of contamination and its transport in the surrounding area of Kasur, site characterization is done by considering all the possible sources and their possible effect on one another. There are three main types of contaminations soil contamination, groundwater contamination and surface drains contamination, basically originating from the tannery effluent either coming directly in contact with soil through overflow and open disposal into stagnant ponds or it may be through drains from which it may percolate down into soil and then mixing with groundwater. Fig. 6.1 shows the overall contamination mode and its extent along with maximum, minimum and average values obtained at the specific location irrespective of the time parameter.

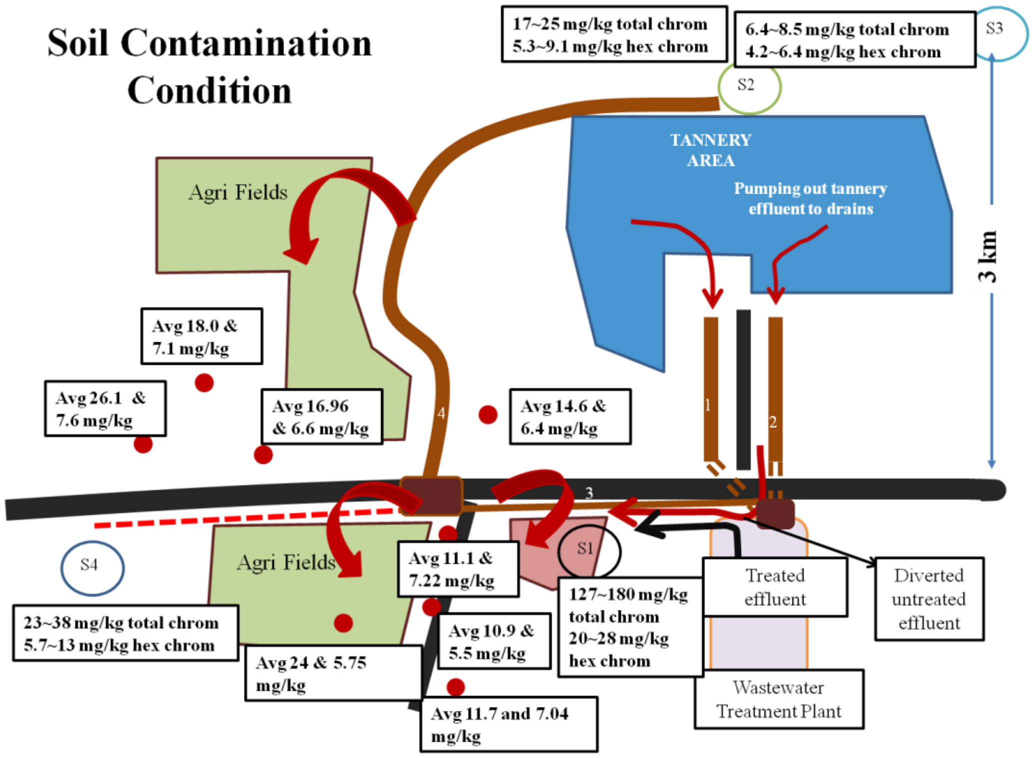


Fig.6.1 (a)

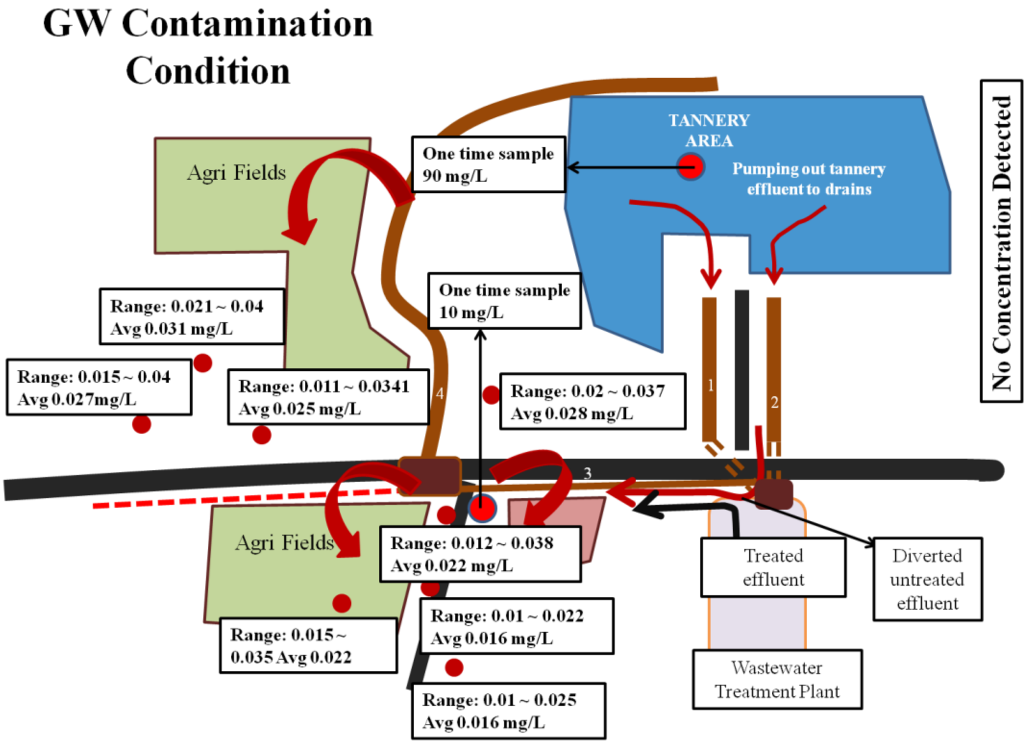


Fig. 6.1 (b)

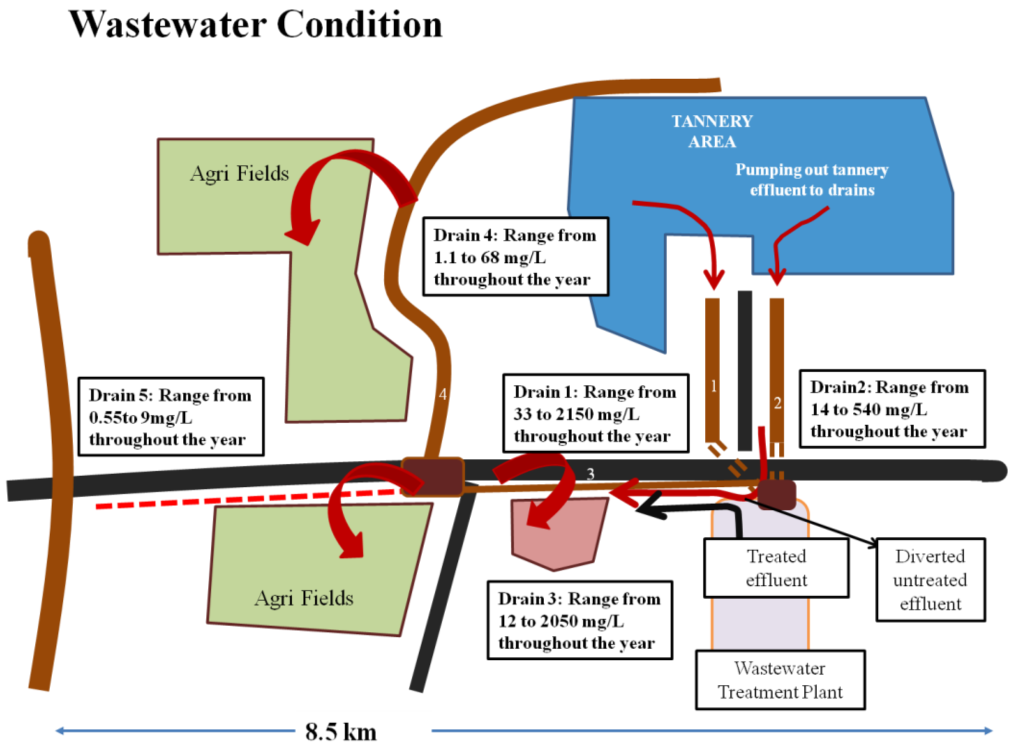


Fig. 6.1(c)

Fig. 6.1: (a) Soil contamination in Kasur tannery area (b) Groundwater contamination in Kasur tannery area (c) Wastewater condition in drains of Kasur tannery area

In Fig. 6.1 (a) soil contamination in Kasur tannery area and adjacent areas have been shown in detail based on its location wise existence and extent. From this part of figure an overall visualization can be achieved about the areas of wise distribution and possible justification regarding some potential source from which it has been caused. Soil contamination has been analyzed on wide range of area, for example four sampling sites S1, S2, S3, S4 were selected in order to observe top layer soil contamination extent, besides 8 soil bores were conducted up to depth of 30.5 meters in the peripheries of Drain 3 and Drain 4 (Drain Rohi) with the purpose to investigate depth wise contamination profile for total chromium and hexavalent chromium.

From Fig. 6.1 (a) two types of main findings can be drawn, first is that top surface has comparatively higher concentrations of total and hexavalent chromium in the surroundings of drains nearer to tannery area while second finding is that although in very minor amounts, still deeper soil layers up to 30.5 meters have shown significant amount total and hexavalent chromium when observed on average basis in the eight (8) soil bores around Drain 3 and 4 near junction.

Observing the groundwater contamination situation from Fig. 6.1(b) a similar contamination trend can be found in study area. Field observations from eight (8) monitoring wells installed exactly at the same location from where soil bores were conducted for depth wise soil sampling on average basis showed the existence of total chromium in groundwater samples, however not in alarmingly high concentrations.

A significant trend of total and hexavalent chromium upto the depth of 30.5 meters on average basis at the every depth of 1.5 meters can be observed in Soil Bore 2, 24 mg/kg and 5.5 mg/kg; Soil Bore 4, 16.96 and 6.6 mg/kg; Soil Bore 7, 18.0 and 7.1 mg/kg and in Soil Bore 8, 26.1 and 7.6 mg/kg of total and hexavalent chromium respectively. While from Fig. 6.1 (b) more or less similar trend of increasing concentrations of total chromium can be found on average basis along with an increase in range as well. These monitoring wells are MW 2 with average value of 0.22 mg/L ranging between 0.015 and 0.035 mg/L, MW 3, with average value of 0.22 mg/L ranging between 0.012 and 0.038 mg/L, MW4, with average value of 0.025 mg/L ranging between 0.011 and 0.034 mg/L, MW 6 with average value of 0.028 mg/L ranging between 0.02 and 0.037 mg/L, MW 7 with average value of 0.031 mg/L ranging between 0.021 and 0.04 mg/L and MW 8 with average value of 0.27 mg/L ranging between 0.015 and 0.04 mg/L.

Thus from this comparison correlation between soil and groundwater contamination can be presented in the surrounding areas of Drain 3 and Drain 4, near junction of these drains.

This correlation can be confirmed and explained by wastewater pollution condition as illustrated in Fig. 6.1 (c). Drain 3, which carry wastewater treated effluent from treatment plant along with diverted untreated effluent from tannery area, have been observed to be over flowing most of the time during the year on either sides but mostly towards left of the flow direction into the agricultural fields and open places. This overflow is subjected to excessive discharge in the drain along with the chocking on the downstream side due to solid waste disposal. With concentrations of total chromium ranging between 12 and 2,050 mg/L along the year, during both minimum production and peak production duration, there is high probability of seepage of chromium contamination into soil and groundwater throughout along the length span of 2.5 kilometers of the drain. This is evident by maximum observed concentrations of total and hexavalent chromium in the top layer soil analysis adjacent to Drain 3 and tannery area equal to 180 mg/kg and 28 mg/kg respectively. Similarly as far as groundwater contamination is concerned, one time soil sample analysis at shallow depth of below 30.5 meters have provided value of 10 mg/L at the bank Drain 3 Furthermore extending along the Drain 3 towards the end, the junction of Drain 3 and Drain 4 is another very critical location. It is due to the cracked concrete structures, exposed to high rates of percolation of contamination into soil and most likely to be probable source of direct intervention into groundwater. From the observation of the depth wise soil analysis data and groundwater monitoring data in the surrounding of this location, the seepage of contamination is undeniable fact. Accumulations of total chromium as observed in Soil Bore 2, 4, 6 and 8 provides a clear evidence of the seepage into deeper layers irrespective of the fact how small the retained concentrations may be. However up to the maximum of 91.2 mg/kg and 16.1 mg/kg for total and hexavalent chromium has been observed in Soil Bore 8 at the depth of 16.8 meters.

6.3 Conceptual Model Development of Kasur Site

In order to interpret the sources of contamination and its transport in the surrounding area three scenarios were developed. For each case the sources of contamination and the concentration contamination were specified along with defining the boundary conditions of the model. In the decade of 1970s when “chrome tanning” was adopted by the tannery units to enhance the quality of leather production and its finishing, the tannery business flourished tremendously thus resulting in increase in subsequent environmental issues. As described before there was no proper disposal mechanism before year 2000. Until then all the industrial wastewater was thrown in open fields. Even now the situation could not have improved even by channelizing the wastewater from the tannery units to the treatment plant with the help of two drains. However the severity of the environmental conditions has been reduced to large extent. It has been mentioned earlier that the major issues is the lack of proper industrial waste management system. The adverse wastewater and solid waste situation in the areas adjacent the tannery units have been shown in Fig. 6.2.

Fig. 6.2: Adverse conditions of improperly disposed tannery waste in open fields adjacent to tannery units (pictures taken in November 2015)

Furthermore it has been observed that as there was lack of solid waste management since the very beginning, the tannery solid waste kept on accumulating on the roads and theirs sides, which was frequently used by the passengers thus creating an exposed health risk to them as obvious in Fig. 6.3. To worsen the situation the tannery effluent also got mixed with the solid waste dumped in the fields.

Fig.6.3: Hazardous solid and wastewater from tannery units in open fields (pictures taken in November 2015)

Fig. 6.4: Mixed wastewater and solid waste from tannery units and households indicating an open threat to health and environment (Pictures taken in November 2015)

The existing situation of the tannery areas and the residential areas adjacent to the tannery units has presented very unhygienic conditions. Even after the provision of drains to carry wastewater from tannery area, still the wastewater is not being properly collected and carried to final disposal. Therefore all the measures which had been taken to reduce the impact of wastewater on subsurface strata and surrounding environment could not fulfill the purpose successfully. Such adverse condition could be observed in Fig. 6.4 and such environmental conditions provided the basics for development of third scenario presenting the factual conditions after the measures had been taken to control the adverse scenario before year 2000.

6.3.1 Adverse Contamination Scenario

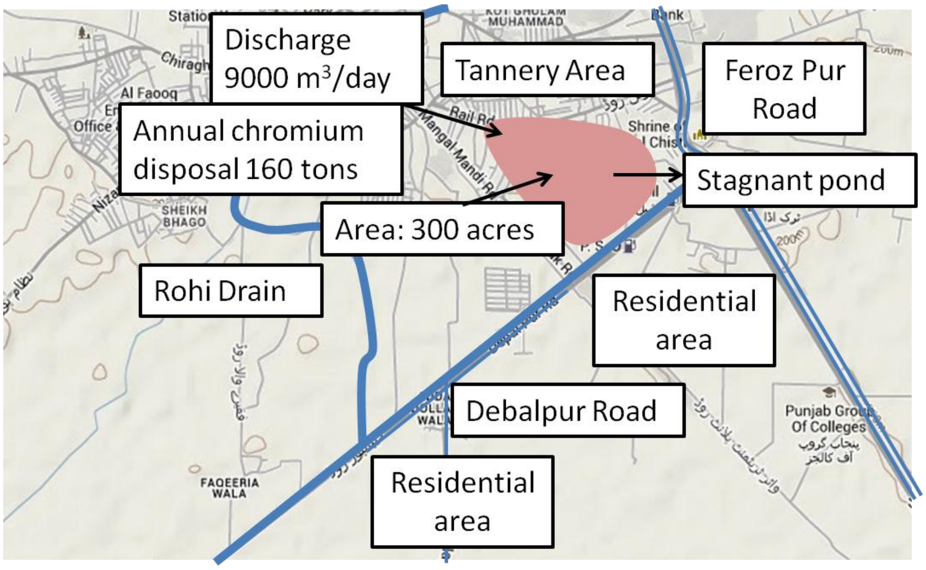


Fig. 6.5: Schematic diagram of adverse contamination scenario

In order to model the contamination and its sources at Kasur tannery area, there is one main assumption to simulate for adverse contamination scenario. In this scenario one major stagnant pond is considered as source in which the tannery effluent of all the tanneries gets accumulated. It is assumed that the total area of the stagnant pond is 300 acres and the discharge of effluent into the pond is 9000 m^3/day. It is also fixed that total chromium load disposed into wastewater is 160 tons annually.

The schematic diagram of adverse contamination scenario is shown in Fig. 6.5. This is one aspect of contamination to consider a stagnant pond as main source of contamination receiving the entire tannery wastewater load from where it seeps down into soil and groundwater. But as a fact of matter there has never been a single potential source at Kasur tannery site rather than dispersed sources all around.

One main reason for these wide spread clusters of contamination in Kasur tannery area is the old history of tannery industry in Kasur. Earlier residential area and tannery area was combined as tannery units were working within the houses as small industries and therefore the waste disposal was also combined. At that time the industrial units were limited and were not involved in large productions. It was because all the tannery processes were handled manually and there was no chemical introduction in tannery industry. Vegetable tanning was in practice in all the industries. But this situation was not anymore prevailed since 1970 onwards.

From early 1970s a new era initiated with the construction of new tanneries on the outer boundary of city along the main road linking major cities like Lahore. But it was not a planned industrial area and there were no sewerage system developed for it and considering barren lands of not any use, the tannery wastewater was directly disposed into the open fields, which finally converted into lake of tannery effluent (usually in rural areas the wastewater is dumped into open ponds).

It almost took 20 years to realize the severity of problem related with sanitation and public health when serious health concerns started occurring in the area due to continuously existing stagnant ponds with heavy bulks of wastewater

In order to investigate the main source of contamination in the entire tannery area, these stagnant ponds adjacent to the tannery area are the most critical one. Initially there were no drains and no treatment plant therefore the entire area of 300 acres was the only waste disposal site for effluent discharge.

For this scenario 20 years period was assumed as this situation persisted until year 2000 when rehabilitation activities started in the area. Initially there were 150 to 180 tannery units existing in this site discharging effluent at the rate of 9000 m^3/day with annual load of chromium equal to 160 tons disposal into environment. Considering the worst possible scenario it was assumed that all the waste disposed was a leached into the soil along with discharged wastewater.

6.3.2 Improved Condition Ideal Scenario

This scenario started after the construction of drains in the tannery area and evacuation of the stagnant ponds, which were dried by disposing the stagnant pond wastewater after treatment into the farther drain from where it was carried to the River Sutlej.

There were two drains, named Drain 1 and Drain 2 which carried the pumped wastewater to the wastewater treatment plant, from where after treatment; the treated effluent was carried through another Drain 3 to a junction of Drain 3 and Drain 4. Drain 4; basically a storm water stream carried the municipal wastewater from the city along with tannery effluent from tannery units which existed on the banks.

During this duration it was assumed that there was high rate of contamination reduction in the surrounding areas of tanneries as all the stagnant ponds got dried and the wastewater was properly collected and carried to treatment facility.

