CHARACTERIZATION OF METALLIC POLLUTANTS IN PAHARANG DRAIN, FAISALABAD

By

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This is to certify that the

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All praises to Almighty Allah, Who bestowed the man with intelligence, knowledge, sight to observe and mind to think and judge. Peace and blessings of Allah be upon the Holy Prophet, Muhammad (PBUH), who exhorted his followers to seek for knowledge from cradle to grave.

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APPROVAL SHEET

Certified that the contents and form of thesis entitled “Characterization of Metallic Pollutants in Paharang Drain, Faisalabad” submitted by Mr. Ghulam Mustafa have been found satisfactory for the requirement of the degree.

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DEDICATION

Dedicated to my loving parents

DECLARATION

I hereby declare that I am the sole author of this thesis and the work represented here has not been published anywhere else before. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

Ghulam Mustafa
(MS-12)

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LIST OF ABBREVIATIONS

AAS	Atomic absorption spectroscopy
BAF	Bioaccumulation factor
BOD	Biochemical oxygen demand
COD	Chemical oxygen demand
Cusecs	Cubic feet per second
EF	Enrichment factor
EPA	Environmental protection agency
EPD	Environmental protection department
FAAS	Flame atomic absorption spectroscopy
HACA	Hierarchical agglomerative cluster analysis
ICP-OES	Inductively coupled plasma optical emission spectroscopy
Igeo	Geoaccumulation index
MGD	Million gallons per day
NEQS	National environmental quality standards
PCRWR	Pakistan council for research of water resources
PLI	Pollution load index
RCRA	Resource conservation and recovery act
TDS	Total dissolved solids
TOC	Total organic carbon
TP	Total Phosphorous
TSS	Total suspended solids
WASA	Water and Sanitation Agency
XRF	X-Ray Fluorescence

ABSTRACT

Metals in the untreated combined wastewater pose a serious threat to the soil and water environment in general and to human health in particular. Samples from Paharang Drain, Faisalabad, one of the major carriers of combined industrial, predominantly textile, and municipal effluents, were collected from six different locations between July 2008 and December 2008. The objective was to examine the state of metallic pollution and its variation with time and space. Metal concentrations in separate industrial and municipal streams falling into the Paharang Drain, were also studied independently for the baseline development. Metals selected for scrutiny were Cr, Ni, Cd, Mn, Zn, Cu, Fe, Pb, As and Hg. Standard Methods were adopted for sample collection, preservation and analysis. Benthic zone soil samples were also analyzed for the same metals by using the Flame Atomic Absorption Spectrometer (FAAS) and X-ray Fluorescence technique. Concentrations of most of the metals were found below Pakistan National Environmental Quality Standards (NEQS) in the Paharang Drain wastewater. Effects of seasonal variations on metal concentration in the drain water have also been elucidated. In addition, correlation between metals concentration and other physicochemical parameters such as pH, total suspended solids and total organic carbon etc. were examined. Good exponential correlation was found between metal concentrations and total suspended solids (TSS). Metal concentrations were found to be more sensitive to temporal variations than spatial ones. The pollution load indices, bioaccumulation factors, enrichment factors and geoaccumulation indices of selected metals were also assessed for benthic soil of the drain.

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Chapter 1

INTRODUCTION

1.1 BACKGROUND

Following the green revolution, most Asian economies emerged as “food self-sufficient” in the 1970s and 1980s. The large scale irrigation projects executed during this period increased the crop yield and helped in reducing poverty. Due to vastly practiced flood irrigation system, water consumption has also increased many folds in Asia.

Availability of water in the desired quality and quantity plays a key role for sustainable health, irrigation and environment. Both, qualitative and quantitative parameters require regular monitoring for efficient water management.

Punjab Irrigation System comprises of a network of freshwater canals and natural as well as man made drains. Most of these drains were originally constructed to counter the problems of water logging and to collect the surplus saline and flood water. In Punjab, the total length of such surface drains is 3883 km (Irrigation and Power Department, 2007). In the present scenario, due to increased population and industrialization, these drains mainly carry the industrial and municipal effluents that are ultimately carried to the rivers.

1.2 WASTEWATER DISPOSAL IN FAISALABAD

Faisalabad, with an estimated population of 2.66 million (within municipal limits) is Pakistan’s third largest city. The city is located in the center of the Punjab province, equidistant from the Ravi and Chenab rivers and is famous for its textile industry. Traditionally, textile wastewater contains substantial pollution loads in terms of COD, BOD, TSS, TDS and heavy metals.

In Pakistan there is a lack of wastewater treatment facilities due to poor legislative enforcement, shortage of financial resources and non-availability of technically trained manpower (CPP, 1999). Current practice is that effluent is being discharged into streams or canals after retention period of some hours in stabilization pond without any secondary or tertiary treatment (Aslam *et al*., 2004). Such untreated or partially treated wastewater has negative impacts on underground and surface water bodies and it also adversely affects the aquatic ecologically. Effluents from textile mills contain chromium, which has a cumulative effect, and higher possibilities for entering into the food chain. Due to usage of dyes and chemicals, effluents are thickly colored, which blocks the passage of sunlight into the water and thus obstruct natural disinfection. This also hampers the photosynthesis process, causing alteration in the botanical habitat (Pak-EPA, 2002-2003).

This situation combined with rapid population growth has placed an especially heavy strain on the city’s water environment.

The estimated sewage generation in Faisalabad is about 250-260 cusecs, of which 150-160 cusecs is municipal wastewater and the rest comes from industrial establishment (Ijaz, 2003).

The sewerage system laid down in early sixties is now badly damaged, blocked and undersized. Open drains passing through the city are used for solid waste and sewage disposal; thus causing sewer blockage problems, and environmental degradation. The existing sewerage system of Faisalabad is in extremely poor condition and needs extensive rehabilitation (Hashmi, 2007). The existing sewerage and drainage system is divided into two distinct zones (Eastern and Western) formed by the Rakh Branch Canal passing through the city as shown in the land use map in Figure 1-1 and drainage system in Figure 1-2.

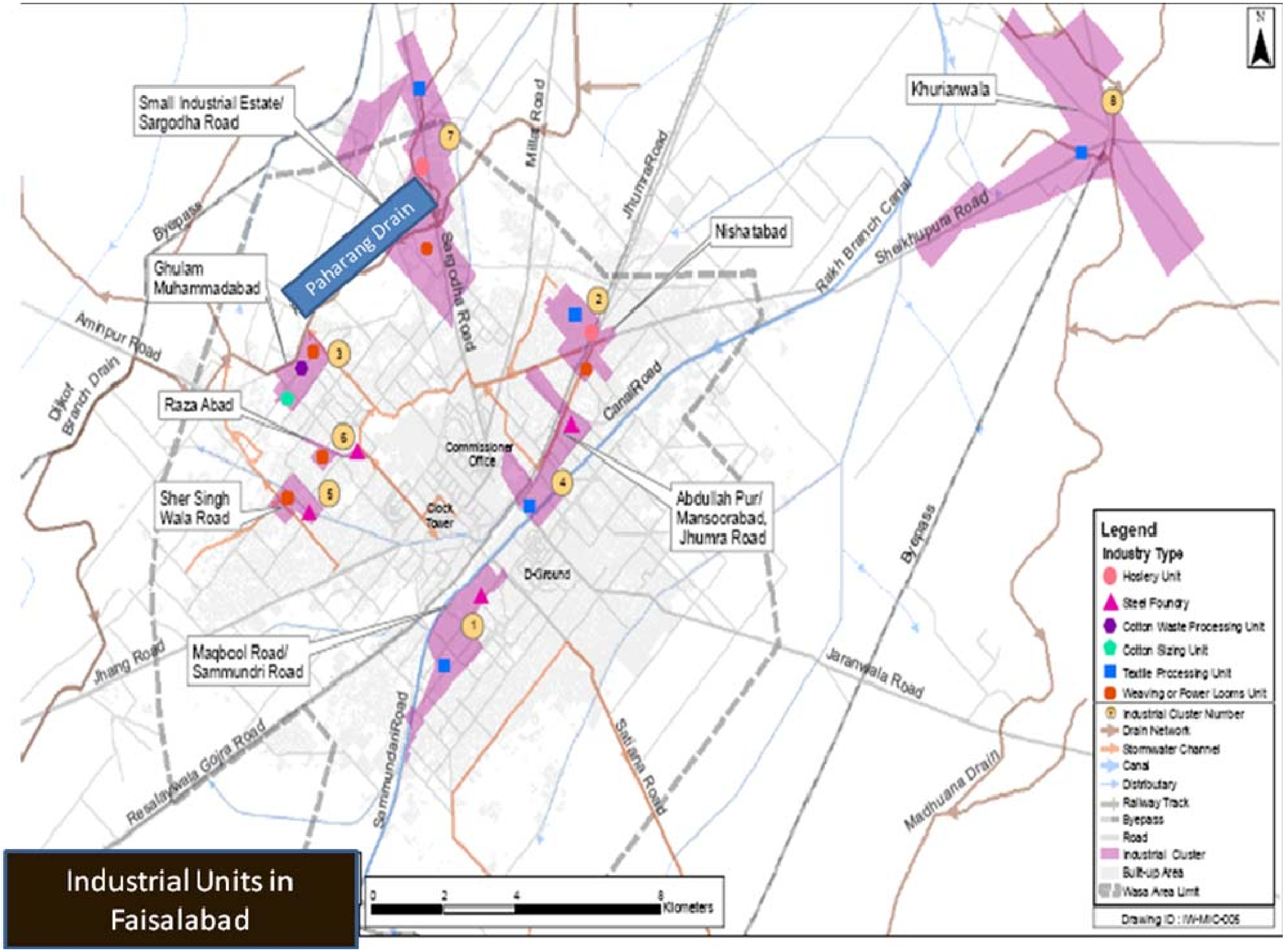


Figure 1-1: Land use map of Faisalabad (source: pre-feasibility study for urban transport and industrial waste management Faisalabad, 2010)