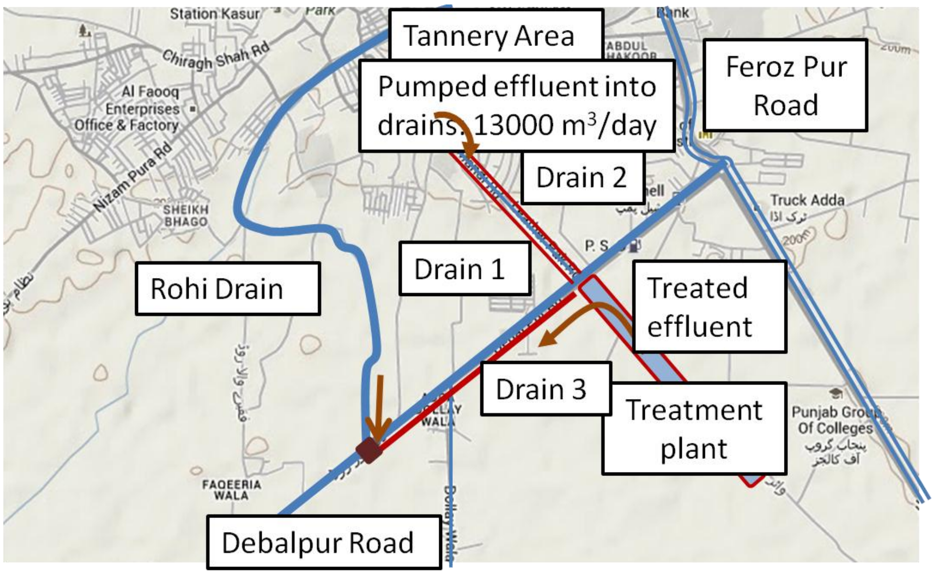


Fig. 6.6: Schematic diagram of improved condition ideal scenario

This second scenario indicates the condition after starting the government activities to cope with severity of health related problems. The major steps included construction of drains in the area to drain out the stagnant ponds, construction of a biological wastewater treatment plant to treat the wastewater from tanneries, development of an agency to manage the wastewater treatment related activities. In this scenario it is assumed that all the tannery waste being properly collected and pumped into Drain 1 and 2 for carriage to wastewater treatment plant, from there treated effluent carried through Drain 3 for final disposal into main drain and then to the river Sutlej. The drains are carrying effluent discharge of 13,000m^3/day in order to incorporate the increased load from increased number of tanneries. It is assumed that all the waste is properly handled and there is no leakage or over flow from drains or construction units. It is also assumed that wastewater treatment plant is working with 100 % efficiency and all the chemicals and organic load are removed before the treated effluent is further carried away. The schematic diagram of improved condition scenario is presented in Fig. 6.6.

6.3.3 Factual Scenario

This scenario is the reality based scenario completely depicting the present situation at site. Main features include the over flow from drains, especially from Drain 3 which is also carrying diverted untreated wastewater before entering treatment plant thus carrying heavy contaminant loads. It is assumed that 1 % of the total discharge i.e. 13,000 m^3/day is being over flowed into the fields on the sides. The third scenario is represented in Fig. 6.7. This overflow being not so regular could not be precisely calculated. In this case the area affected by overflow was also a variable parameter as it was mainly dependent upon the flow rate and causes of overflow. However based on the site observations the flow was assumed to be 130m^3/day, covering an estimated area of 22,500 meter square. In this scenario it was also assumed that the main stagnant pond that once was considered as main source of contamination had been closed and no more in operation.

This scenario was assumed from 2005 to 2011 for duration of 7 years. It was based on assumption that for first four years treatment plant has worked well and proper carriage of effluent took place. But after 4 years, overflow in drains created lot of area into stagnant pond, which however had its effect on soil contamination as the drains were carrying heavy chromium concentrations.

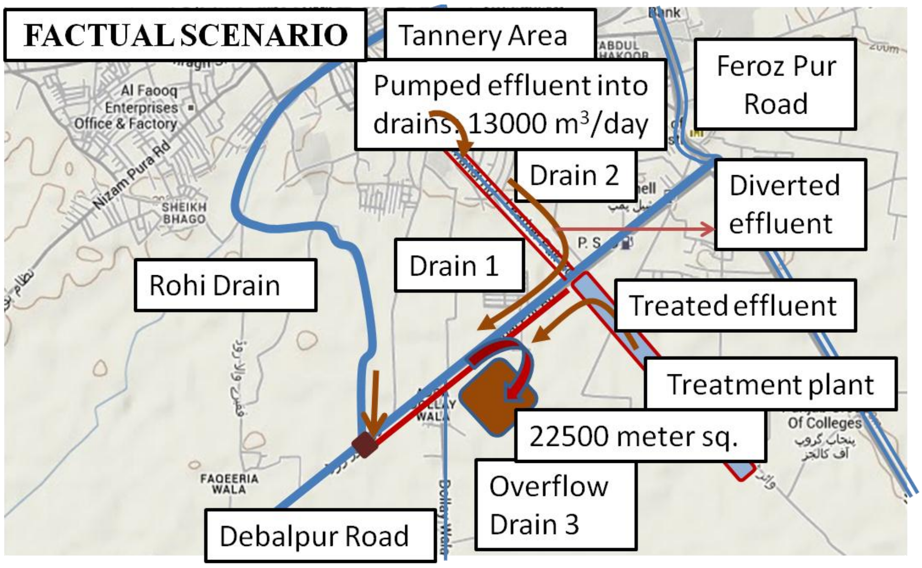


Fig. 6.7: The schematic diagram of factual Scenario of contaminant transport

6.4 Development of FEMWATER Model

In this study FEMWATER model was used for simulating the groundwater contamination due to total chromium subjected to leachate from the drains and stagnant ponds in the research area as described in the three scenarios.

6.4.1 Validation of FEMWATER Specifically with reference to Research Site

In order to obtain specific research objectives based on the existing site conditions FEMWATER model was considered to be the most suitable tool to be applied for exploring the research site at Kasur thoroughly. FEMWATER is a 3D finite element, saturated/unsaturated, density driven, flow and transport model. It's a Finite Element Model of water flow through both saturated and unsaturated media. As main source of contamination lies in the filtration of effluent from soil medium therefore FEMWATER was found more suitable to conduct simulation with particular reference to existing site conditions. The applied model was found to be the most suitable option regarding site characterization, groundwater modeling and contaminant transport to be conducted simultaneously. It has the ability to model saturated and unsaturated areas both.

FEMWATER was selected on the basis of available literature and its suitability for developing model and it simulation. FEMWATER has been used to develop model domains and some of its features facilitate the utilization of soil texture characteristics to construct the model domain. This could be done using Stratification, one of the significant features of FEMEWATER. It was an important characteristic which was necessary to understand the sub soil characteristics and expanding them to larger areas. The most significant feature of FEMWATER which validate the application of this model for the research area is advanced 3-D soil analysis. This can be conducted by using stratification which helps in generating complex soil profile domain of the area under investigation.

6.4.2 Formulation of FEMWATER

GMS includes a graphical interface to the groundwater model FEMWATER. It is a 3D finite element, saturated or unsaturated, density driven, flow and transport model. It is designed to solve the following system of governing equations along with initial and boundary conditions, which describe flow and transport through saturated-unsaturated porous media (Lin et al, 1997)

6.4.2.1 Governing equations for flow

$$\frac{\rho}{\rho_o} F \frac{\partial h}{\partial t} = \nabla . \left[K . \left(\nabla h + \frac{\rho}{\rho_o} \nabla z \right) \right] + \frac{\rho *}{\rho_o} q \qquad \text{————————} \qquad (1)$$

$$F = \alpha' \frac{\theta}{n} + \beta' \theta + n \frac{dS}{dh} \qquad \text{————————————} \qquad (2)$$

Where

F = storage coefficient

h = pressure head (Length)

t = time

K = hydraulic conductivity tensor

z = potential head

q = source and/or sink

ρ = water density at chemical concentration C

ρ_0 = referenced water density at zero chemical concentration

P* =density of either the injection fluid or the withdrawn water

θ = moisture content

α‘ = modified compressibility of the medium

β’ modified compressibility of the water

n = porosity of the medium

S = saturation

The hydraulic conductivity K is given by

$$K = \frac{\rho g}{\mu} k = \frac{(\rho/\rho_o)}{(\mu/\mu_o)} \frac{\mu g}{\mu_o} k_s k_r = \frac{\rho/\rho_o}{\mu/\mu_o} K_{so} k_r \qquad \text{———————} \qquad (3)$$

μ = dynamic viscosity of water at chemical concentration C

μ_o = referenced dynamic viscosity at zero chemical concentration

k = permeability tensor

k_s = saturated permeability tensor

k_r = relative permeability or relative hydraulic conductivity

K_{so} = referenced saturated hydraulic conductivity tensor

6.4.2.2 Governing equations for transport

$$\theta \frac{\partial C}{\partial t} + \rho_b \frac{\partial S}{\partial t} + V.\nabla C - \nabla.(\theta D.\nabla C) = -\left(\alpha' \frac{\partial h}{\partial t} + \lambda \right)(\theta C + \rho_b S) - (\theta K_w C + \rho_b K_s S) + m - \frac{\rho^*}{\rho} qC + \left(F \frac{\partial h}{\partial t} + \frac{\rho_o}{\rho} V.\nabla \left(\frac{\rho}{\rho_o} \right) - \frac{\partial \theta}{\partial t} \right) C$$

$$\text{———————} \qquad (4)$$

S = K_dC For linear Isotherm

$$S = \frac{S_{\max} KC}{1 + KC}$$

For langmuir Isotherm

S = KC^n For Freundlich Isotherm

θ = moisture concentration

ρ_b = bulk density of the medium (M/L^3)

C = material concentration in aqueous phase (M/L^3)

S = material concentration in adsorbed phase (M/M)

t = time (T)

V = discharge (L3/T)

∇ = del operator (vector differential operator)

D = dispersion coefficient tensor

α' = compressibility of the medium (LT^2/M).

h = pressure head (Length)

λ = decay constant

m = q C_{in} = artificial mass rate

q = source rate of water

C_{in} = material concentration in the source

K_w = first order biodegradation rate constant through dissolved phase

K_s = first order biodegradation rate through adsorbed phase

F = storage coefficient

K_d = distribution coefficient

S_{max} = maximum concentration of medium in the Langmuir nonlinear isotherm

n = power index in the Freundlich nonlinear isotherm

K = coefficient in the Langmuir or Freundlich nonlinear isotherm

The dispersion coefficient tensor D in Equation (4) is given by

$$\theta D = a_T |V| \delta + (a_L - a_T)\frac{VV}{|V|} + a_m \theta \tau \delta$$

|V| = magnitude of V

δ = Kronecker delta tensor

a_T = lateral dispersivity (L)

a_L = longitudinal dispersivity (L)

a_m = molecular diffusion coefficient

τ = tortuosity

6.4.2.3 Initial conditions for transport equation.

The initial conditions for the transport equation are given by Equation (4)

C = Ci(x, y, z) in R

where R is the region of interest and Q is the prescribed initial condition, which can be obtained by either field measurements.

6.4.2.4 Boundary conditions for transport equation.

The boundary conditions for the transport equation are given in the following equations.

***a.* Dirichlet conditions:**

C = Cd(xb, yb, zb) on Bd

b. Variable conditions:

$n.(VC-\theta D-\nabla C) = n.VCv(xb, yb, zb, t)$ if $n.V \leq 0$

$n.(-\theta D. \nabla C) = 0$ if $n.V > 0$

c. Cauchy conditions:

$n.(VC-\theta D-\nabla c) = qc\ (xb, yb, zb, t)$ on Bc

d. Neumann conditions:

$n.(-\theta D. \nabla C) = qn(xb, yb, zb, t)$ on Bn

where

(x_b, y_b, z_b) = spatial coordinate on the boundary

n = outward unit vector normal to the boundary

Cd = concentration on the Dirichlet boundary

Cv = concentration of water through the variable boundary

Bd = Dirichlet boundary

Bv = variable boundary

qc = total flux through the Cauchy boundary Bc

qn = total gradient flux through the Neumann boundaries Bn

6.4.3 FEMWATER Model Construction

FEMWATER is applied in the research area with the main objective to use the simulation for prediction of chromium contamination to move off site and travel upto farther distances. This approach can used to adopt best management practices in the affected area by taking preventive measures in terms of direct usage of soil and groundwater. It is particularly significant as most of the inhabitants are dependent upon the groundwater as one of the major sources of water. Water supply scheme from the municipality is still not available in the peripheries of the tannery area. Furthermore contamination of soil is also one of the major parameters which must be considered along with the groundwater contamination as the tannery area is surrounded by agricultural lands. People use the land as major source of income and different crops and vegetables are cultivated in the agricultural lands just adjacent to the tannery area. It must also be considered that farmers in the vicinity use the tannery effluent directly for irrigation purposes without any treatment. Thus it poses a direct health hazard due to its immense reliability on tannery effluent as wastewater. The modeling outcome is to be used so as to define the boundary of highly contaminated plume. It will restrict the seriously contaminated area and its radius of influence. Thus boundaries can be predefined for future tube well (pump) installations so that contamination free water can be drawn for the different uses including household usage, drinking water and irrigation etc. Studies of system dynamics have an application forward to understanding the complexities of existing contamination scenarios.

The data obtained from the particle size distribution of soil samples collected at fixed interval of 1.5 meters upto the depth of 30 meters during manual soil boring helped in obtaining basic information about lithology of subsurface and ultimately in the description of layers formation. The groundwater characteristics and stratification obtained through the boring analysis are used to describe the vertical extent of the conceptual model. Overall 500 mm precipitation per year and 1500 mm evaporation was considered on annual basis.

The model domain was selected in order to represent the flow processes and contaminant transport pattern in the study boundary. The model domain included the hydrological features and the main sources of contamination within the area. The total length along east west was 2,750 meters while along north south was 2,000 meters.

Using the borehole data obtained during site investigations as described earlier, soil layer data and water table elevations were imported using model, ,to develop firstly solid data for the entire area up to the depth of 100 meters and then generating a 3D mesh from using same borehole defined horizons data. The vertical extent was totally based on soil bores conducted in the research area. On the basis of soil texture the soil layers were divided into seven main classifications consisting of sand, sandy loam, loamy sand, loam, clay loam, silty clay loam and silt loam. On the basis of these soil textures material properties were input into model which is described in Table 6.1 (Lin et al., 1997).

Table 6.1: Parameter values for different soil textures used in model

Materials	**Saturated Water Content [ND]**	**Residual water content [ND]**	**Empirical constant Alpha[1/cm]**	**Empirical constant (n)**	**Hydraulic Conductivity (m/yr)**	**Bulk Density (kg/m^3)**
Silt Loam	0.45	0.067	0.02	1.41	39.4	1380
Sand	0.43	0.045	0.145	2.68	2601.7	1690
Loam	0.43	0.078	0.036	1.56	91.1	1430
Sandy Loam	0.41	0.065	0.075	1.89	387.2	1510
Silty Clay Loam	0.43	0.089	0.01	1.23	6.1	1270
Clay Loam	0.41	0.095	0.019	1.31	22.7	1300
Loamy Sand	0.41	0.057	0.124	2.28	1277.5	1630

The objective to use groundwater model was to interpret and characterize the site regarding potential to contaminate the subsurface considering different contamination scenarios describing the realistic conditions of possible sources of contamination and their effect on soil and groundwater.

6.5 Hydrogeological Characteristics and Determination of Input Data for Mass Flux

Interaction between different hydrological units within the study area was studied in order to understand the total water flux and its movement in soil and aquifers.

6.5.1 Determination of Initial and Boundary Conditions

6.5.1.1Boundary Conditions

Following boundary conditions were applied to the model. Significant hydrogeological features of the model domain are shown in Fig. 6.8.

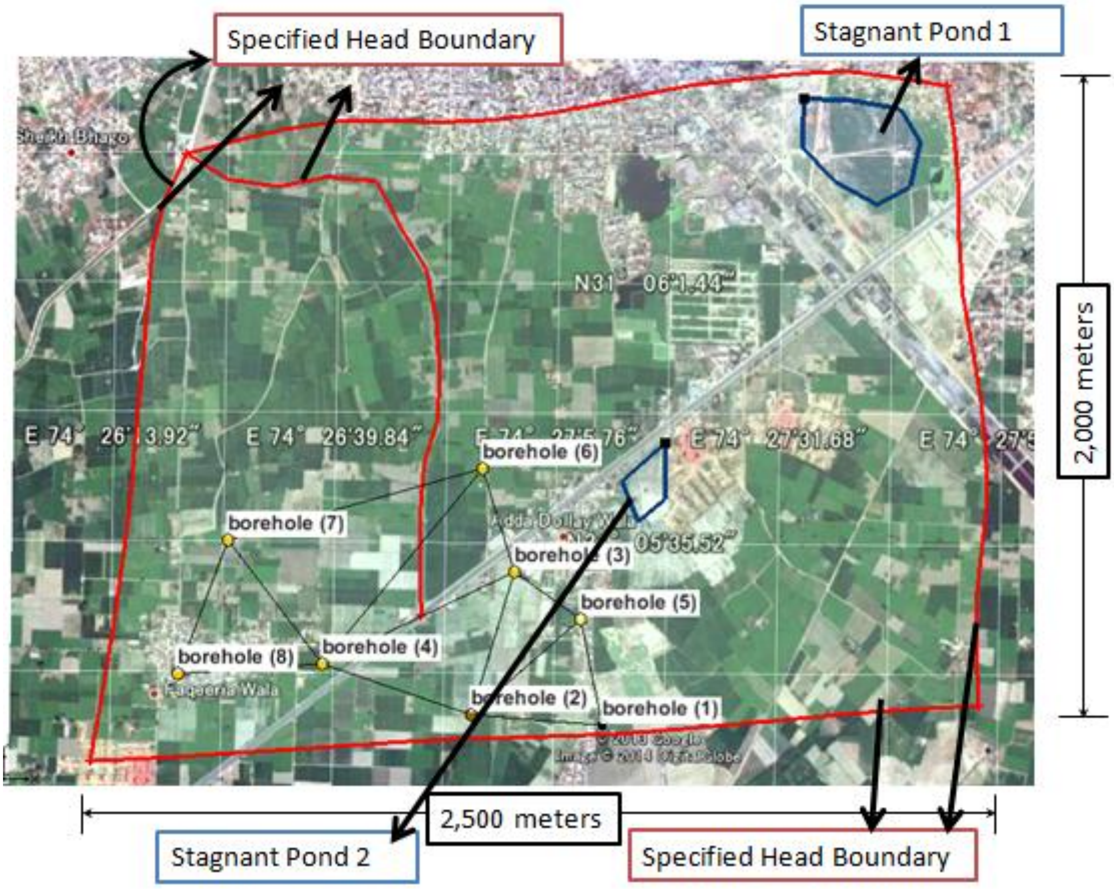


Fig. 6.8: Model domain presenting significant hydrogeological features and boundary conditions

(a) Specified head boundary

This boundary condition was given to all the four sides of the model and to Drain 4 by providing head values on each end of the respective arc for the boundary.

Most realistically the data obtained from field investigations and experimentation was used to describe the boundary conditions of the model domain. Arcs representing the boundary domain of model are described as specific head with maximum head of 2 meters diagonally in south – west direction. The major component of the model domain is “stagnant ponds” represented by polygon. Total area covered by the polygon in the field is 400 acres or 1.62 x 10^6 m^2 and it mainly constitutes tannery effluent released from the tanneries before the proper construction of wastewater treatment plant and the effluent carrying drains. Previous studies indicated that about 74 kg of total chromium was being disposed on daily basis by the tannery units. The data utilized is obtained from the previous research work available in literature. Therefore it was assumed that this stagnant pond remained a continuous source of subsurface contamination until year 2000 when the drains were constructed to dry the stagnant pond and wastewater treatment plant was developed in year 2003.

Groundwater level, as measured in an observation well, reflects the amount of water in storage in the monitored aquifer. When recharge exceeds natural discharge plus abstraction, groundwater levels rise. When recharge into soil is less than natural discharge plus abstraction, groundwater levels fall.

Comparison of measured groundwater levels with long term averages provide an indication of the state of groundwater resources within an aquifer. Observation over several years allows the prediction of aquifer response to current climatic and hydrological conditions. First of all the water table readings were measured in feet and then converted to meters to maintain general format.

(b) Flux boundary

In order to incorporate flux, due to evapotranspiration and discharge flow rate, flux boundary conditions were applied at the surface of model. For variable concentration as used for contaminant transport phenomenon, transient concentration was applied at the element faces for accommodating the step wise provision of contaminant mass, for both the polygons representing stagnant ponds.

6.5.1.2 Summary of Calculations for Model simulation.

Data Calculations are as follows

- Total area of stagnant pond = 400 acres (1.62 km^2)
- Initial Discharge rate from the tannery units before year 2000 = 9000 m^3/day
- Assuming per day chromium load into the effluent = 74 kg (literature available)
- Contamination flux = 0.67 m / year
- Discharge / area
- 3000 x 365 m^3 / year x 1 / 1.62 x 10^6 m^2
- **0.67 m / year**
- Annual ppt flux into soil = 0.575 m / year

- **TOTAL = 1.245 m / year**
- Specific Mass Flux for Polygon (Stagnant Pond)
- Conversion to Kg/m2/year for defining the infiltration rate
- 74 kg / day / 1.62 x 10^6 m^2
- = 0.0167 kg/m2/year
- Water table variations during the study period of 1 year

Table 6.2: Water table levels and its yearly based comparison

Bore Hole	Elevation from Sea Level	Water table Level 2009		Water table 2010	
		First WT	**Second WT**	**First WT**	**Second WT**
BH 1	197 m	185. 7 m	169.6 m	185. 7 m	169.6 m
BH 2	197 m	185 .7 m	169.6 m	185 .7 m	169.6 m
BH 3	198 m	186.1 m	170.6 m	186.1 m	170.6 m
BH 4	197 m	185.7 m	169.6 m	185.7 m	169.6 m
BH 5	198 m	186.1 m	170.6 m	186.1 m	170.6 m
BH 6	197 m	185.7 m	169.6 m	185.7 m	169.6 m
BH 7	199 m	185.3 m	171.6 m	185.3 m	171.6 m
BH 8	198 m	185.2 m	169.6 m	185.2 m	169.6 m

Soil bores conducted in the research area are shown in Fig. 6.9, describing the wide distribution and location of the bores for soil and water analysis. Soil texture and stratification of the subsurface is shown in Fig. 6.10 and Fig. 6.11. Mostly the soil texture observed is of loamy or sandy in nature. However the top elevation being generally flat, similar trend is water table elevations can be observed. First Water table level on average exists at 10.7 meters while the second water table level on average lies at 27.4 meters.

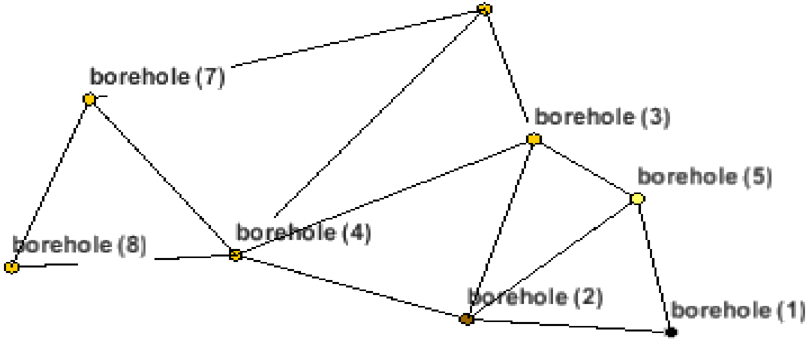


Fig. 6.9: Soil bore mapping for stratification

6.6 Model Simulation for Three Scenarios

The three contamination scenarios were used to develop the model. The model was simulated for duration of 31 years, representing the time frame from 1980 to 2011. It was assumed that stagnant pond originated in 1980 due to continuous discharge of initial ten years from 1970 to 1980. It is also assumed that after 20 years presence the stagnant pond was dried in year 2000 by constructing drains. Initially amount of 73 mg/l of chromium was used as variable concentration for contaminant mass in pond on yearly basis for the predefined area. After 20 years the supply of discharge to the pond was stopped. For duration in between 2001 to 2004, four years were considered to be improved condition scenario as ideal case in which no source of contamination existed at site, due to working of treatment plant and construction of drains for carrying the effluent. But again in the model contamination was input from overflowing of Drain 3 in the form of polygon, representing pond with same concentration input as initially provided for first stagnant pond as it was carrying untreated effluent. This condition was assumed to be continuous until the model time frame finished in year 2011 after 7 years presence of second source of contamination from pond created due to overflow. Therefore the supply of discharge was not stopped at the polygon mesh element boundary face until the model run time ended.

It was attempted to obtain the most realistic outcome of the model simulation so as to determine the pattern of contaminant transport in the study area minimizing the irregularities in the contamination behavior along with reducing the chances of exaggerated assumptions based on the facts that no literary evidence of level of contamination could be obtained.

The most important factor is the precise description of the soil strata and its characteristics in order to obtain more realistic model simulation. In this regard Fig. 6.10 showed the geographic position of the Soil bores based on which lithology of the subsurface was defined. The geological profiles of the lithology of the area have been shown in Fig. 6.10 & 6.11. The differentiation is based on the upstream side of the drains and on the downstream side. Both cases it can be observed from the Fig. 6.10 & 6.11 that the dominating soil texture is exiting in terms of sand layers while other soil characteristics are not that much in extent to be significant enough so as to have any impact on the behavior of the contaminant with the soil strata. However remarkable characteristics variations could be observed on the downstream side in all the Soil Bores that is Bore Hole 2, 4, 7 and 8. This could be one of the confirmations of the retention of contaminant in the deeper layers, particularly in Soil Bore 8.

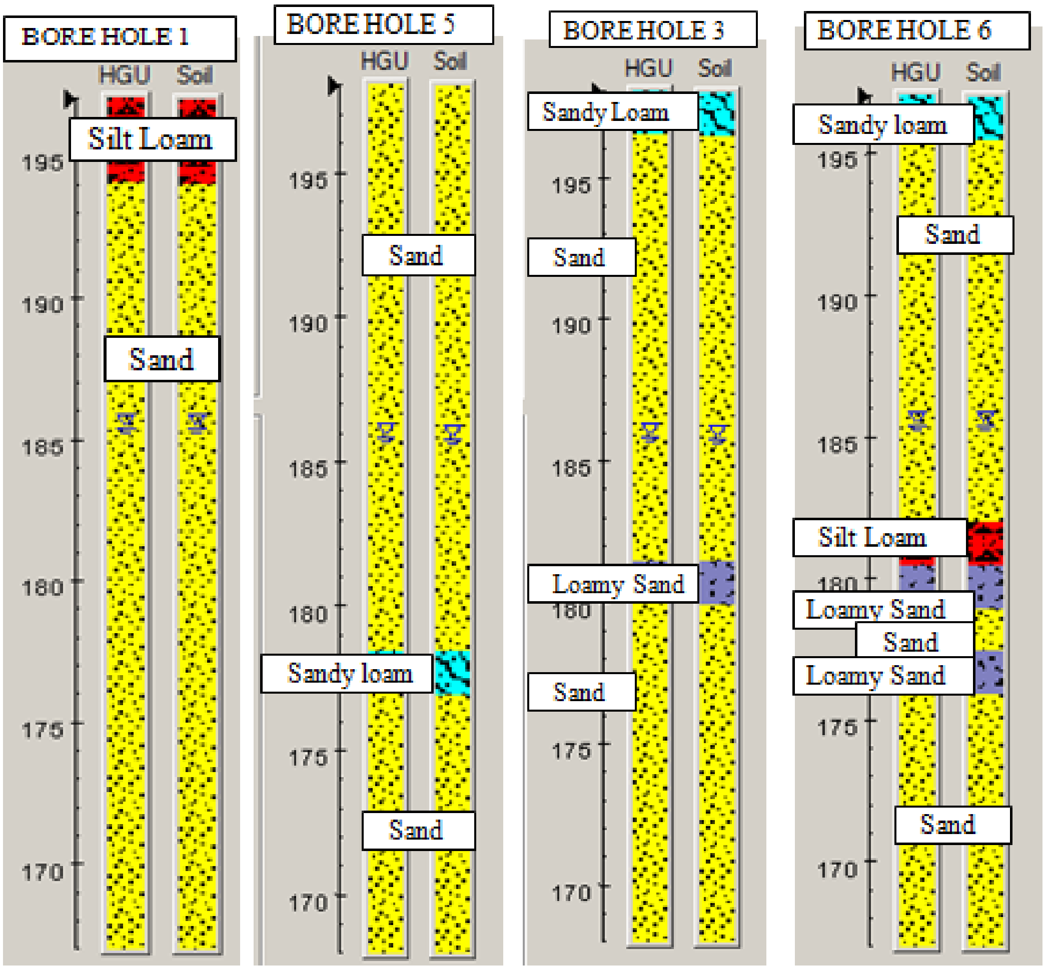


Fig. 6.10: Geological profiles of studied area on upstream side of drains

There have never been any investigations conducted in this study area previously for its subsurface geological investigations. Therefore validation of the data with the previous available studies outcome could not be conducted. However localized experimentations as conducted by environmental scientists and agronomists have shown sufficient reliability of the data. And most of the soil layers have been declared to be sandy loam or loam in its characteristics. Particularly this finding can be justified by the topography and its existence in between the alluvial soil of two main rivers the Ravi and Sutlej.

Using Stratification technique application in the model FEMWATER, subsurface strata was expressed based on the boring log data. However the depth of the domain was fixed to be up to 30.5 meters (100 feet). Due to the unavailability of the boring locations at a wider range and difficulty in moving the mechanical bore machinery to remote areas along with power supply issues, soil bores on extensive level could be conducted. However these soil bores were supported by further additional 6 soil bores at the extended boundaries of the study area so to validate the soil stratification behavior as described in the domain of the model. These extended soil bores were conducted to calibrate the groundwater flow direction as well.

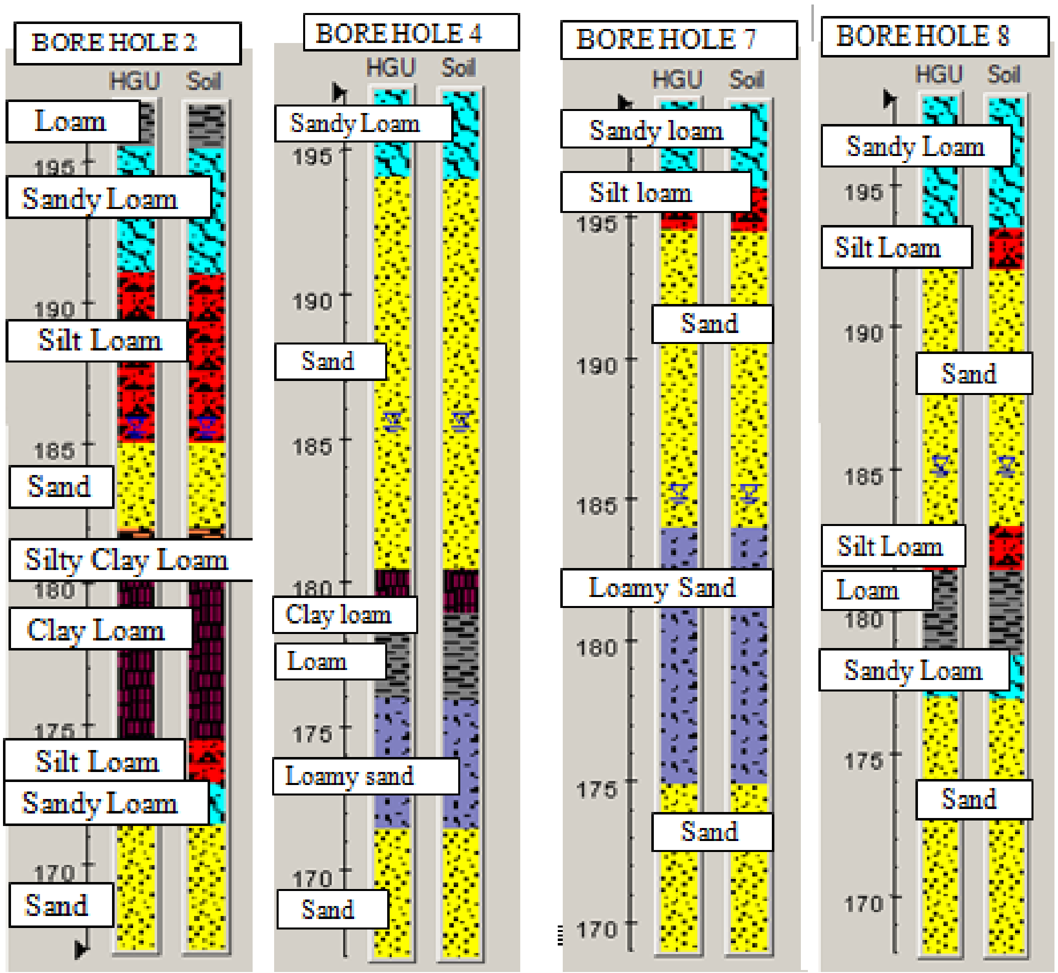
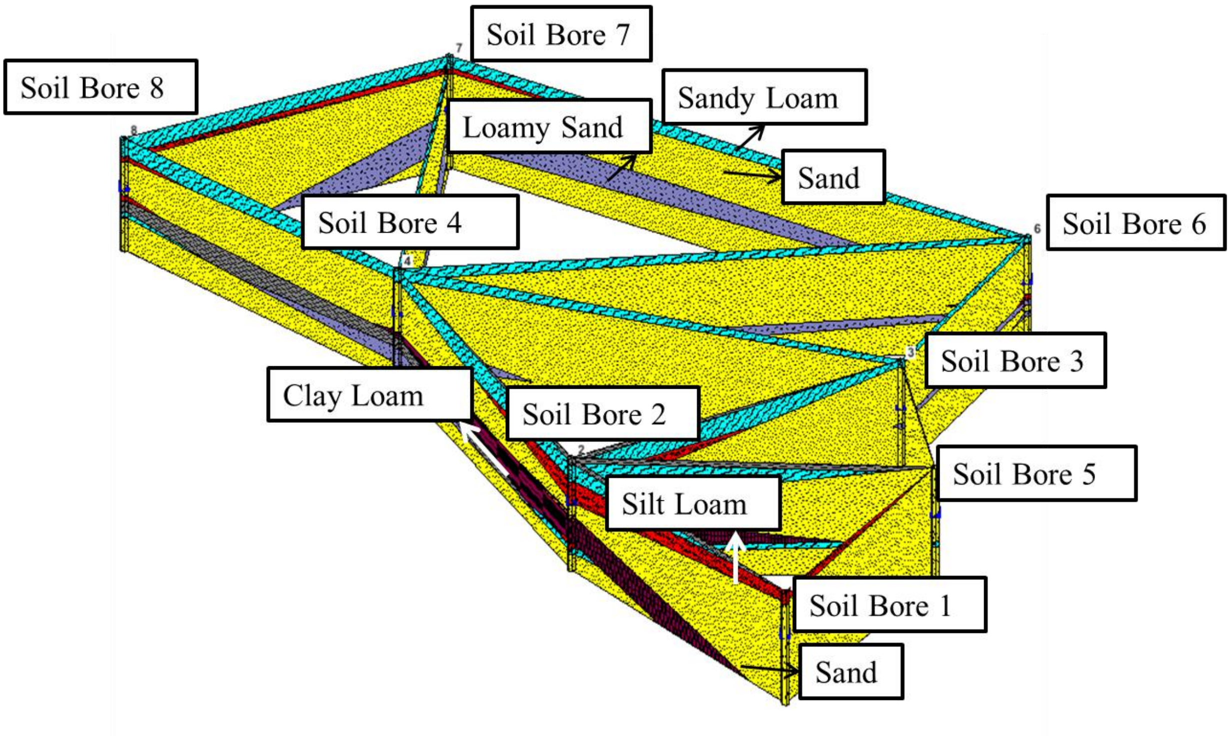


Fig. 6.11: Geological profile of studied area on the downstream side of drains

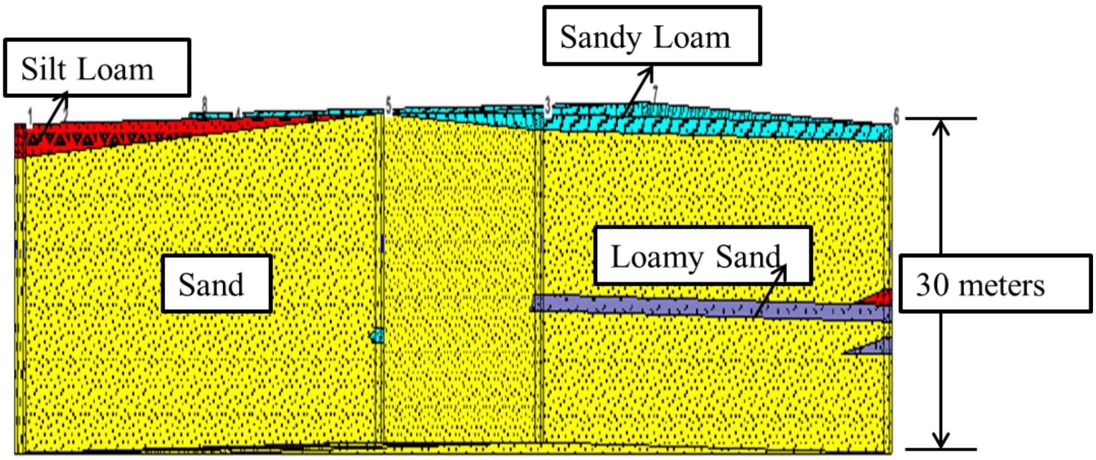
Fig. 6.12 described the ortho projections of soil bore log data as obtained from the field and investigated for the soil texture analysis in the laboratory. Stratigraphic framework of the three (3) dimensional cross section can be observed in these figures.

6.6.1 Steady State Simulations & Calibrations

The data files were prepared pertaining to the required information regarding the mass flux and infiltration. Furthermore based on the information related to the hydraulic head in the study area, as obtained from the observation wells (monitoring wells) was simulated for the given boundary of the conceived model for a period of One year. Discrepancies were observed in the smooth flow pattern of groundwater due to unsymmetrical directions of nodal velocity vectors. It was mainly subjected to uncertainty in the data related to the mass influx and infiltration rates. There was no previous data available on the hydraulic head in the study area to cross check the consistency in the data related to head values in the observations wells. Rate of infiltration into the soil layers was also very inconsistent with reference to smooth and continuous recharge in the soil medium and the groundwater aquifer. Mass flux which was used to define the initial conditions of the contaminant concentrations being entering into the model domain were also unreliable due to non-availability of the previous information about the discharge of effluent and constantly changing contamination transport scenarios. There was intermittent discharge of effluents from the tannery units therefore to ensure the uniformity of the contamination behavior was not feasible. Observation heads obtained in year 2009 was the only source of determination of hydraulic head to work out the groundwater flow directions, which were counter checked next year in 2010 and were found to be same as before. Thus hydraulic head was observed to be almost horizontal. In the Table the difference in the water table for two years can be observed. In order to overcome the uncertainty in the data, head values were fixed on trial and error basis to maintain the steady flow conditions. The discrepancies as discussed in CHAPTER 5 regarding smooth groundwater flow movement were overcome by the use of FEMWATER.



(a) Lithology of the Soil Bores (Ortho Projections) Showing overall trend of the soil texture showing dominating sand layers with thin bands of Loam and Silt clay



(b) Lithology of the Soil Bores (Side View) Dominating the Sand layers

Fig. 6.12: (a) and (b) Soil profile describing the soil texture distribution along the depth

Fig. 6.13 described the year wise model simulations for the total chromium transport based on the predefined soil and hydrological conditions. As the simulation was governed by three different contamination scenarios therefore the behavior of the contaminant transport was also very much divergent, particularly numerous uncertainties also were a major factor while demonstrating the impact of contaminant on the study area.

The main source of contamination in the study area was found to be present in the form of clusters rather than showing a specific source of contamination may be in the form of spillage. Neither the source could be clearly described and measured for its impact on soil and groundwater contamination. There was an intermittent supply of contaminants to the study area being influenced by so many external factors. Inappropriate data and its authenticity was always a big question mark in obtaining the rational outcome of the model simulation which was run for the whole duration while the contamination was being fluxed into the soil and groundwater considering different scenarios which actually prevailed during this time duration.

The main source was considered to be the stagnant ponds which were used for disposing the tannery effluent since 1970. It can be observed in Fig. 6.13 for year 1 simulation that gradually the concentration is increasing and after the time interval of 10 years the contaminant from the contaminant source has sufficiently spread out in the nearby vicinities. This was the time when the residents started having the adverse effect of these contaminants and groundwater contamination as it was the only source of water available at that time in 1980s. The flow of contaminants is under the influence of so many factors mainly affected by the soil characteristics and hydrogeological formations. However the previously run model for calibration purpose and defining a symmetric groundwater flow conditions only has shown the same trend of contaminant as governed by the groundwater movement. It can be observed in Fig. 6.14, where nodal velocities of the groundwater flow are in accordance with the contaminant transport model simulation as shown in Fig. 6.13.

As described earlier that there was a huge variation in the observations for different scenarios, thus the simulations are also exhibiting the same variation trends in terms of contaminant transport for the desired time duration for regular time intervals. The model simulations for year 31 can be observed as combination of all the different scenarios which are varying from time to time.