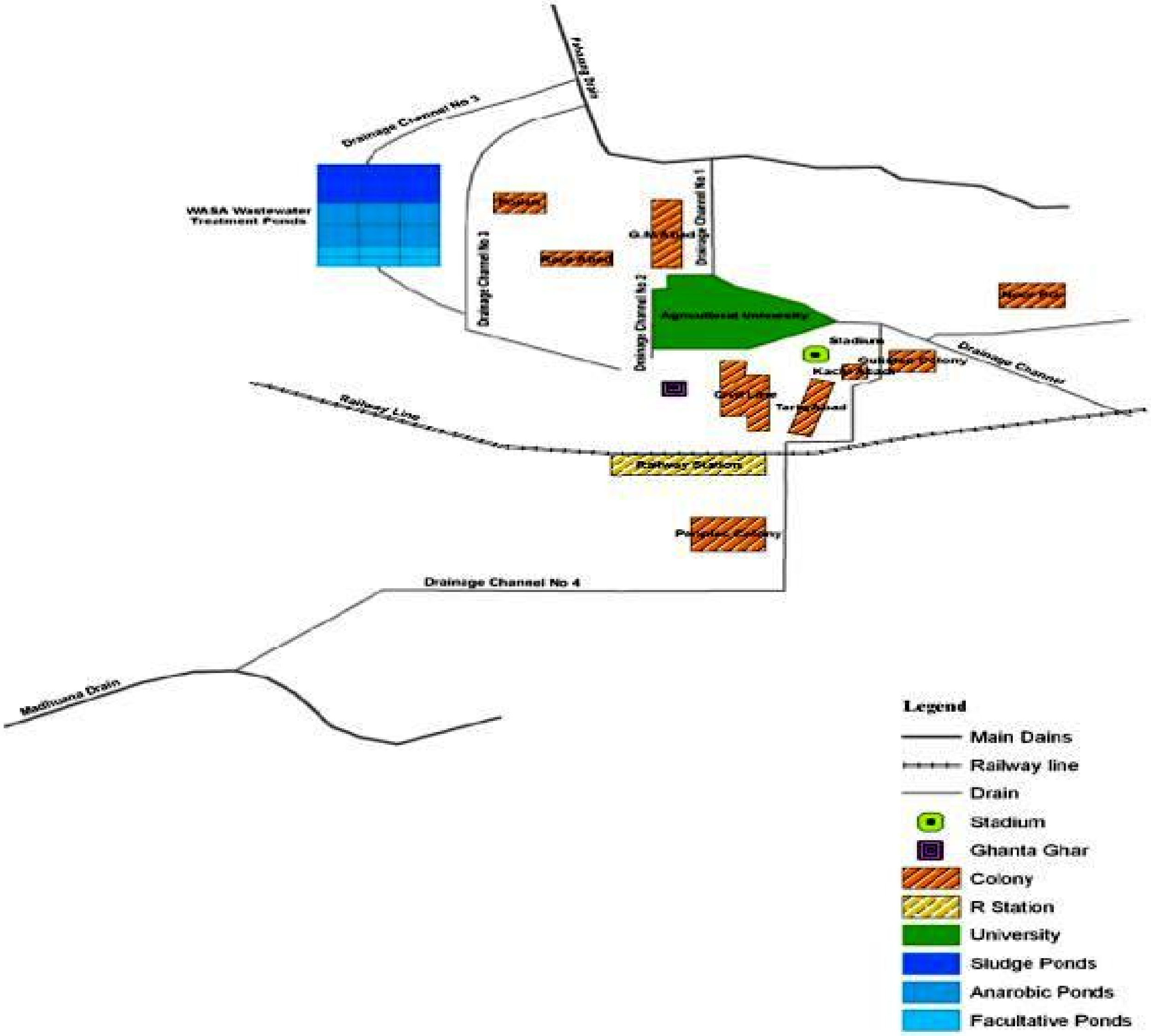


Figure 1-2: Drainage system of Faisalabad (Source: Kahlown *et al*., 2006)

The population of the Western Zone is twice that of the Eastern Zone. Presently, untreated wastewater from the Eastern Zone is collected and carried through an open storm water channel to the Madhuana Drain, which finally discharges into the River Ravi.

Around 5% of the wastewater from the Western Zone is treated through a system of stabilization ponds. The treated and the rest of the untreated wastewater are being discharged into the Paharang Drain, which ultimately flows to the River Chenab.

1.3 THE PROBLEM

As all metals are a part of earth's crust, they occur naturally. Water bodies receive these metals from natural and anthropogenic sources. Metals such as Chromium (Cr), Copper (Cu), Iron (Fe), Zinc (Zn), Cobalt (Co), and Manganese (Mn) are needed in trace quantities by living beings. Other metals such as Cadmium (Cd), Mercury (Hg), and Lead (Pb) are not needed and are harmful even in trace quantities. Some of these metals are found in aquatic systems in concentrations which are toxic to the organisms. This excessive discharge is usually associated with human activities.

While the proportion of anthropogenic or natural sources for these metals are different in different regions, a better strategy may exist in the identification of both sources and components, causing metals discharge in water resources. In addition to discharge from industrial sources, high concentrations of a few metals are also present in urban runoff (U.S. EPA, 2005). EPA's 1998 list of priority pollutants of 53 chemicals included metals such as Cd, Cr, Cu, Hg, Ni, Pb, and Zn. The contamination of crops, water resources and soil by these metals is a major concern because of their toxicity, persistence and non-degradable nature.