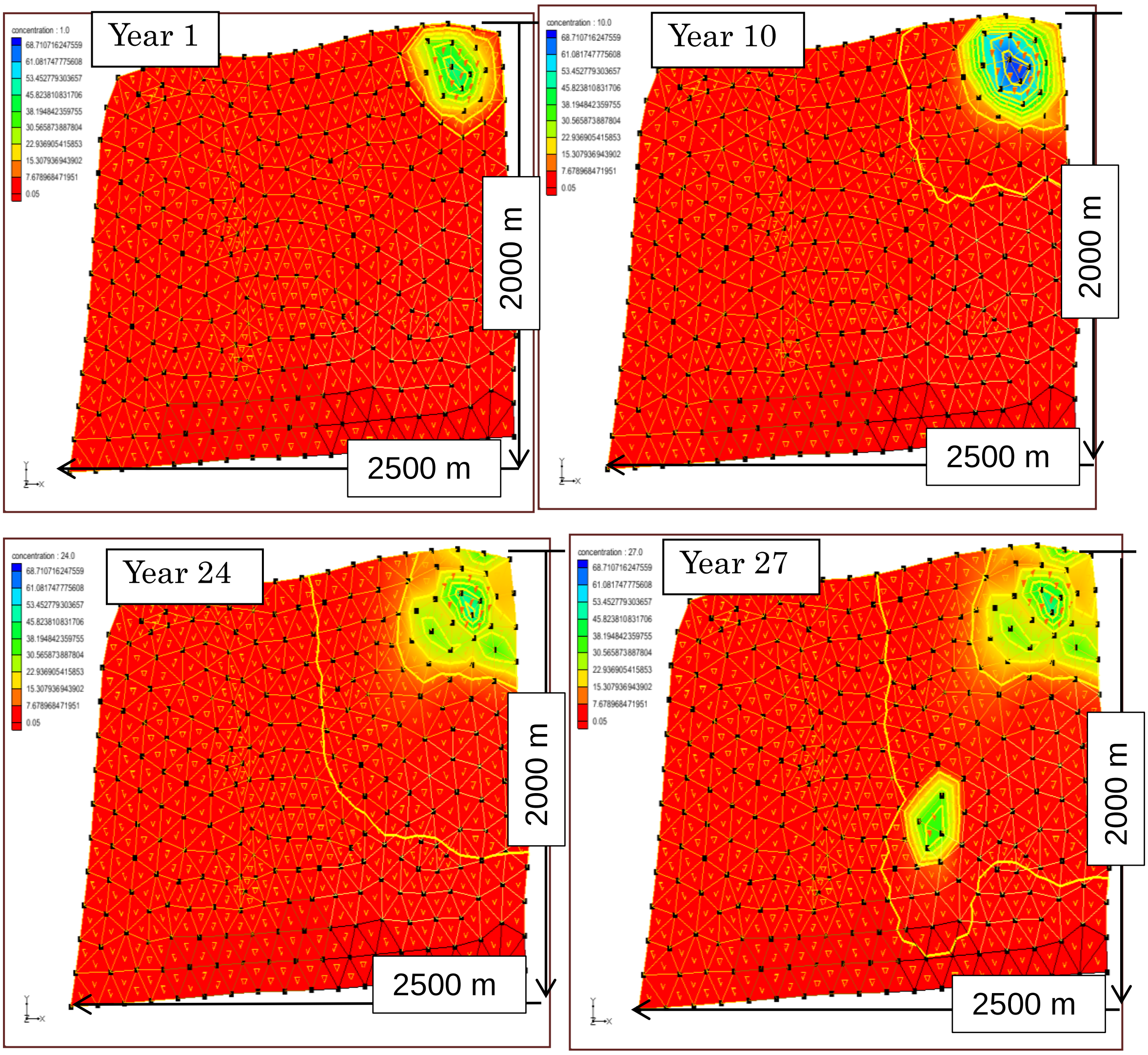


Fig. 6.13: Concentration variations at different time intervals and its movement graphics

The total time period of 31 year with 1 year time step was simulated for all the three contamination scenarios simultaneously as explained earlier in one simulation to observe combined effect of overall contamination condition at site. The demonstration of the model simulation as given in Fig. 6.13 is more accurately described in Fig. 6.15, 6.16, 6.17 and 6.18. The nodal simulations for all the different scenarios can be very understood from these figures which are actually showing the contaminant movement following the pattern of groundwater flow directions as shown in Fig. 6.14.

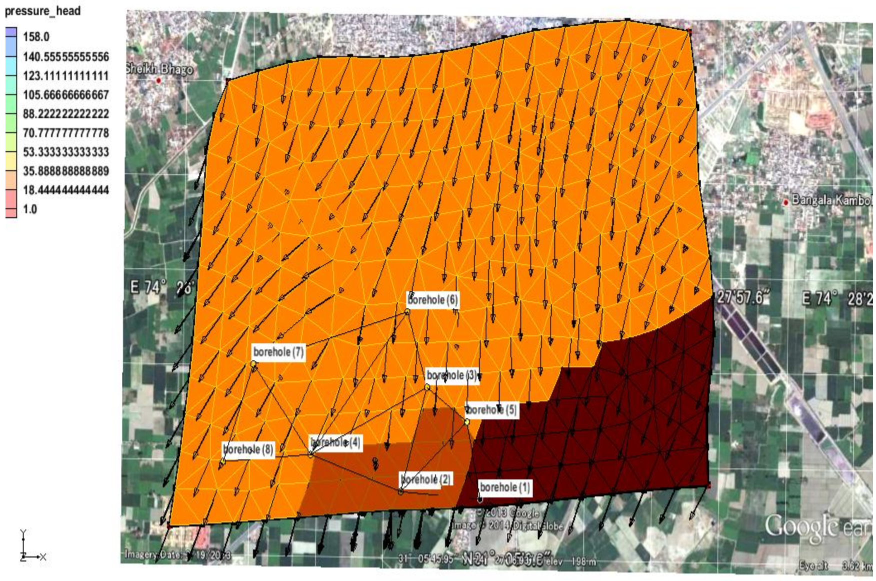


Fig. 6.14: Nodal velocity vectors showing groundwater flow directions

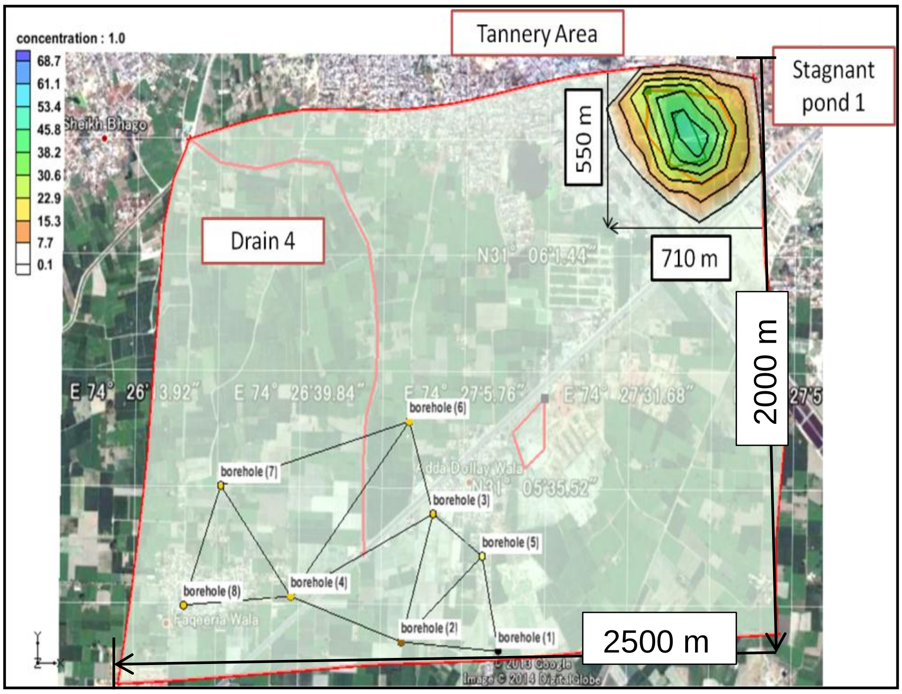


Fig. 6.15: Concentration contours for stagnant pond 1 after time step of 1 year

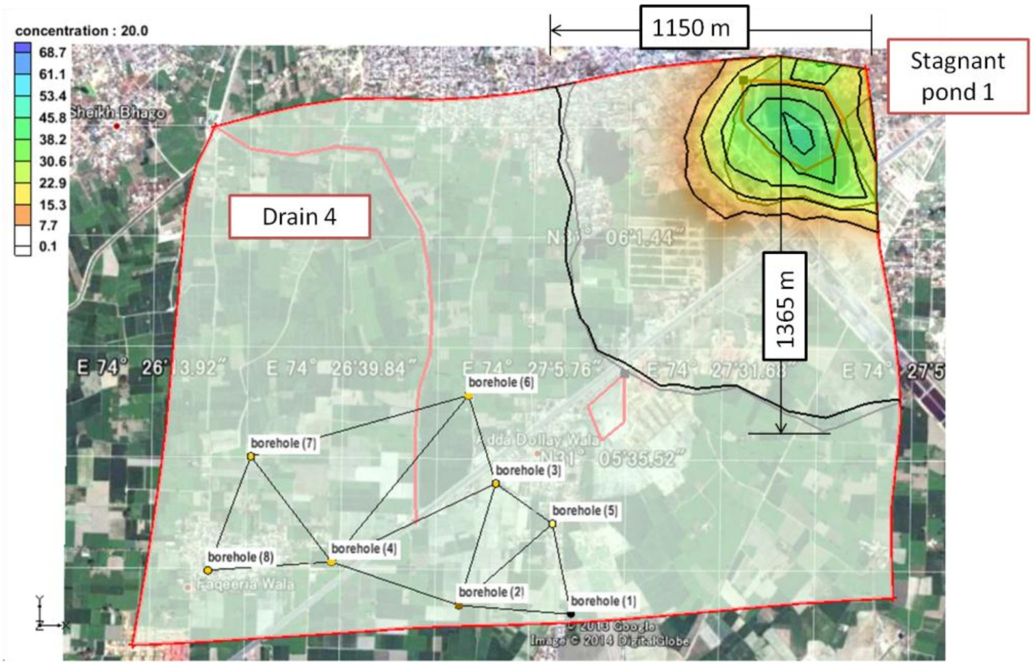


Fig. 6.16: Concentration contours for stagnant pond 1 after time step of 20 years

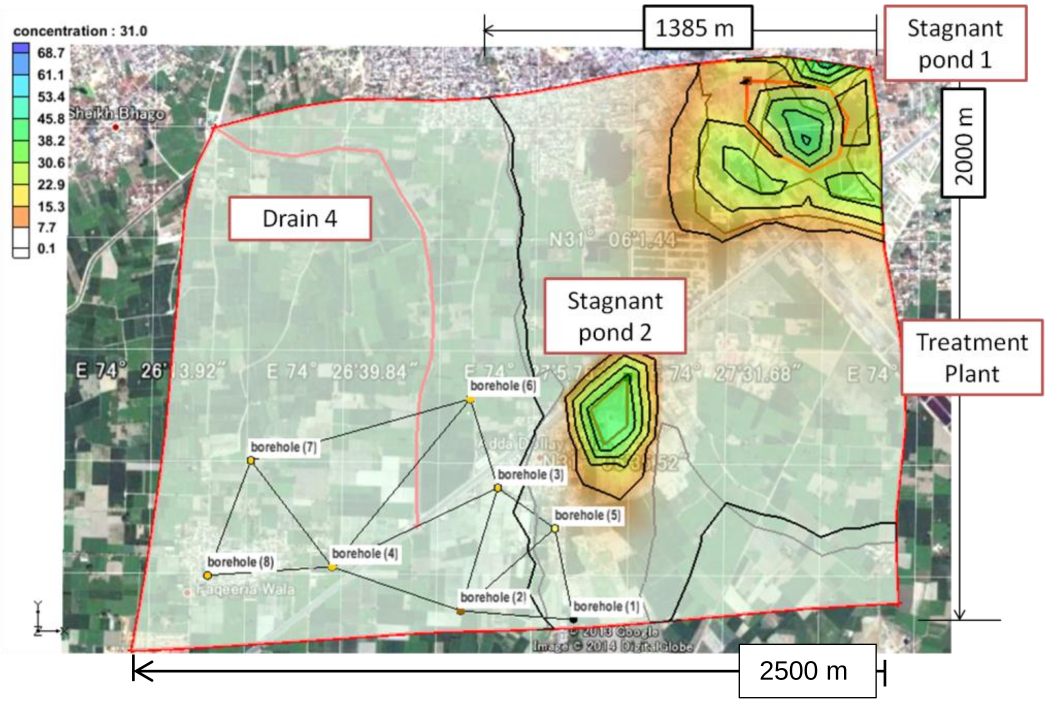


Fig. 6.17: Concentration contours for stagnant pond 1 & 2 after 31 years

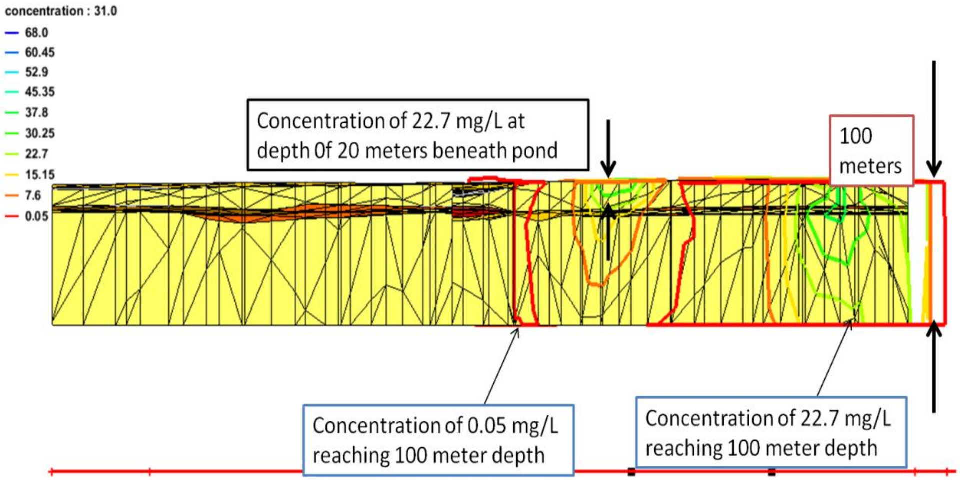
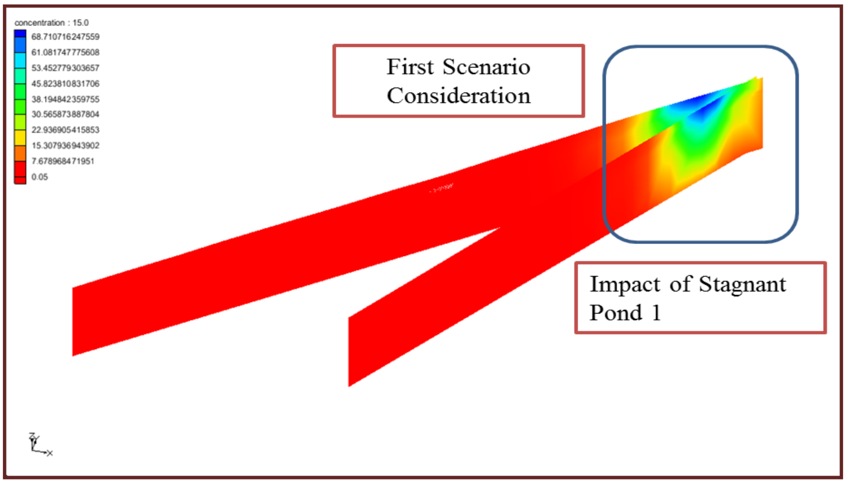
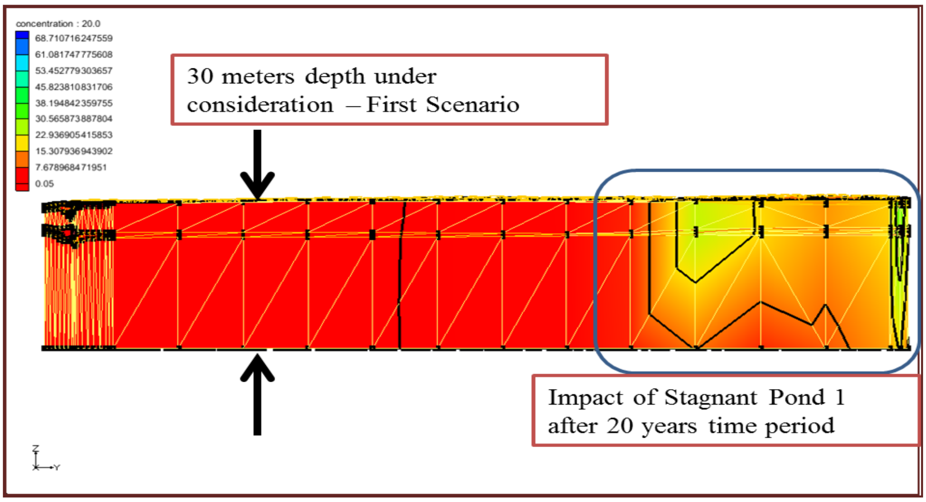


Fig. 6.18: Concentration contours for stagnant ponds 1 & 2 from side view of model



(a) Cross Section along Section AA’ and BB’ at the time interval of 15 years.



(b) Side view of the Model Simulation at the time interval of 20 years

Fig. 6.19: Different pictorial projections of model simulations at significant time intervals

Considering multi factors which are affecting the contaminant coupled movement of groundwater, the subsurface groundwater aquifers become highly significant no matter how much concentration of chromium is present in soil and groundwater. This argument is further augmented by the typical nature of the soil strata which is varying so abruptly within the study area. Huge variation in the soil content and its behavior towards the contaminants from tannery effluent exists as major uncertainty to accurately define the contaminant transport mechanism in the study area. The soil formation varied from fine to coarse particles therefore developing not completely impermeable rather slightly permeable.

6.7 Results of Simulation

The model run for time duration of 31 years showed the output in the form of nodal velocities and concentration contours for every unit time step. From nodal velocity vectors presentation the groundwater flow direction obtained as shown in Fig. 6.14. Following the groundwater direction normal contaminant flow trend can anticipated. In Fig. 6.15 the flow pattern of contaminant for year 1 time step can be observed. First scenario is presented only for stagnant pond 1, therefore the results are show slight movement of contaminant plume following the groundwater flow directions as guided by nodal velocity vectors. Fig. 6.11 showed the contaminant plume for time step of 20 years. It was observed that plume shifted only up to 1150 meters in x-axis while along y-axis the plume moved up to 1365 meters distance. After 20 years' time period no further discharge was assumed to enter stagnant pond 1 but still there is obvious movement of plume following the direction of groundwater both along x-axis and y-axis as clear from Fig. 6.17. Stagnant pond 2 started discharge into soil after time step of year 25, therefore combined effect of both ponds can be observed in Fig. 6.17.

It can be observed that overall groundwater movement is very slow. Table 6.2 indicated that there was no groundwater movement observed during the monitoring period of one year from December 2009 to December 2010. This flat groundwater level was subjected to low precipitation on average 500 mm per year and complex geological formation. Combined plume of both the ponds just travelled the distance of 1385 meters along x-axis and 2000 meters along y-axis and hardly reached monitoring wells location with minimum concentration of 0.1 mg/L (Fig. 6.17). Therefore it can be assumed that presently the stagnant ponds are not causing any serious threat to downstream areas. However high movement of concentrations to deeper depths are evident from Fig. 6.18 showing the front view of model indicated concentration of up to 22.7 mg/L reaching 100 meter depth for stagnant pond 1, while for stagnant pond 2 this much concentration level is at 20 meters depth from surface beneath the stagnant pond.

6.8 Summary of Chapter 6

This chapter mainly constitutes of development of contaminant transport model and execution of simulations for different scenarios which were considered during conducting investigations.

Initially in this chapter, existing situation regarding soil contamination, groundwater contamination and wastewater condition was described in such a way so as to present the realistic site characterization approach at the research area. The purpose was to build a firm foundation regarding the level of contamination as well the different sources of contamination so that the contaminated site of Kasur Tannery area may be thoroughly assessed. As there was lack of authentic background information about the site, these site conditions provided a reliable source of information so as to lead towards model development procedures.

FEMWATER module was selected for the purpose of evaluating contaminant transport modeling in the study area. In this regard main contaminant considered was total chromium. The data previously obtained from the site investigations was used as input data for the model running and simulations. Basic physical and chemical properties of the soil and other parameters which were necessary for the development of realistic conditions in the model were conducted and analyzed. This data was used to describe a realistic soil profile existing beneath the ground surface. Based on these readings model domain was defined and initial and boundary conditions were allocated to this domain.