Metal salts are often used in textile finishing industry as oxidizing agents, metal complex dyes, dye stripping agents, fastness promoters, and finishers (Zeiner *et al*., 2007). Such waters, when in contact with human body may lead to a variety of diseases as toxic effects of some metals on human health are well documented (Duruibe *et al*., 2007). Studies have shown that some metals interfere with essential dietary metals like Zn, Ca, Fe, Cu, Se, Cr, and Mn. Most commonly reported impacts of metals on human health include, damages to body organs, disorder in the respiratory tract, dysfunction of the heart and blood producing organs, disorder in the nervous system, lung diseases, skin diseases, abnormalities in fertility and pregnancy etc (Chowdhury and Chandra, 1987). According to Ohe *et al*. (2004) high concentrations of metals in textile wastewater have adverse impact on the soil and water environment in general, and, on the aquatic biota in particular. Bioaccumulation of metals in body tissues and their binding to enzymes disrupts the functioning of cells, which also leads to tumors or cancers (Marquadt *et al.,* 1999). Noticeable concentrations of such pollutants may adversely affect the biological treatment of wastewater (Spellman, 2003).

According to Environmental Protection Department (EPD), Punjab, approximately 9000 industries are operating in Faisalabad city including those in residential localities, majority of which are related to textile.

These industrial units discharge untreated effluent containing high levels of soluble salts, metals, aromatic dyes, inorganic salts, and organic materials (Nosheen *et al*., 2000) directly into municipal sewers and open surface drains (Madhuana and Paharang Drain), ultimately draining into the rivers.

Of the existing water supply system in Faisalabad, that approximates to 62 million gallons, 56 million gallons are obtained from tube-wells installed near the Chenab River which is receiving untreated sewage and industrial wastewater from six districts of Punjab including Gujrat, Mandi Bahauddin, Jhang, Multan, Hafizabad, and Sargodha (Raza, 2009). Paharng Drain also discharges into this river and this study will help in determining the level of pollution being contributed to the river by this drain.

The negative impact on ground water quality is evident from the fact that groundwater quality has shown improvement as the distance from the drains/sewers increases. These effluents are also damaging the aquatic life and ecosystem of the river. Roughly 62,000 hectares around Faisalabad is irrigated with raw effluent for growing crops particularly vegetables (Ahmad *et al*., 2004).

Among metals generally zinc, copper and manganese concentration in soils have been found above the safe limits set for growing food and fodder crops. The salinity, sodicity and toxic metals values in soil profile were higher in the surface soil than sub-surface soil (Kahlown *et al*., 2006). It has been found that a number of inhabitants living in villages around Paharang Drain are affected by different diseases related to stomach and digestive system (Diarrhea, Dysentery and Diarrhea with fever) which are the direct effect of the use of polluted water for drinking as well as the direct exposure to the wastewater (Mahmood and Maqbool, 2006).

The above findings show that Paharang Drain wastewater is contaminating the groundwater, surface water, crops, vegetables, soil, River Chenab and causing different diseases in human population of the area. This study will focus on the characterization of the drain water and its benthic soil with respect to metallic pollutants.

1.4 OBJECTIVES OF THE STUDY

Interestingly all of the studies related to the contamination of drains and ground waters in their vicinity have focused on only 3 to 4 metals without discussing the temporal and spatial variations of these metals. This research aimed at;

- Study of spatio-temporal variations of metals in the Paharang Drain wastewater
- Estimation of metallic pollution level in the benthic soil
- Correlation of the metallic pollutants with physicochemical parameters

1.5 APPROACH

Wastewater and soil samples were analyzed using Flame Atomic Absorption Spectrometry (FAAS), and Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). Soil samples were analyzed qualitatively using X-ray Fluorescence (XRF) while quantitative analyses were carried out using FAAS.

1.6 SIGNIFICANCE OF THE STUDY

- The study will provide a complete chemical profile of the drain along with seasonal variations
- It will give a clear picture to devise a treatment terrain.
- Metals are often used as oxidizing agents, as metal complex dyes, dye stripping agents, fastness improvers, and finishers. Thus, they act as hazardous sources throughout entire textile processing. Toxic effects of some metals on humans are well documented. Therefore, it is important to monitor such metals.
- It has been proved that accumulation of certain metals in body tissues and their binding to enzymes disrupts the functioning of cells, which also leads to tumors or cancers. For this reason, it is important to monitor such metals in/on textile materials.

1.7 MISCONCEPTION OF THE TERM "HEAVY METALS"

The term "heavy metals" has been used increasingly in various publications and in legislation related to chemical hazards and the safe use of chemicals. As many as forty different definitions of the term have been found in the scientific literature (Duffus, 2002). The term is often used as a group name for metals and semimetals (metalloids) that have been associated with contamination and potential toxicity or ecotoxicity. At the same time, legal regulations often specify a list of "heavy metals" to which they apply. Such lists may differ from one set of regulations to the other, or the term may be used without specifying which "heavy metals" are covered. In other words, the term "heavy metals" has been used inconsistently. This has led to general confusion regarding the significance of the term. There is also a tendency to assume that all so-called "heavy metals" have highly toxic or ecotoxic properties. This inconsistent use of the term "heavy metals" reflects inconsistency in the scientific literature.

Therefore, this term will not be used and a more scientific and technical approach for the classification for the selected metals is being adopted in this study. The classification for selected metals is as below;

Hard Metals: Fe

Soft Metals: Cu (I), Ag, Cd, Hg, Pb (II)

Borderline Metals: Cr, Mn, Fe (II), Co, Ni, Cu (II), Zn, Pb (IV)

Chapter 2

REVIEW OF LITERATURE

Globally, land, air and aquatic systems have been contaminated with heavy metals through various anthropogenic discharges. Intake of toxic metals as a result of moving up the food chain, have become a major human health hazard. Increased awareness of the harmful effects of environmental pollution caused by heavy metals is because of the vast research that has been carried out in this field.

This chapter reviews the approach and findings of the research that has been carried out in the recent past, particularly relevant to the objectives of this study.

2.1 DETERMINATION OF METALLIC POLLUTANTS IN DRAINS

Various national and international studies have been conducted to find out how metallic pollution is determined in drains.

The concentration of Fe, Cu, Cr, Zn, Cd and Pb in effluent from Makera Drain in Kaduna, Nigeria was determined seasonally by the use of Atomic Absorption Spectrophotometer (Ali *et al*., 2005). The monthly levels of the metal concentrations and the mean metal concentration at four sampling stations showed that Fe>Cr>Cu>Pb>Zn>Cd. The concentrations of some of these metals were higher than those recommended by World Health Organization (WHO) for drinking water. There was significant variation between stations, months and seasons, except for Zn, which had significant variation between months and insignificant variation between seasons. This study highlights the implications of the high concentration of these metals on the biota and consequently on human being who is at the end of the food chain.

Dakan *et al*. (2008) while working on Jakara wastewater channel near the Airport Road Bridge, Kano metropolis collected wastewater and vegetable samples. Samples were also collected to determine the most common physicochemical parameters. In addition, metals like Cu, Co, Cr, Fe, Mn, Mg, Ni, Cd, Pb, Na, K and Ca were also determined. Levels of physicochemical parameters were higher than the maximum permissible limits set by Federal Environmental Protection Agencies (FEPA) Nigeria. The concentrations of the metals in the wastewater and vegetables samples were higher than limits set by WHO and the maximum contaminant levels.

Sarfaraz *et al*. (2007) conducted a similar study on Nullah Dek and wastewater was analyzed for electrical conductivity (EC), residual sodium carbonate (RSC), sodium adsorption ratio (SAR), pH and metals in irrigation water from the nullah. The results showed that the concentration of all the metals analyzed especially Cu, Mn, Cd and Sr was within the safe limits or NEQS.

Qadir *et al*. (2008) studied the spatio-temporal changes in water quality of Nullah Aik, a tributary of the Chenab River, Pakistan. Samples collected at seven sampling sites of the nullah were analyzed for twenty four (24) parameters including metals. Most significant parameters which contributed in spatiotemporal variations were assessed by statistical techniques such as Hierarchical Agglomerative Cluster Analysis (HACA), Factor Analysis/Principal Components Analysis (FA/PCA), and Discriminant Function Analysis (DFA). The study identified distinct spatial and temporal variations of water quality measurements and also highlighted the spatial heterogeneity in terms of surface water pollution related to anthropogenic factors.

Badar *et al*. (2006) conducted analysis to determine the seasonal variation of pH, dissolved oxygen, trace metals (Fe, Zn, Cd, and Pb) and major cations in surface and bottom water of El Rahaway drain at the point of its discharge with the Nile water and also before and after the discharge point. These results were compared with five selected locations along the River Nile at the bifurcation. Fe, Pb, and Cd concentration exceeded the upper limit of standard at most sites along the River Nile especially in summer.

2.2 ESTIMATION OF METALLIC POLLUTANTS IN INDUSTRIAL WASTEWATERS

Zeiner *et al*. (2007) tested several analytical procedures for the determination of metals. The advantages and disadvantages of various analytical techniques such as TLC, UV-VIS, GF-AAS, ICP-OES, and ICP-MS methods were discussed. The study showed that the best results for sample analysis are usually achievable by combining different methods. For instance, simple and rapid thin layer chromatography can be applied as a fast screening method prior to ICP-OES or GFAAS measurements. In the first step, the metals should be determined qualitatively and their concentration ranges should be estimated. Thereupon, the method for an exact quantification may be chosen depending on the analytical task.

Frank and Harangozo (1994) determined metals in industrial wastewaters and studied their influence on activated sludge biocenose. Radionuclide X-ray fluorescence method with a Si/Li semiconductor detector and ^{238}pu exciting source was used for the determination of Cr, Fe, Ni, Cu, and Zn content in industrial wastewaters.