Three different model scenarios were considered for running the model. These three scenarios were Adverse, ideal and factual condition based scenarios which were used to describe the overall changing conditions at the site during different periods of time, where maximum time simulation was decided to be 31 years starting from 1980 to 2011. These changing scenarios actually showed the variations in the input levels of contamination in the form of influx into the subsurface and changing conditions of different sources of contamination as well at the site during the assumed period of model simulations.

Main features of the model development include the conditions like stagnant pond adjacent to the tannery area as the main source of contamination for the first 20 years of the model simulation. Later the drains were constructed to carry the wastewater for final disposal to treatment plant. Furthermore the extensive flow of the effluent worsens the existing situation and described the inefficiency of the treatment plant and inadequacy of the wastewater management approaches at the site. Another important feature is the flat subsurface soil profile showing minimum availability of head to facilitate movement of groundwater in the aquifer, which left intense impact on the movement of contaminant as justified with the model simulations.

Subsurface soil profile and nature of the soil exhibits very tough conditions for the movement of contaminant into the soil or along with groundwater aquifer. Simulations for 31 years duration depict very slow movement of contaminant i.e. only 1.38 kilometers along x – axis and 2.0 kilometers on y – axis direction. Therefore most of the contamination is basically due to localized interference of source of contamination with the groundwater aquifer or loose subsurface soil strata as described in the previous chapter. Evapotranspiration is also one of the major factors which facilitated the drying and evaporation of the contaminant due to extremely adverse hot weather of the study area during the summer season.

The simulation of total chromium for a period of 31 years, based on different scenarios finally concluded complex subsurface conditions leading to slow movement contaminant on lateral and vertical direction. The major focus of simulation studies was to forecast the extent of spreading of the contaminant in the surrounding areas of the city and the tannery units. It was found that, considering the three possible scenarios as explained, total chromium has not been transported to longer distances than 1.38 km in the East west direction i.e. lateral movement, while maximum limit for contaminant transport is 2.0 kilometers on north south side i.e. vertical direction along the drains for a simulation period of 31 years. These results can be explained and justified with reference to the findings of site characterization as described in previous chapter in detail. In this regard the results of groundwater analysis as monitored periodically and soil sample analysis for total chromium retention (Aqua Regia Acid Digestion) as well as mobility (TCLP) reasonably explain the present conditions of contamination. Considering the average values and ranges of groundwater samples as described in Fig. 6.1(b), the total chromium concentration is gradually describing a reducing pattern as justified by the simulation results shown in Fig. 6.17.

CHAPTER 7

HEALTH HAZARD STUDIES

This chapter is based on the health hazard investigations conducted in the research area in order to find out the effect of contaminated groundwater on the human body.

With the purpose to investigate the effect of drinking contaminated groundwater, health survey was conducted in the study area. It was aimed to correlate the existing adverse environmental conditions due to improper tannery waste management with groundwater contamination followed by health issues among residents of the nearby vicinity.

7.1 Chromium and its Exposure Modes to Humans

A possible flow diagram of exposure of chromium to body is described in Fig. 7.1. The exposure path of chromium to humans is identified. Human beings can be affected from all means including soil, water and air. But in case of chromium soil and surface water plays significant role in exposing human beings to health threats due to chromium. From soil, chromium may percolate and from the root zone taken up by the crops, the fruits of which are extensively used by humans. This mode is highly vulnerable as most of the crops are irrigated by wastewater including tannery effluent and municipal wastewater. Other possibilities are through usage of groundwater, which are also a major threat as more than 50 % population rely on groundwater for daily usage. Direct interaction of chromium with human body may cause skin diseases like dermatitis. While inhaled in excessive amounts chromium may cause nasal and lungs infection through air.

7.2 Health Survey Approach and Methodology.

The objective for health hazard studies in Kasur study area was to confirm the effects of exposure to chromium, along with other tannery based contaminants, on the health of the inhabitants of nearby vicinities of tannery area. Besides it was also aimed to obtain statistical facts and figures regarding health conditions of people living in these areas.

In this regard three localities in the surrounding areas of tanneries were selected with the purpose to conduct health survey. These localities are, Basti Kambohan Wali, Dole Wala and Faqire Wala as shown in GIS map in Fig. 7.2. Basti Kambohan Wali is located in the South of the tanneries. It is basically a newly settled locality at the same place were once stagnant ponds of openly disposed tannery effluent used to exist. The history of this locality is no more than 12 years therefore people living in this locality have maximum exposure time of 12 years to adverse environmental conditions. While the other two localities Dole Wala and Faqire Wala are actually villages on the bank of Drain Rohi and people living there are settled for decades.

In order to conduct survey, a “Health Survey Proforma” was prepared, which is shown in Fig. 7.3. It includes basic introduction about household unit being surveyed. Regarding health data, questions related to the health issues which could probably originate from drinking water and those diseases which were linked with existence of chromium in water were particularly emphasized.

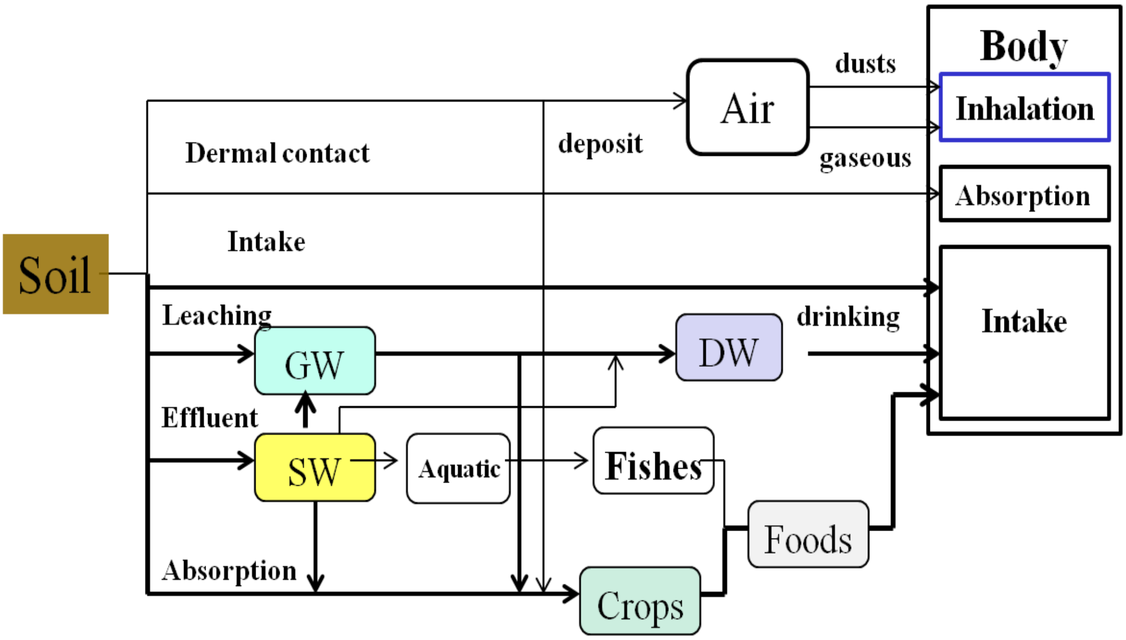


Fig. 7.1 Identification of exposure pathways to chromium by human body

7.3 Toxicology of Chromium

The primary health impacts from chromium are damage to the gastrointestinal, respiratory, renal and immunological systems, as well as reproductive and developmental problems. Chromium VI is a known human carcinogen, and depending on the exposure route, can increase the rate of various types of cancers.

Based on the health survey which was conducted in the research area, a wide range of impacts were observed on the health of residents of the study area. All the diseases from which the residents of the research area were suffering are related to tannery based effluents in one way or the other. The findings of the health impact survey of the area clearly identify the toxicity level of chromium in the research area. It also describes that how the residents are exposed to the intense adverse effects of the tannery waste on the human beings living in the nearby vicinity. It can also be compared with site investigations as described in Chapter 3, which covers level of exposure of the pollutants released from the tanneries.

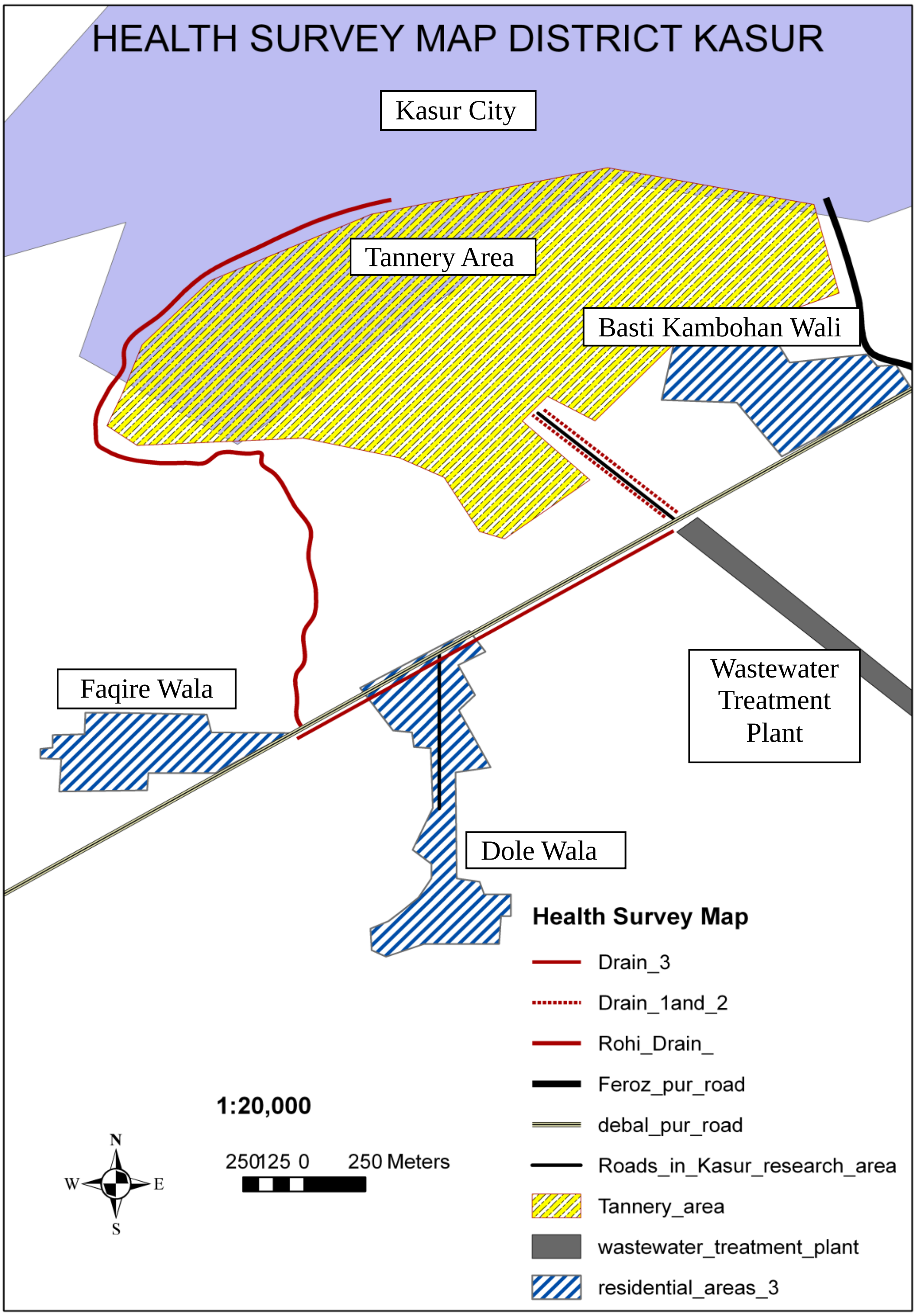
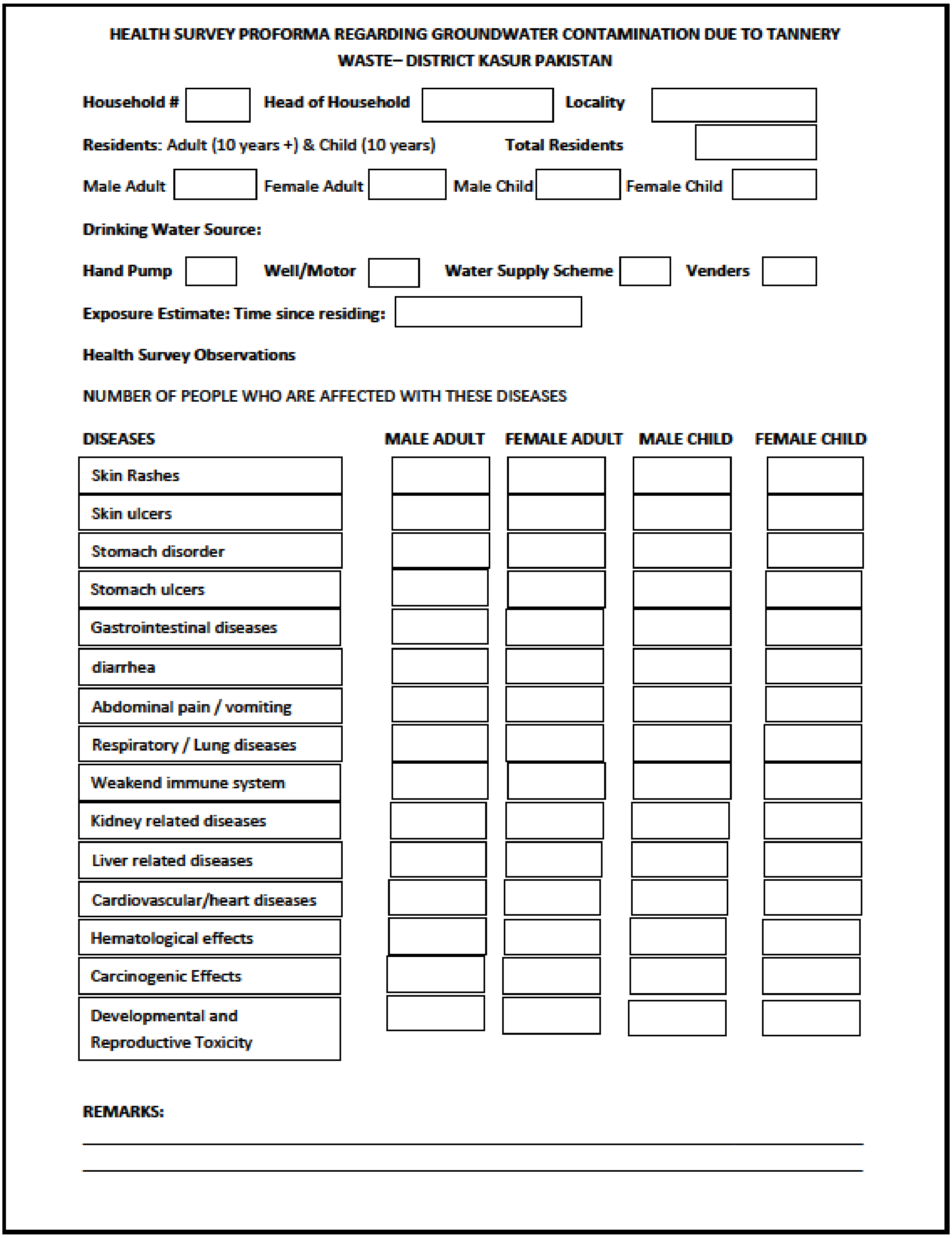


Fig. 7.2: GIS map of Kasur study area showing three localities for health surveys due to groundwater contamination



HEALTH SURVEY PROFORMA REGARDING GROUNDWATER CONTAMINATION DUE TO TANNERY WASTE– DISTRICT KASUR PAKISTAN

Household # ☐ **Head of Household** ☐ **Locality** ☐

Residents: Adult (10 years +) & Child (10 years) **Total Residents** ☐

Male Adult ☐ **Female Adult** ☐ **Male Child** ☐ **Female Child** ☐

Drinking Water Source:

Hand Pump ☐ **Well/Motor** ☐ **Water Supply Scheme** ☐ **Venders** ☐

Exposure Estimate: Time since residing: ☐

Health Survey Observations

NUMBER OF PEOPLE WHO ARE AFFECTED WITH THESE DISEASES

DISEASES	**MALE ADULT**	**FEMALE ADULT**	**MALE CHILD**	**FEMALE CHILD**
Skin Rashes				
Skin ulcers				
Stomach disorder				
Stomach ulcers				
Gastrointestinal diseases				
diarrhea				
Abdominal pain / vomiting				
Respiratory / Lung diseases				
Weakend immune system				
Kidney related diseases				
Liver related diseases				
Cardiovascular/heart diseases				
Hematological effects				
Carcinogenic Effects				
Developmental and Reproductive Toxicity				

REMARKS:

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Fig. 7.3 “Health Survey Proforma” for conducting health hazard studies

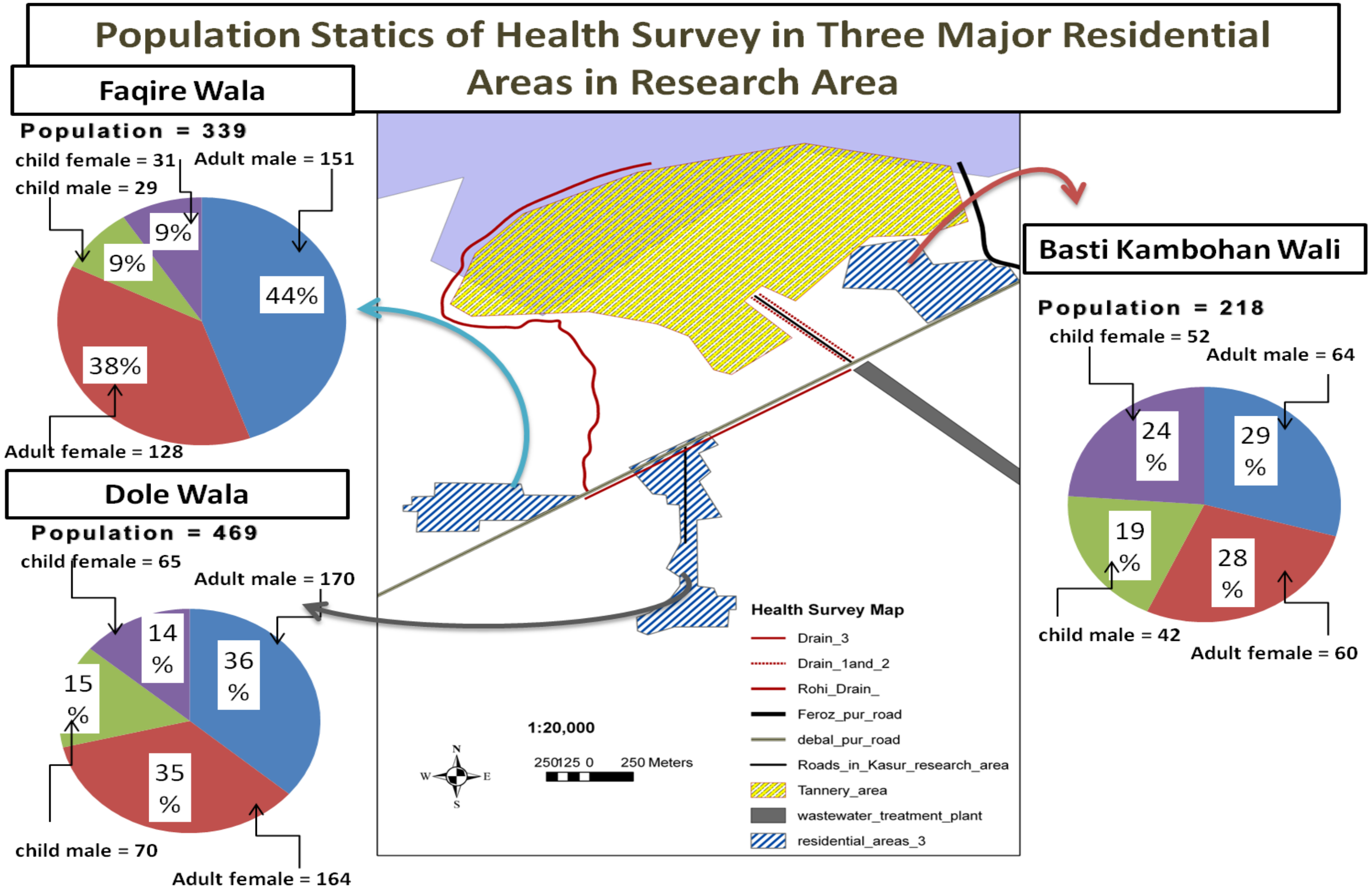

Fig. 7.4: Population statics for three localities surveyed for health hazard studies