V and CP (2006) determined the concentration of metals, like As, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn in industrial wastewaters. As, Cd, Cr and Pb were not found in any sample, while some of the metals ranged as: Cu (0.0 - 1.0 mg/L), Fe (0.1 - 0.4 mg/L), Mn (0.0 - 0.4 mg/L), Ni (0.01 - 0.07 mg/L) and Zn (0.68 - 60.84 mg/L). Cu, Fe, Mn and Zn were found above the standard limits recommended by IS: 3307 (1977). However, Nickel was found below the regulated safety values in all the samples.

Yusuff and Sonibare (2004) characterized effluents from five major textile industries of Kaduna (Nigeria). Al, Mn, and Zn were detected and found within WHO limit in 80% of the samples, while Fe was detected in 60 % of the samples. Cu was detected in 80 % of the samples with limit exceeding about 3 folds on the average.

The concentration levels of twelve selected metals were studied in textile effluents, adjoining soil and groundwater samples in Nattai Industrial Estate, NWFP, Pakistan by Manzoor *et al*. (2006). Metals were analyzed by using FAAS System with automatic background compensation. The results showed elevated levels of Cr, Pb, Ni, Co, Fe, Ca, Na, K and Zn in the selected soil and water media, following the order: soil > effluent > groundwater. Comparison with background and international data revealed that textile effluents were contaminating the soil and groundwater; Cr and Pb were dominant toxic metals in soil samples, while Co, Cd, Zn, Ni, Mn and Fe were found to be higher than background levels in ground water. Descriptive statistics, along with correlation coefficient and linear regression supported the fact that elevated concentrations of the metals in textile industrial effluents lead to the contamination of the soil and groundwater in its proximity.

Laser Induced Breakdown Spectroscopy (LIBS) System was used (Hussain and Gondal, 2008) for determination of toxic metals in liquid samples and the system was tested for analysis of wastewater collected from dairy products processing plant. The plasma was generated by focusing a pulsed Nd:YAG laser at 1064 nm on wastewater samples. Optimal experimental conditions were evaluated for improving the sensitivity. The Laser-Induced Breakdown Spectroscopy (LIBS) results were then compared with the results obtained using standard analytical technique such as Inductively Coupled Plasma Emission Spectroscopy and it was found that the result obtained by both techniques were similar.

Miranzadeh (2005) obtained composite samples from Kashan Textile Sewage (KTS) for metallic and physicochemical analysis. The average concentration of BOD_5, COD and TSS was 109, 583, 169 and 108 mgL^{-1} respectively. The average concentration of metals was less than Iranian reuse standards, except for cobalt.

Wastewater mixed with industrial effluent used for irrigation in the vegetable growing area of Korangi was tested for its metal contents by Saif *et al*. (2005). As many as 24 samples from different drains were collected and analyzed.

Concentration of various metals was found in the rages given below;

Table 2-1: Concentration ranges of the metal and percent exceeding

Metal	Concentration Range (mg/L)	NEQS (mg/L)	Percent Exceeding
Zn	0.005-5.5	5.0	4
Cu	0.005-1.19	1.0	4
Fe	0.04-5.58	8	4
Mn	0.01-1.79	1.5	7
Cd	0.004-2.4	0.1	21
Cr	0.004-5.62	1.0	4
Ni	0.02-5.35	1.0	14
Pb	0.05 to 2.25	0.5	36

A study was conducted in Hayatabad Industrial Estate, Pakistan by Khan *et al*. (2002) to investigate the individual industrial effluent load. Physicochemical parameters along with metal concentrations were studied. Samples were collected from end-up-pipe of each industrial process. Pb, Cr and Ni were found above NEQS in effluents of all types of industries in the industrial estate.

Sial *et al*. (2006) collected industrial, sewage and tap water samples for the analysis of various physicochemical parameters and metals. The effluents of ghee and textile industries were highly alkaline. EC and TSS loads of ghee and textile industries were also above the National Environmental Quality Standards (NEQS), Pakistan. Total toxic metals load in all the effluents was also above the limit i.e. 2.0 mg/L. Copper in effluents of textile and sewage, manganese in ghee industry effluents and iron contents in all the effluents were higher than NEQS. BOD and COD values of all the industries were also above the NEQS.

Hanif *et al*. (2005) investigated effluents from seven industries including ghee, Ni-Cr plating, battery, tannery and textile in city zone of Faisalabad, Pakistan. Quantitative analyses were performed on nickel, zinc, copper, iron and other physicochemical parameters. Results revealed that effluents from all of the above industries were causing severe toxic and metal pollution. Analysis of physicochemical parameters showed that all industries were causing some type of physicochemical pollution except textile industry where almost all physicochemical parameters were above permissible limits.

2.3 DETERMINATION OF METALLIC POLLUTANTS IN DOMESTIC EFFLUENTS

Rojas and Ojeda (2005) comprehensively summarized effluent analysis of most of the parameters based on various methods and techniques described in the literature since 1975. They classified pollutants in municipal wastewater into four main categories: (1) physical and chemical properties (2) inorganic metals analysis (3) inorganic non-metallic analysis (4) organic analysis.

Zhefeng and Xiaotao (2002) developed a method for the determination of Cu, Zn, Fe, Ni and Pb by inductively coupled plasma emission spectrometer after pre-concentration on a column containing saccharomycete immobilized on silica gel. Optimum pH value, amount of adsorbent, elution solution and flow rate was obtained for the elements. This method was successfully applied to the determination of trace metals with relative error lower than 5%.

Abulude *et al*. (2007) determined the concentrations of physicochemical parameters and trace metals in water samples from Akure, Nigeria using atomic absorption spectrophotometery. Results indicated low variations between physicochemical parameters such as; pH, temperature, conductivity, dissolved oxygen and nitrate. In water samples, oil and grease, taste and odor were not detected .The mean levels of the metals in mg/L were; 4.8(Fe), 0.3 (Cr), 0.1(Cd), 0.2(Pb), 0.2(As), 0.1(Ni). However, Co and Zn were not detected.

Huang and Wang (2001) studied the distribution of metals, namely, Ag, Cd, Co, Cr, Cu, Hg, Ni, Pb, and Zn in 4 municipal wastewater treatment plants as a function of several parameters including pH, COD, ionic strength and SS. There were variations in pH, alkalinity, COD and ionic strength and wastewater samples containing less than 5 g/L suspended solids were of similar characteristics. Correlations between metal distributions (as the ratio between dissolved to total metals) and wastewater characteristics were attempted. Correlation between the parameters monitored and metal distribution is poor. Metal distribution relies almost entirely on the concentration of solids in wastewater samples.

Shomar *et al*. (2004) investigated wastewater and sludge chemical characteristics in a 3-year monitoring program. Twelve elements (Ag, Al, As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn) were analyzed in 120 composite samples of influent and effluent wastewater.

The results revealed that domestic wastewater influent contains considerable amounts of metals.

2.4 DETERMINATION OF METALLIC POLLUTANTS IN SURFACE WATERS

Metals in the water, plants and sludge were determined by Moodley *et al*. (2007) using an inductively coupled plasma-mass spectrometer (ICP-MS). The concentrations of metals in the water were found to be well within the limits set by the South African National Water Act of 1998 for discharge of water into rivers. Furthermore, the results of this study were compared with those from model studies.

Sahin *et al*. (2008) developed a co-precipitation method for the determination of Cr, Mn, Fe, Co, Cu, Cd and Pb ions in aqueous samples by flame atomic absorption spectrometry (FAAS). The obtained co-precipitates were dissolved with nitric acid and measured by FAAS. The results showed that the proposed separation/preconcentration procedure for the determination and enrichment of Mn, Co, Cu, Cd and Pb ions from seawater samples and of Cr, Mn, Co, Cu, Cd and Pb ions from dialysis solutions yielded satisfactory results. The proposed method for the determination of Fe in aqueous solutions is only valid when the sample volume is less than 50 ml. Enrichment factors of 50 to 75 could be achieved for the elements studied, except for iron, by choosing proper sample and final measurement of volumes. The proposed method has good recovery and detection limit values, i.e., 96 – 101% and $\leq$2.44 μg/L, respectively.

A method for the determination of Cu, Pb, Ni, Cd, Mn and Fe was developed by Tokahoglu *et al*. (2002) using flame atomic absorption spectrometry (FAAS) after pre-concentration on Amberlite XAD-16 resin, using hexamethyleneammoniumhexamethylenedithiocarbamate (HMA-HMDTC) as a chelating agent, and NH_3/NH_4Cl buffer solution (pH 9). Influence of various analytical parameters such as pH, concentration of nitric acid, amount of analytes, diverse ions and sample volume were investigated. The method provided an effective preconcentration and separation procedure for the determination of Cu, Pb, Mn, Cd, Ni, and Fe metals in seawater and wastewater samples. For the analytes of interest, the preconcentration factor was 150 and 75 for the seawater and the wastewater samples, respectively.

Daifullah *et al*. (2003) determined iron, manganese, zinc, copper, lead and cadmium in water samples collected from surface and bottom layers of River Nile using atomic absorption spectrophotometery (AAS). Seasonal variations of iron were found to be within the range of 0.46- 4.18, 0.37 - 2.84 mg/l. The values of manganese concentration were found to be in the range of 54.2 - 194.8, 187- 387 µg/l. Also, copper concentration was varied in the range of 5.0 - 63, 6.0 - 74 µg/l. Zinc concentrations were varied between16.0 - 396.9, 14.0 - 148 µg/l. However, the lead concentration fluctuates in the range of 27.8 - 148.9, 60.0 - 153.6 µg/l. As well as, the concentrations of cadmium were found to be in the range of 5.5 - 12, 12.5- 46 µg/l for the different stations and drains respectively during different seasons. In general, the concentration of these metals was higher than the permissible levels due to the discharges of two industrial companies in this area.

Eletta (2007) determined Fe, Mn, Pb, Zn, Cr and Cu concentrations in Asa River (Nigeria) using Atomic Absorption Spectrophotometery (AAS) and X – ray fluorescence (XRF). Statistical analysis showed that there was no significant difference in the concentrations of Cr, Zn, Pb and Cu using the two techniques but significant differences were observed at 5% probability level for Mn and Fe.