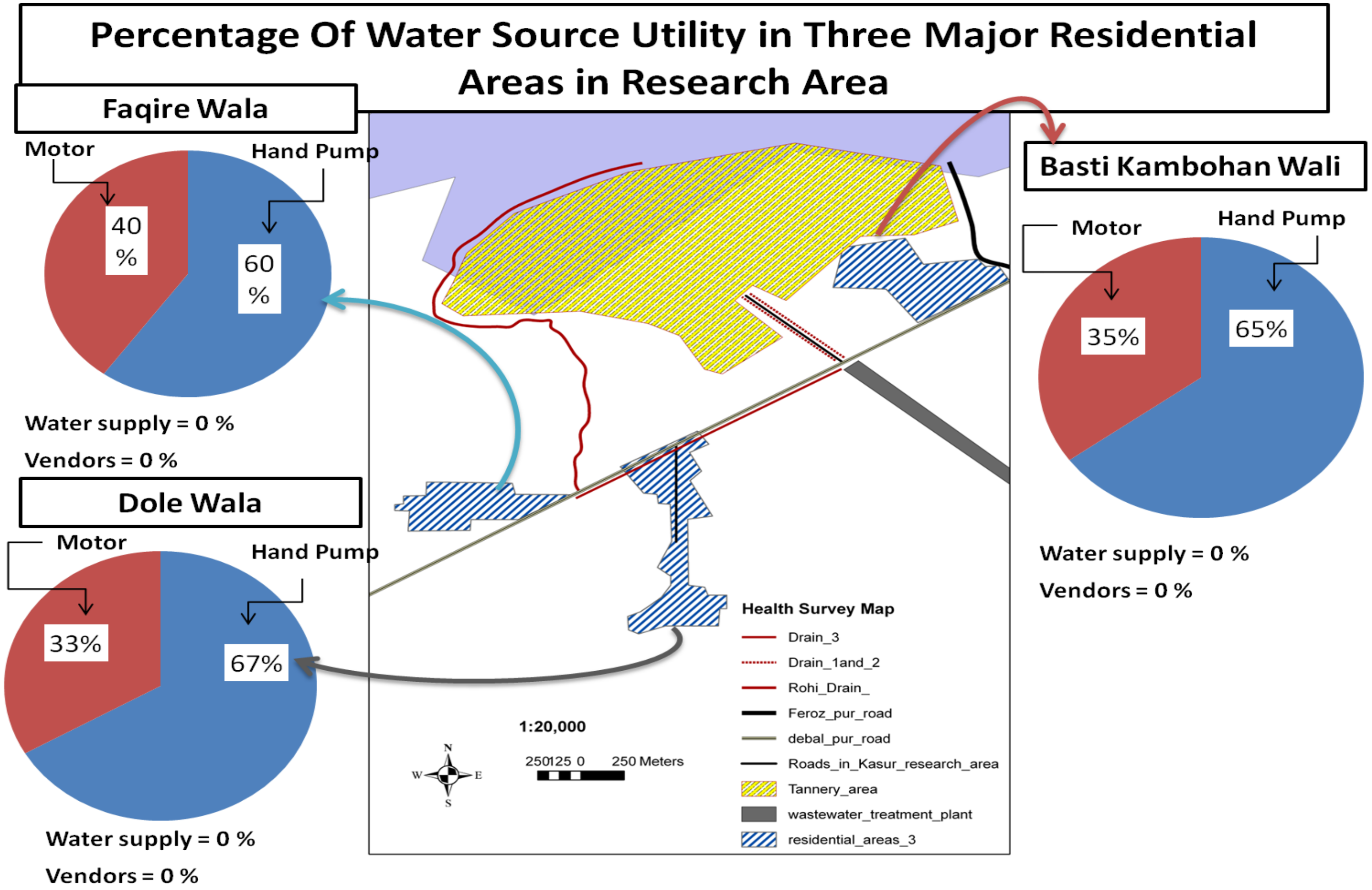

Fig. 7.5: Percentage of water source utilization in three localities for health hazard survey

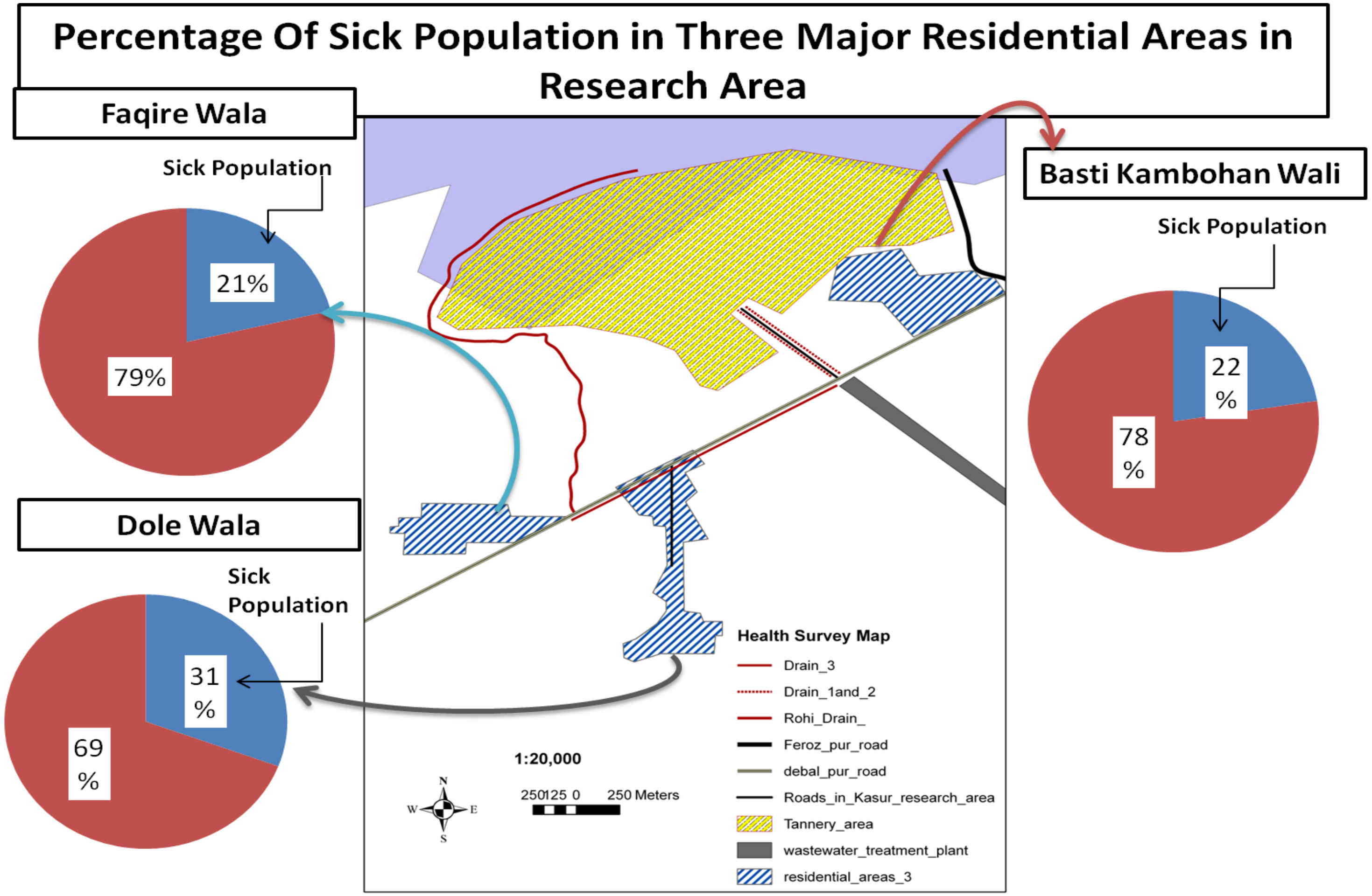

Fig. 7.6: Percentage of sick population in surveyed localities

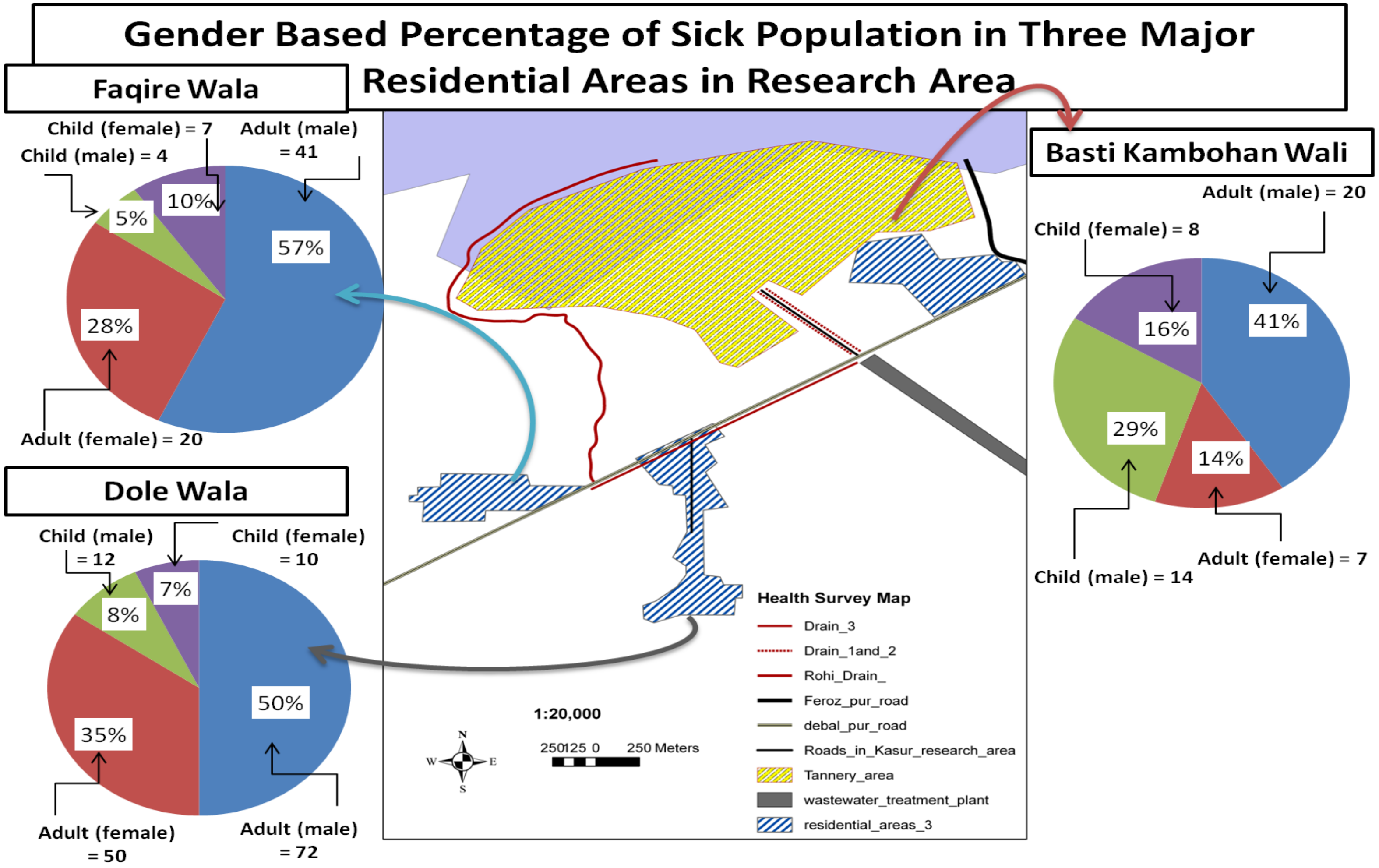

Fig. 7.7: Gender based percentage of sick population in three localities for health hazard studies

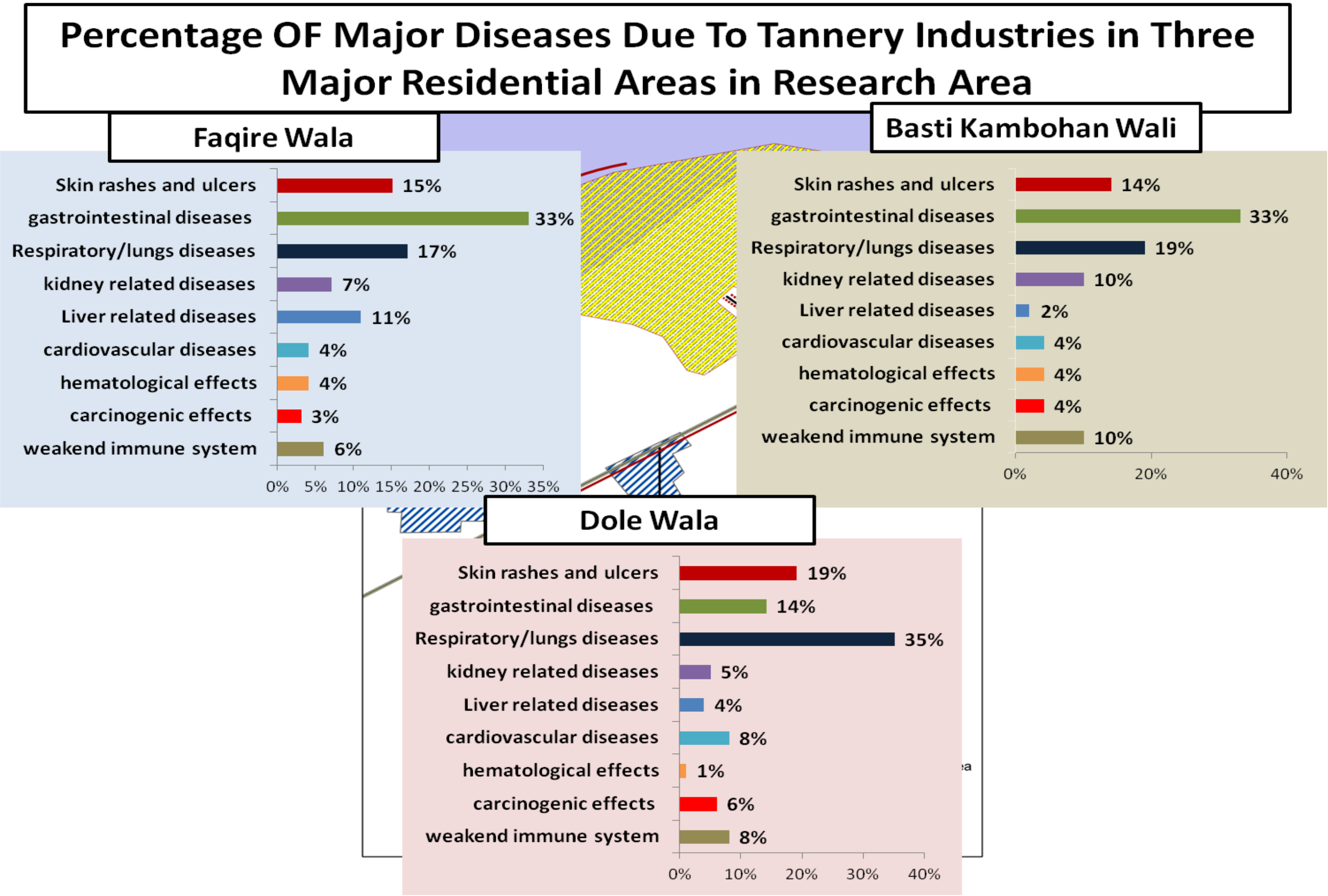

Fig.7.8: Percentage of population suffering from major diseases in three localities

7.4 Comparative Analysis of Health Risk among different research sites

Three different localities which were selected for the studies, including, Basti Kambohan Wali, Dole Wala and Faqire Wala were the most dominant residential areas in the surrounding vicinity of tannery area. 50 household units were selected from each locality on random basis to collect the required information. A comparative analysis has been presented in Table 7.1 to understand the existing health conditions and its relevance with the tannery waste contamination as a source.

Table 7.1 Comparative analysis of health risk among different research sites

Parameters \ SITES	**Basti Kambohan Wali**	**Dole Wala**	**Faqire Wala**
household units surveyed	50	50	50
Population investigated	218	469	339
%shallow water usage	65	67	60
%water supply usage	0	0	0
%age Sick Population	22	31	21
%age Male adult Sick	41	50	57
%age Female adult Sick	14	35	28
%age male child Sick	29	8	5
%age female Child Sick	16	7	10
Skin rashes & ulcer	14	19	15
Gastrointestinal diseases	33	35	33
Respiratory diseases	19	35	17
Kidney related diseases	10	5	7
Liver related diseases	2	4	11
Cardiovascular diseases	4	8	4
Hematological diseases	4	1	4
Carcinogenic diseases	4	6	3
Weekend immunity	10	8	6

Data as obtained from the health survey and summarized in Table 7.1 has described that Dole Wala which is the oldest residential area in the vicinity was thickly populated and due to their longer exposure to the industrial sources of contamination has more probability towards health risks exposure to the residents of all ages but elderly people more particularly. Significant parameters have been highlighted in Table 7.1 for their comparative analysis and risk factors.

Bastil Kambohan Wali has shown the least % age of sickness as compared to other places among elder people which can be justified by its being a newly established residential area. However the children were having higher percentage of sickness to extremely unhygienic conditions due to poor sanitation facilities. Fig. 2.9 and Fig. 4.5 have shown the adversities of the area clearly. Furthermore as this site is at upstream side of Drain 3 and initial groundwater sampling in this area has shown satisfactory results as presented in Fig. 5.1 to Fig. 5.4.

Dole Wala site being the oldest village in the research site has shown very congested population as obvious from Table 7.1 and it has a distance of only 2.5 kilometers from the tannery area. This residential area has shown higher level of shallow groundwater contamination and thus indicating poor quality of groundwater as obvious from initial groundwater analysis as described in Fig. 5.1 and 5.2. Drain 3 which is passing just adjacent to Dole Wala has been the major source of groundwater contamination. Results related to Total chromium concentration could be observed from Table 5.1 which have shown chromium concentration upto 10 mg/L. Due to this reason the diseases related to tannery effluent have been in higher percentage as compared to other areas.

Third residential area, Faqire Wala being situated at a distance of about 3 kilometers from tannery area has also congested population like Dole Wala. Most of the residents belong to the profession of farming and domestic wastewater coming from Kasur city through Drain 4 has been directly used by the farmers to meet their water demands for agriculture. Due to this reason the soil has shown higher levels of chromium contamination as obvious from Fig. 5.10 for Soil Bore 8. It has shown maximum level of chromium retention in shallow soil layers as well as presence of hexavalent chromium in higher levels at groundwater table. Initial groundwater analysis for Faqire Wala has also shown considerable groundwater contamination in Fig. 5.3. Groundwater analysis for total chromium has also shown higher levels upto 0.04 mg/L as described in Fig. 5.19. People are suffering from diseases related to tanneries and also due to other unhygienic conditions.

Another crucial factor which increased the health risk was more than 60 % dependency on groundwater for drinking purpose and other household usage. Had there been alternative and safe drinking water sources, the level of health issues would have been much lesser. Almost one third population was suffering from gastro problems in all the three localities. It indicated equally severe conditions related to hygiene along with chronic sources of contamination in soil and groundwater.

7.5 Findings of Health Hazard Survey

According to International Union for Conservation of Nature (IUCN) in 1993 atleast fifty thousand workers and residents living in and around polluted areas are at direct risk of cancer and other chronic diseases associated with pollution caused by tanning industry in Kasur (Rehman, 2004). Therefore it was required to find out that how much % age of people are suffering from diseases caused by contaminated drinking water in areas other than tanneries but in the nearby peripheries. Overall sample data from 150 household units in total was collected from the three localities with surveyed population of more than one thousand (1000).

There is an increasing trend of health risk associated with chromium concentrations in environment associated with tannery industries in Kasur. The residents and particularly the tannery Industries workers are exposed to serious threat of health risk in the tannery area and the nearby vicinities. While there are so many other pilferages in the system (sanitation and soil waste disposal) still it can be considered that tannery effluent is the main source leading to cause number of environmental hazards. It includes mainly soil and groundwater contamination originating from tannery areas. People residing in the tannery areas and the adjacent areas along with tannery industry workers are found to be greatly affected from the hazardous tannery waste. As it is found in this research that both soil and groundwater are not only remarkably contaminated by industrial effluent but chromium, which is so extensively used in the tannery industries is observed in alarmingly high concentrations. Thus while discussing the effect of tannery waste; the hazardous impact of chromium is highly significant. Industrial effluent contains immense quantities of chemical pollutants along with chromium. Thus while understanding the health impact of tannery industries both chemical pollutants and heavy metals should be considered as main source of environmental degradation in the tannery areas and adjacent regions. However in this research it was planned to investigate health risk impacts due to chromium only due to its significant potential hazard to cause chronic health issue in human beings who are exposed to the threat. the nature of the threat can be through drinking contaminated water, through consumption of contaminated wastewater irrigated crops and vegetables and fruits or may be due atmospheric exposure to improperly disposed hazardous chemical waste from the tannery industries.

A detailed exposure assessment of total and hexavalent chromium being released from the tannery industry was conducted through different approaches. It include, field visits, soil waste dumping site facilities, effluent carrying drains, groundwater and soil investigations and above all conducting field survey and interview to doctors, hospitals, clinics, personal one to one based interview to residents, data collection related to their health issues and health status and its statistical based evaluation.

However there was lack of previous data availability for cross checking the findings and for baseline data preparations, still the data collected presented a comprehensive and factual based health report of the residents of the tannery areas and surrounding localities. Such intense and detailed investigation regarding effect of chromium in the tannery industrial area were conducted for the first time as earlier this area has been deprived off from the basic facilities of life. Still there is no proper provision of basic needs of life including health, safe drinking water and proper sanitation but gradually the improving communication has resulted in awareness and now residents on self-support basis are getting involved in those activities which are initiated for betterment of quality of life. It include private vendors for clean drinking water supply, initiation of water supply scheme from reliable source, lining of wastewater carrying drains and health care activities etc.

A very significant study conducted by medical researchers (Khan, 2013) revealed a very crucial aspect of tannery contamination on human health. Although this research was conducted in another cluster of tannery units in Pakistan this is in district Sialkot but the results regarding the impact can be generalized as similar conditions prevail in study area Kasur as well. In this study total of 240 study samples were collected; 120 of which were male workers from tanneries while same number of samples were collected as control. Blood complete counts, high-sensitive C-reactive protein, malondialdehyde and routine biochemical tests were carried out by routine procedures. Chromium levels in blood (BCr) and urine were analyzed using graphite furnace atomic absorption spectrophotometer Perkin Elmer analyst-200. Results revealed that all the workers were male with average age of 33 years and 15 (13%) had skin rashes, 14 (12%) had chronic bronchitis, 10 (8%) had gastritis and 4 (3%) conjunctivitis. The tannery workers had significantly raised median (interquartile range) of BCr 569 (ranging in between 377–726) nmol/L as compared to 318 (ranging in between 245–397) nmol/L in the control ($p<0.001$). Sixty-five (54%) workers had BCr levels above the upper limit set by Agency for Toxic Substance and Drug Registry (ATSDR). The urinary chromium excretion was significantly high in workers 131 (46–312) nmol/L as compared to 13 (3–26) nmol/L in controls ($p<0.01$). The workers had hematological, hepatic and renal function impairment because of oxidative stress on body systems. It is concluded that about half of the workers had excessive exposure to chromium in the tanneries at Sialkot. They had significantly raised chromium levels in their biological fluids and adverse health effects due to enhanced oxidative stress and inflammatory changes.

7.5.1 Health Survey of Basti Kambohan Wali.

The location of this residential area is very significant as it is encompassed by two main roads on east and south side while in the north side there is tannery area (Fig. 7.3). The total population surveyed in Basti Kambohan Wali is 218 (Fig. 7.4). Another significant finding is related to water supply system in this area and it has been observed that 65 % of people are using hand pumps while 35 % are using centrifugal pumps or motors (Fig. 7.5). Average water drawing depth for hand pumps is below 30 meters while motors are in the range of 35 to 45 meters. Data obtained regarding health aspects revealed that only 22 % (Fig. 7.6) of surveyed population has illness out of which adult male are in highest percentage of 41 (Fig. 7.7). For data related to diseases, gastrointestinal diseases were in the highest percentage of 33, followed by Respiratory and lungs diseases which were 19 % and then skin rashes and ulcers, which were 14 % (Fig. 7.8).

7.5.2 Health Survey of Dole Wala

This is basically an old village, which now has converted to suburbs of Kasur city.

The significance of this area is its location which exists in the catchment area of all the drains. Its location is just next to junction of Drain Rohi and Drain 3, which carried tannery effluent and treatment plant effluent. During all seasons the surroundings of Drain 3 remain soaked in effluent which overflowed due to chocking and excessive discharges. The surveyed population in this area is 469 people (Fig. 7.4). In this locality again there is no water supply scheme for clean drinking water and no venders are available in this area. 67 % of houses use hand pumps while motors are used by 33 % household units (Fig. 7.5). About 31 % of population has health problems with leading percentage of 50 of male (adults) (Fig. 7.6 & 7.7). Highest percentage of diseases is related to respiratory and lungs i.e 35 % while Skin rashes and ulcers are 19 % and gastrointestinal diseases are 14 % (Fig. 7.8).

7.5.3 Health Survey of Faqire Wala

Faqire Wala is an old locality in the South west of Kasur city adjacent to Drain Rohi with people settled here for decades**.** The surveyed population in this area is 339 (Fig. 7.4). There is also no water supply scheme and 60 % people are dependent upon hand pumps while remaining 40 % use centrifuge pumps or motors (Fig. 7.5). About 21 % of population was facing health problems (Fig. 7.6) with major proportions of gastrointestinal diseases i.e 33 % followed by respiratory and lungs diseases and skin rashes and ulcers 17 and 15 % respectively (Fig. 7.8).

7.6 Summary of Health Survey

As high concentrations of total chromium do exist in the shallow groundwater aquifer in Kasur study area it was most likely to have effect on the groundwater consumers. From the survey conducted it can be observed that 60 to 67 % of population is dependent upon shallow groundwater aquifers in order to obtain drinking water by using hand pumps less than 30 meters. Chromium is also one of the causes for major diseases from which people are suffering in these areas, which include gastrointestinal diseases, respiratory and lungs diseases and skin rashes and ulcers. Therefore high possibility exists that health conditions are related to major diseases caused by groundwater contamination due to tannery effluent. Therefore it can be concluded that although there could be many possible sources of contamination of drinking groundwater still groundwater quality deterioration in the study area mainly due to tannery based source. Major diseases found in the area are closely associated with the toxic pollutants found in groundwater originated from tannery waste.

Hexavalent chromium compounds as they are carcinogen based on the epidemiological research on workers is a huge threat to the lives of inhabitants of the area.

Clear accumulation of hexavalent and total chromium as observed through the intense investigations in Chapter 5 and 6 upto alarmingly high concentrations finally pose a severe potential of health hazard in the tannery area and the surrounding areas upto the lateral distance of about 2.0 kilometers towards south and 1.5 kilometers on east western side. The model simulation has shown movement of contaminant to even farther areas but the level of contamination is not that alarming. This is due to very slow movement of ground water flow, suggesting that the plume of high concentration might approach the surrounding area. Therefore long term monitoring of GW quality should be done. Reducing the spreading of contaminant in different media is very difficult. In the particular site, natural attenuation is only feasible measures for the GW contamination in the deep depth. To reduce the health impact of the GW contamination by natural attenuation, removal of the critical contaminant source of GW pollution is the most effective and essential method, as discussed in Chapters 5 and 6.

CHAPTER 8

CONCLUSIONS AND RECOMMENDATIONS

The present study illustrates the site characterization of Kasur tannery area regarding soil and groundwater contamination due to tannery effluent. Detailed site investigations regarding soil, groundwater and wastewater were conducted along with health survey and modeling the site for contaminant flow. Conclusions of the research are summed up as follows.

8.1 General Concluding Statement

"Tannery based contamination in Kasur study area does not exist at particular location rather present in the form of widely spread clusters of contamination; nature of groundwater contamination is also not consistent and totally dependent upon location from drains and depth from where water is drawn, nearer to the drains, samples showing higher groundwater contamination at shallow depths; besides the area adjacent to tanneries soil at deeper depth has not shown significant contamination, however all the drains in the study area are continuous potential threat for aquatic life, flora and fauna and crops in their surroundings due to carriage of extremely heavy loads of chromium."

8.2 Conclusions of Soil Analysis

For soil samples collected from eight (8) soil bores in the surrounding area of drains, up to the depth of 30.5 meters no significant value for both total and hexavalent chromium could be observed for leaching test done by using Toxicity Characteristics Leaching Procedure. Maximum concentration of total chromium was observed to be 0.05 mg/L while that of hexavalent chromium was 0.035 for leaching test collected from top soil layer for Bore 1, these are within the standard permissible values.

Soil sample analysis for total chromium content retained in soil conducted by aqua regia acid digestion method for all the right (8) soil bores in areas adjacent to drains also showed no significant results with maximum concentration of 91.2 mg/kg for total chromium and 16.2 mg/kg for hexavalent chromium in Bore 8. It is important to mention that although these values are far less than the standard permissible values for chromium content retention in soil still these values and other values observed in other samples are in excess of background values obtained for this area, which are 8.5 and 6.4 mg/kg for both total and hexavalent chromium respectively. It depicts that the surrounding area of the drains is somehow influenced by the continuous spillage of tannery effluent and chronic stagnant ponds of wastewater prevailing in the area for decades. Thus higher levels of soil contamination were observed mainly due to localized factors in the form of chocking of drains and stagnant pond formation. It is worth mentioning that samples collected from near the tannery area showed the highest concentrations in the whole study area up to 180 mg/kg and 28 mg/kg for total chromium and hexavalent chromium respectively. Such high values are subjected to immense overflow from drains and direct disposal of tannery effluent into open fields.

From the observed values of total chromium content retained in soil, among the soil samples collected from right (8) soil bores it was found that samples with higher silt and clay proportions have shown relatively higher concentrations of the hexavalent and total chromium.

8.3 Conclusion of Wastewater Analysis

From the chemical analysis and chromium analysis in wastewater samples obtained from all the five drains in the study area revealed that parameters BOD_5, COD, Sulphides, Sulphates, and total chromium all are present in extremely high concentrations and exceeding the permissible limits by NEQS set by Pak EPA.

The values of total chromium in wastewaters were specifically found in high concentrations in all the drains, ranging between 68 & 2,152 mg/L. Such alarmingly high values of total chromium in wastewater are a potential risk for the groundwater contamination

Concentrations of total chromium investigated in wastewaters twice a year during peak production duration i.e. May to September and minimum production duration in January, reveal that throughout the year the wastewaters contain concentration of chromium higher than the standard limit by NEQS i.e. 1.0 mg/L, although these values were lesser than those obtained during peak production period.

8.4 Conclusion of Groundwater Analysis

Two extremely high concentrations of total chromium in groundwater sample from existing sources first at tannery area with concentration of 90 mg/L and second at Dole Wala near Drain 3 with concentration of 10 mg/L depict an alarming situation regarding chromium concentrations in groundwater.

It describes direct interference of wastewater being carried in drain with groundwater aquifers. It is because soil medium has not shown any significant results regarding chromium retention or mobility through soil layers. Thus high levels of chromium at particular locations, i.e. near to Drain 3 or at junction of Drain 3 and 4 were most likely due to the unlined drains, leaking and cracked sewers.

Groundwater sampling analysis from the monitoring wells installed in the surrounding area of drains exhibit varying concentrations of total chromium during six months. The results do not depict any uniform trend throughout the period of six months rather varies abruptly for every month. It may be due to seasonal changes and direct intervention of fresh contamination through unlined drains, leaking and cracked sewers and destructed structures. However dividing the monitoring wells in downstream and upstream side, it can be observed that downstream side has moderately higher values of chromium on average throughout the monitoring period of six months.

Maximum concentrations of 0.04 mg/L are observed from the Monitoring well 4 and 8 on the downstream side in February when sampling was done in post rainy season.

8.5 Conclusion of Site Characterization

There are different clusters spread throughout which act as contamination source varying time to time in concentration. These sources include stagnant ponds, unlined drains and overflowed drains.

Initially higher concentrations have contaminant have leached into soil from stagnant ponds considering them as major contamination source, since there were neither drains nor wastewater treatment plant which could carry the effluent discharge in a proper manner for treatment or final disposal until year 2000.

Gradually with the construction of treatment plant and drains and drying out of stagnant ponds, overall the condition improved to some extent after year 2000. But still with the passage of time major issues are present which are related to inefficiency of wastewater treatment plant as it is unable to handle the excessive and increasing discharge loads of tannery effluents, high discharge rates of overflow in drains due to blockage and inadequacy of drains and finally the unlined drains from which percolation may be a continuous threat to soil and groundwater contamination.

The levels of contamination are spreading towards farther distances away from tannery area, which once were limited to only tannery area due to direct disposal of effluent into stagnant ponds. Now through movement of groundwater and contaminant flow through drains, the contamination has shifted to adjacent peripheries.

Due to overflow from Drain 3, percolation through Drain 4 and deteriorated concrete structure, especially at junction of Drain 3 and Drain 4, the surrounding area is more exposed to soil and groundwater contamination as it is evident from the 8 monitoring wells analysis for six months and depth wise chromium concentration profile for 8 soil bores in areas of

Dole Wala and Faqire Wala. Although not present in alarmingly high values, both soil and groundwaters are equally observed contaminated especially on the downstream side along Debalpur road.

Concentration of total chromium in wastewater for Drain 3 is also in range of 12 to 2,050 mg/L, which is most of time overflowing resulting in soil contamination in the side of drain. Maximum total and hexavalent chromium retention level have been observed in the top soil layer at this location i.e. 180 mg/kg and 28 mg/kg respectively. Therefore basically the source of contamination is the untreated effluent which is overflowing in excessive amounts with high concentrations of total chromium.

The groundwater samples collected from upstream of drains in the north eastern side did not show any detection of chromium, similarly soil samples collected from these areas were also with very minute levels of chromium up to 21 mg/kg.

It has been found that correlation do exist at the entire site among the wastewater, groundwater and soil with respect to the levels of contamination regarding chromium. All the three media are interrelated in terms of distribution contamination up to remote places.

8.6 Conclusion of Health Hazard Studies

The main finding of the health survey is that residents are dependent upon groundwater for drinking and daily household use due to which chromium concentration in groundwater and other groundwater quality parameters became significant from health aspects on the residents. More than 60 % of population is using shallower depth of groundwater for drinking purpose through hand pumps. The quality of shallow waters has been shown adversely affected due to industrial effluents in Chapter 5. The maximum level of total chromium has reached upto 10 mg/L along with other parameters also in excess at Dole Wala site along Drain 3. Such high levels of total chromium and other parameters in groundwater, specifically when 60 to 65 % of the residents are relying on groundwater for daily use directly relates to poor health conditions in the study area.

The observation that people living at Dole Wala and Faqire Wala localities are suffering more from drinking water and chromium related diseases was mainly due to overflowing drains and leaky structure at junctions. On the other side residents of Basti Kambohan Wali (BKW) are facing water related diseases due to their localized unhygienic conditions as it is a newly developed residential locality right at the place where there was stagnant pond 1. But still as there existed huge blockage of household waste being mixed with tannery waste. It explained the reason for majority of residents particularly children in excess being suffered from diseases related to tannery waste along with other water borne diseases.

8.7 Conclusion of Contaminant Transport Modeling

31 years simulation considering stagnant pond 1 as the main contamination source did not reveal contaminant transport to farther distances as it travelled only 1385 meters along x-axis and 2000 meters along y – axis with contaminant concentration of 0.1 mg/L per liter at top layer. However most probably due to heavy flow rate most of the contaminant moved vertically downward with concentration of about 23 mg/L at the depth of 100 meters.

After year 2004 the generation of stagnant pond 2 due to heavy overflow also could not create any farther movement horizontally. As a combined effect of both ponds contaminant moved with concentration of 0.1 mg/L and reached residential area of Dole Wala after 31 years at a distance of 1385 meters.

This could be reason of low concentrations of chromium observed in monitoring wells and soil analysis for retention of chromium and its leaching probability in soil.

Minor higher values in subsoil samples could be due to local effects of drain overflows and some direct intervention of contamination into groundwater may be due to some leakage or percolation.

TCLP analysis showed high leaching value of chromium of 0.05 for Soil Bore 1 in top layers which could be justified by model result interpretation as contamination only in top layer has reached in Dole Wala residential locality. The location of Soil Bore 1 is just in the beginning of dole Wala area where the contamination plume is approaching.

8.8 General Conclusions

Soil analysis has not shown serious level of contamination except the nearby vicinity of drains that is also subjected to extensive over flow of the effluent from drains.

Groundwater has shown some variation trend based on seasonal variation however so abrupt variations could be due to direct intervention of contamination with groundwater.

Groundwater in tannery area is highly polluted even at deeper depths of 45 meters with concentration as high as 90 mg/L, while at the distance of 3 kilometers from tannery area the groundwater is contaminated with chromium upto 0.04 mg/L concentration but still with safe limit at the medium depth of 30 meters.

Health and provision of safe drinking water are the main issues to be addressed in Kasur along with overall betterment of environmental conditions.

The current soil contamination might not be a serious source of the groundwater contamination in the future. Therefore by focusing on the chemical treatment of the tannery effluent and on the seepage prevention of the untreated effluent from the drains or leakages from the concrete made sewers, further spreading of the groundwater contamination could be controlled up to large extent. Once the source of contamination has been stopped and controlled, the groundwater contamination might reduce by exhibiting natural attenuation.

8.9 Recommendations for Future Studies

The wastewater in the drains is being used for irrigation at many places along the drain length. It is said that as the wastewater contains high loads of organic matter therefore it works as natural supplement for crops and enrich the process of crop cultivation. However as there is high concentration of total chromium in wastewater it is suggested for future researchers to investigate the content of chromium or other chemical compounds in the crops.

Considering it as a pilot scale study, similar type of site investigation and characterization studies can be conducted in other contaminated sites in the country as almost similar pattern of contamination do exist in other industrial areas/sites as well.

As initially there was no hydrogeological data available for this site or even any other similar site in Pakistan, it is highly recommended that detailed subsurface and geophysical investigations should be done so as to provide reliable data for future hydrogeological studies in this area.

Not only chromium but other compounds including Magnesium, Iron, Arsenic and fluoride should also be investigated simultaneously in order to study the chemical bonding of these compounds in such a way to affect the retention capacity in soils.

8.10 Recommendations for Site Management Plan

“Key effective contamination management strategy at Kasur tannery site is the source reduction steps accompanied by natural attenuation process for dilution of contaminant in soil and groundwater”

On the basis of this detailed research work conducted in Kasur tannery area, frame work for site management plan in order to cope with the adverse environmental conditions at site can be provided. Here are the detailed step wise recommendations for preparation of site management plan

Step 1: Regular monitoring of groundwater quality and wastewater characteristics and discharge

It is the basic need to establish concurrent data base on regular basis. In this regard groundwater should be monitored periodically on wide range for longer durations from fixed monitoring wells with observation of water table depth as well. Wastewater discharge in the drains should be determined accurately on specific intervals of time in order to incorporate seasonal variations and tannery productivity. Besides wastewater samples from all the drains from fixed sampling locations should be taken and tested for basic chemical parameters and heavy metals.

Step 2: Extension of existing drains, Lining of Drains and repair of damaged structure

As availability of space is not an issue, all the drains should be extended to accommodate excessive amounts of effluent discharges. The most important step in site management plan is concrete lining of the all the drains in Kasur and adjacent areas. It is also utmost required to repair or rebuild the damaged hydrologic structures for example junction of drains. It will help in seepage reduction and direct intervention of effluent into groundwater.

It is also recommended that improved system for collection of wastewater by constructing a network of channels interlinked and collectively carrying the wastewater for final disposal be arranged.

It is also recommended to permanently install monitoring wells on wide range, which should be sampled periodically for long term so as to observe a detailed concentration variation of total chromium in groundwater.

Step 3: Technical workshops and awareness campaigns

On site handling of solid waste, with proper segregation could be a key factor to minimize the waste load in the drains, especially when the solid waste is of hazardous nature as originating from the industrial processes. In this regard technical workshops and awareness campaigns can play vital role in educating the industrial workers and managers about the latest methodologies of industrial and hazardous waste handling.

Step 4: Improving the Efficiency and Capacity of Wastewater treatment plant

Wastewater treatment plant capacity needs to be enhanced in order to address the increasing demands of tannery industry. Once the efficiency of treatment plant is improved, the contaminant loads in the drains can be significantly reduced. Sludge disposal process also needs attention and should be done on regular basis for avoiding the possibility of sludge leachate into soil.

Step 5: Integrated Solid waste management plan and landfill site

In continuation to the previous step, it becomes the duty of the state to establish a proper solid waste management system not only Kasur tannery area but also throughout the city to effectively implement the action plan for solid waste collection and management. Besides a landfill site is extremely needed in order to properly dump the hazardous solid waste from tanneries and from other areas. It should be an engineered landfill site so as to avoid the after effects of a poorly developed dump site which instead of improving the situation would more likely to make it worse.

Step 6: New Sewer Line System in Kasur City & Rehabilitating Drain Rohi into fresh water drain

In order to address the increasing demands of the city, it is recommended to develop a new sewerage system for the city and instead of disposing the municipal wastewater into Drain Rohi, it should be carried through main sewers for final disposal. Drain Rohi should be only used for carrying fresh water for irrigation purposes along with carrying excessive storm water during the rainy season. Once carrying fresh water, Drain Rohi can play a vital role in the natural attenuation of the contaminated soil in the entire research area along the Debal Pur road by seepage through the side walls and bottom of the drain.

Step 7: To ensure provision of safe drinking water supply to Kasur city and nearby localities and regular health checkup activities

Groundwater being major source for household usage and drinking purposes must be replaced by developing a safe drinking water supply scheme. It should be prioritized to make arrangements for supply of treated drinking water to residents of Kasur city and the surrounding localities in order to avoid the hazardous effects of contaminated shallow aquifer due to tanneries. Rather people should be encouraged to rely on other sources of water rather than using groundwater resources so intensively. It is also important to regularly monitor the health situation in the area by arranging mobile clinics as no sophisticated and well equipped health set up is available in the research area.

Step 8: Conservation and safeguarding of eliminated and dried stagnant ponds

It is highly recommended that open fields adjacent to tannery area and along the drains, which are heavily soaked in tannery effluent, once eliminated and dried, should no more be used for any human activity, especially for residential purposes. Rather these open fields and landmarks should be conserved and safeguarded by proper vegetation sheeting and fencing.

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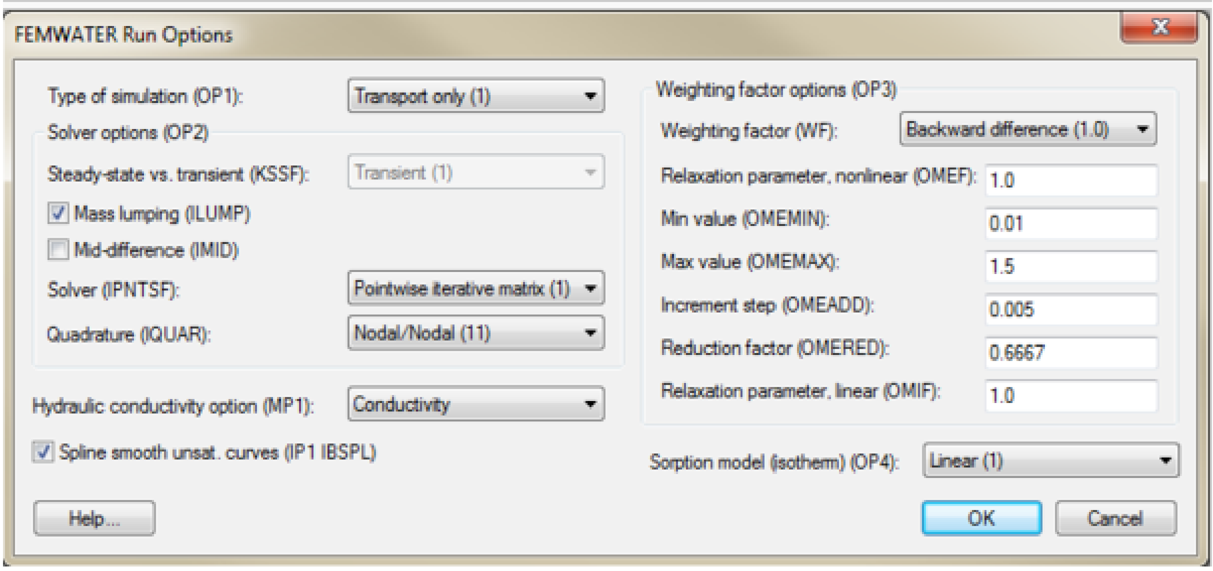
APPENDICES

Appendix I

FEMWATER Model Parameters

A – 1 FEMWATER Run Options



FEMWATER Run Options

Type of simulation (OP1): Transport only (1)

Solver options (OP2)

Steady-state vs. transient (KSSF): Transient (1)

☑ Mass lumping (ILUMP)

☐ Mid-difference (IMID)

Solver (IPNTSF): Pointwise iterative matrix (1)

Quadrature (IQUAR): Nodal/Nodal (11)

Hydraulic conductivity option (MP1): Conductivity

☑ Spline smooth unsat. curves (IP1 IBSPL)

Weighting factor options (OP3)

Weighting factor (WF): Backward difference (1.0)

Relaxation parameter, nonlinear (OMEF): 1.0

Min value (OMEMIN): 0.01

Max value (OMEMAX): 1.5

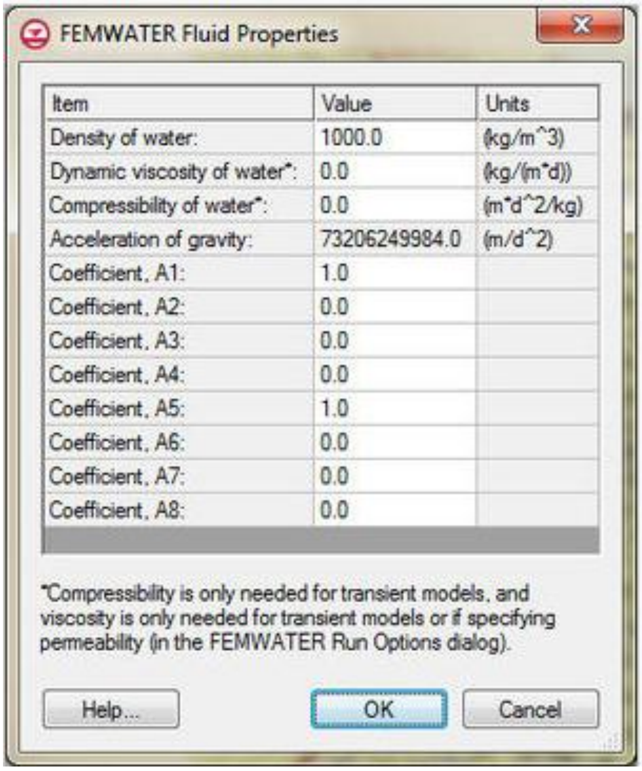
Increment step (OMEADD): 0.005

Reduction factor (OMERED): 0.6667

Relaxation parameter, linear (OMIF): 1.0

Sorption model (isotherm) (OP4): Linear (1)

A – 2 Fluid Properties

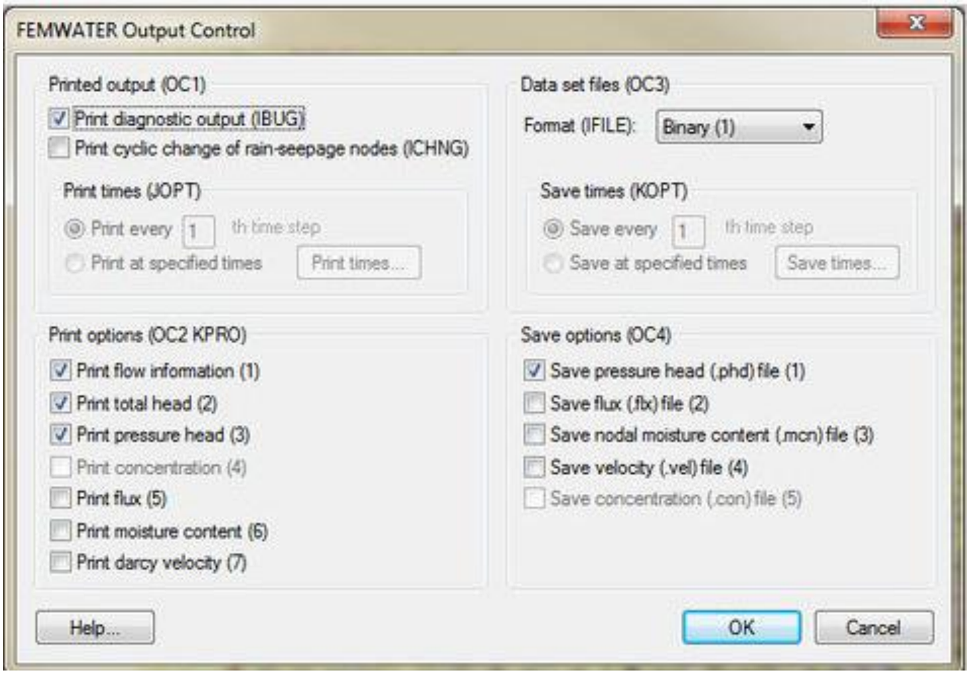


FEMWATER Fluid Properties

Item	Value	Units
Density of water:	1000.0	(kg/m^3)
Dynamic viscosity of water*:	0.0	(kg/(m*d))
Compressibility of water*:	0.0	(m*d^2/kg)
Acceleration of gravity:	73206249984.0	(m/d^2)
Coefficient, A1:	1.0	
Coefficient, A2:	0.0	
Coefficient, A3:	0.0	
Coefficient, A4:	0.0	
Coefficient, A5:	1.0	
Coefficient, A6:	0.0	
Coefficient, A7:	0.0	
Coefficient, A8:	0.0	

*Compressibility is only needed for transient models, and viscosity is only needed for transient models or if specifying permeability (in the FEMWATER Run Options dialog).

A – 3 FEMWATER OUTPUT CONTROL PARAMETERS



FEMWATER Output Control

Printed output (OC1)
☑ Print diagnostic output (IBUG)
☐ Print cyclic change of rain-seepage nodes (ICHNG)

Print times (JOPT)
● Print every 1 th time step
○ Print at specified times

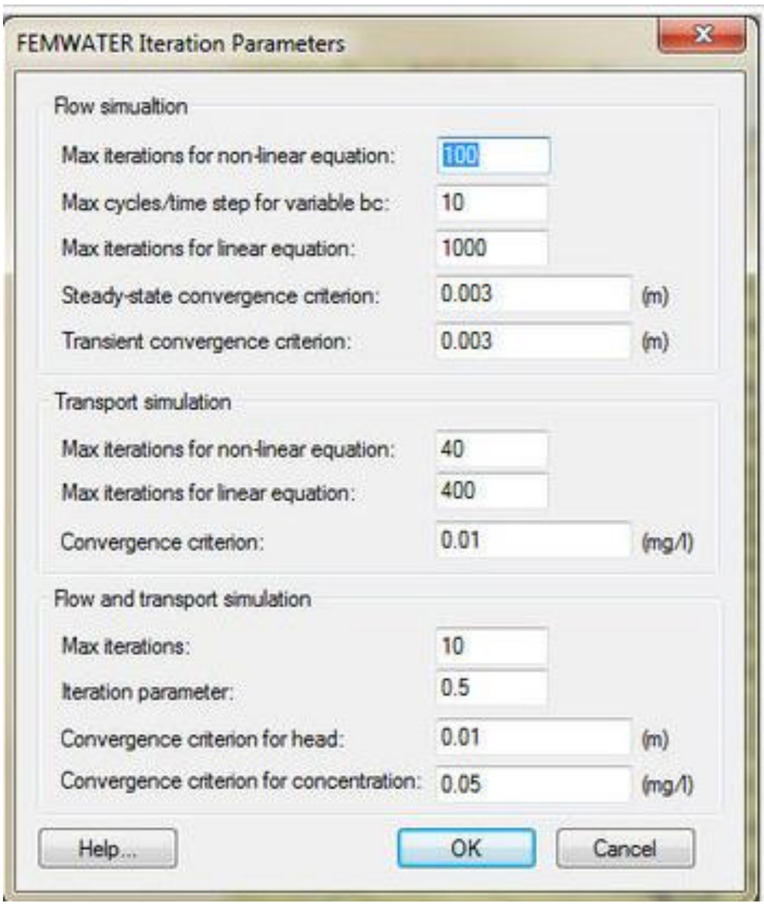
Data set files (OC3)
Format (IFILE): Binary (1)

Save times (KOPT)
● Save every 1 th time step
○ Save at specified times

Print options (OC2 KPRO)
☑ Print flow information (1)
☑ Print total head (2)
☑ Print pressure head (3)
☐ Print concentration (4)
☐ Print flux (5)
☐ Print moisture content (6)
☐ Print darcy velocity (7)

Save options (OC4)
☑ Save pressure head (.phd) file (1)
☐ Save flux (.flx) file (2)
☐ Save nodal moisture content (.mcn) file (3)
☐ Save velocity (.vel) file (4)
☐ Save concentration (.con) file (5)

A – 4 Iteration Parameters



FEMWATER Iteration Parameters

Flow simualtion
Max iterations for non-linear equation: 100
Max cycles/time step for variable bc: 10
Max iterations for linear equation: 1000
Steady-state convergence criterion: 0.003 (m)
Transient convergence criterion: 0.003 (m)

Transport simulation
Max iterations for non-linear equation: 40
Max iterations for linear equation: 400
Convergence criterion: 0.01 (mg/l)

Flow and transport simulation
Max iterations: 10
Iteration parameter: 0.5
Convergence criterion for head: 0.01 (m)
Convergence criterion for concentration: 0.05 (mg/l)

The *FEMWATER Run Options* dialog is used to set the simulation run parameters and to enter a set of general analysis options.

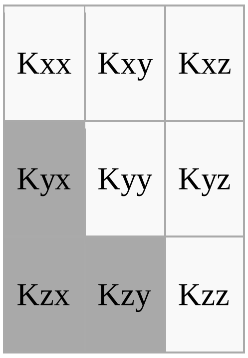
- *Type of Simulation* – Three options are available for designating the type of simulations to be performed by FEMWATER:
    - "Flow only" – This option is used to perform a steady state or transient flow simulation.
    - "Perform a transport simulation only" – For this case, a steady state or transient flow simulation must be performed prior to the transport simulation. The results of this simulation (velocity and moisture content) are then input to FEMWATER as a flow solution initial condition.
    - "Coupled flow and transport" – With a coupled flow and transport simulation, either density-dependent flow or density-independent flow can be simulated. This option is controlled by entering the appropriate parameters defining the relationship between concentration and density and concentration and viscosity. These parameters are entered in the *Fluid Properties* dialog.
- *Steady State vs. Transient* – FEMWATER can be run in either a steady state or transient mode. The steady state mode is only allowed when the *Flow only* option has been selected.
- Units – The Units button brings up the UNITS dialog. This dialog is used to enter the units for length, time, concentration, etc. for the simulation. GMS uses the selected unit options to display the appropriate units next to each input edit field in the other FEMWATER dialogs.
- *Other Options* – The remaining run options are described in the FEMWATER Reference Manual. In most cases, the default values are appropriate.

A – 5 Material Properties

As a 3D finite element mesh is constructed in GMS, a list of materials is defined and each element in the 3D mesh has a material type associated with it. The list of materials is initially created using the MATERIALS dialog accessed through the *Edit* menu.

- *Kxx, Kyy, Kzz, Kxy, Kxz, Kyz* – The hydraulic conductivity tensor is defined via the Kxx, Kyy, Kzz, Kxy, Kxz, Kyz fields. Since the tensor is symmetric only the upper right half of the matrix can be specified.

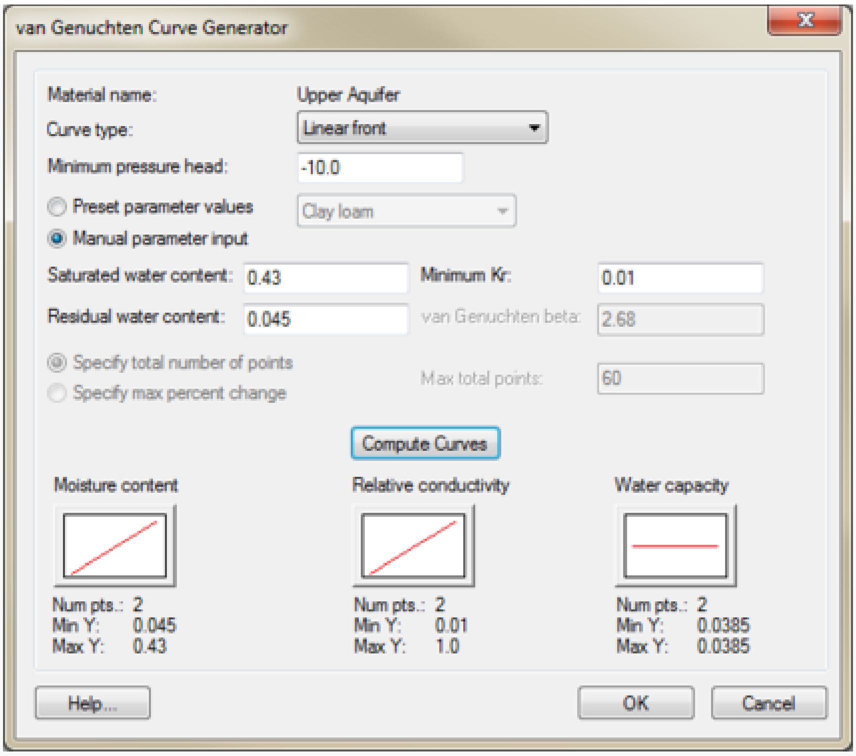
Hydraulic Conductivity Tensor



Kxx	Kxy	Kxz
Kyx	Kyy	Kyz
Kzx	Kzy	Kzz

- *Moisture Content, Relative Conductivity, Water Capacity curves* – These unsaturated zone curves must be defined for each material. The curves can be defined using either the XY Series Editor or the Curve Generator (discussed below). The Curve Generator is accessed via the **Generate Unsat Curves** button in the bottom of the dialog. When that button is selected, the curves that are generated will be associated with the active material, or the material in the spreadsheet row that currently has the focus.

Curve Generator



van Genuchten Curve Generator

Material name: Upper Aquifer

Curve type: Linear front

Minimum pressure head: -10.0

○ Preset parameter values — Clay loam

● Manual parameter input

Saturated water content: 0.43

Minimum Kr: 0.01

Residual water content: 0.045

van Genuchten beta: 2.68

● Specify total number of points

○ Specify max percent change

Max total points: 60

Moisture content
Num pts.: 2
Min Y: 0.045
Max Y: 0.43

Relative conductivity
Num pts.: 2
Min Y: 0.01
Max Y: 1.0

Water capacity
Num pts.: 2
Min Y: 0.0385
Max Y: 0.0385

The FEMWATER *Curve Generator* dialog

In most cases, the simplest way to generate a set of pressure head curves for the unsaturated zone is to use the *Curve Generator*. The **Generate Unsat Curves** button brings up the *Curve Generator* dialog. This dialog is used to automatically generate a set of unsaturated zone curves using the van Genuchten equations described in the FEMWATER Reference Manual. The items in the top of the dialog are used to select the curve type ('linear front' or 'van Genuchten equation') and the max height of capillary rise above the water table. Two methods are available for entering the Van Genuchten parameters: (1) selecting the *Manual parameter input* option and enter the values directly, or (2) selecting the *Preset parameter values* option and choose from a list of pre-defined soil types.

Once the parameters are defined the **Compute Curves** button can be used to generate a set of curves. The curves are displayed in the bottom of the dialog. New values can be entered and the process can be repeated until a satisfactory result is obtained. When the **OK** button is selected, the active curves are assigned to the current material.

Each of the unsaturated zone curves is a piece-wise linear curve defined by a sequence of points. The number of points in each curve is either specified by the user or determined automatically by specifying a *Max percent change*. If the **max percent change** option is used, a new point is added to the curve each time the parameter changes by the Max percent value.

Note that the effective porosity for each material is defined from the pressure head vs. moisture content curve. The value at p = 0 is taken from the curve and is written to the model file as part of the MP2 card.

Note also that GMS assumes that the van Genuchten 'alpha' value is entered in units consistent with the current model units. GMS displays the current model units next to the input field to help the user remember this.