The concentration of metals in the wastewater samples taken from 9 different stations of Biga-Kocabas Stream (Turkey) were determined by Yayıntas *et al.* (2007) after simple pretreatment of samples by the proposed ICP-AES method. Analysis of a given sample was completed in about 15 min using ICP-AES method. The results of metal concentrations in waste water were found between 0.00001–77.69610 mg/l by the ICP-AES technique.

Sial *et al.* (2005) conducted a study to compare the effects of irrigation water with 100% canal water, 50% wastewater (conjunctive) and 100% wastewater on groundwater quality. It was concluded that direct use of wastewater not only produced salinity problem but, also affected the groundwater quality by increasing its sodicity. The plots irrigated with 100% wastewater were deteriorated in terms of measured parameters when compared with 100% canal water. Among metals determined, Fe was in the maximum concentration and it was 56% of the total metal content while Cr was the minimum. Concentration of the metals Mn, Ni, Cr, Pb, Fe and Zn were within permissible limits.

Nazif *et al.* (2006) analyzed metal contents of irrigation water in Akbarpura area of District Nowshera NWFP, Pakistan. Water samples were collected from two irrigation sources (canal and Bara River) with three replications each from Akbarpura, Kurvi and Banda Sheikh Ismail villages. Water samples were collected in clean bottles at 10cm depth. The samples collected were analyzed for copper, lead, zinc, iron, manganese, cadmium, nickel and chromium by Atomic Absorption Spectrophotometer. Metal contents were found much lesser in irrigation canal water as compared to Bara River water. Copper, lead, iron, cadmium, nickel and chromium were found in normal concentrations in both irrigation canal and Bara River, while zinc and manganese were found in deficient concentrations.

Roberto *et al*. (2008) determined the seasonal and downstream water quality variations of the San Pedro River in Chihuahua, Mexico. Water samples were collected monthly in triplicate. The five sampling locations were established. The levels of As, Be, Ca, Cd, Co, Cu, Cr, Fe, Li, Mg, Mn, Mo, Ni, Pb, Sb, Se, Sr, Ti, Ta, V and Zn were measured using an Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) Perkin Elmer 2100. In addition, temperature, pH, electrical conductivity and total and fecal coliformes were determined. The statistical analysis considered a factorial treatment design; where factor A was the location point and factor B was sampling date. In addition, a multivariate technique looking for principal components was performed. The results indicated that some samples exceeded Mexican standards for As, Be, Ca, Cd, Co, Cr, Fe, Mn, Ni, Pb, Sb, Se, Sr and Zn.

Akoto *et al*. (2008) analyzed water samples from five sampling points on four rivers of Ghana for metal (Zn, Cu, Mn, Cu, Pb and As) concentrations and some physical parameters. Of the metals determined in the water samples, Fe, Mn, Zn and Cu concentrations in all the streams were within the acceptable WHO limits, whiles Pb and As appeared to be higher than the acceptable limits in all the streams. The highest concentrations of most of the metals were recorded at the Kronum site on Owabi stream

(Ghana). There was a statistically significant positive correlation between pH and some metals at all sampling points.

Dheri *et al*. (2007) studied metal concentration in surface water, soil, and crops grown in fields near the industrial city of Ludhiana, Punjab, India, which receive irrigation water contaminated with sewer and untreated industrial effluents. The concentrations of Pb, Cr, Cd, and Ni in sewage contaminated water were 18, 80, 88, and 210 times higher than in shallow hand pump water, and 21, 133, 700, and 2200 times higher than in deep tube-well water, respectively.

Pulikowski *et al*. (2007) studied the daily drainage runoff measurements and carried out periodical chemical analyses of water samples from selected drainage plots. Concentrations of metals: Cu, Zn, Pb, Cr and Cd were also measured. They found that drainage waters do not contain significant amounts of metals. Concentration of Zn, which is very common in nature, ranged from 0.018 to 0.675 mg/l while Cd concentration was somewhat larger than 0.001 mg/l.

Gowd and Govil (2008) carried out a study to find out the contamination of surface water bodies due to industrial effluents. The results revealed that the surface water in the area was highly contaminated showing very high concentrations of some of the metals.

Papafilippaki *et al*. (2008) investigated the seasonal variations of five metals (Cu, Zn, Cd, Pb and Cr) in the surface water of the Keritis River, one of the most important rivers in Chania, Greece. The surface water samples were collected at 8 sampling sites in the Keritis river system. Metals were determined by using flame and furnace Atomic Absorption Spectrometry. Ancillary data included water temperature, pH and electric conductivity. Significant variations were observed between the warm period (May to September) and the wet period (October to April), for the studied metals. The relative variability followed the order: Zn>Pb>Cu>Cd>Cr.

Variations of Cd, Fe, Co, Pb, Zn, Co, Cr, Al, Mn and Ni in the suspended particulate material were monthly examined by Türkmen and Türkmen (2004) at five stations in Iskenderun Bay (Turkey). The variations in concentrations of the metals were found significantly different. The bay receives industrial and agricultural metallic pollution from the surrounding facilities and domestic effluents from the cities. The levels of Cd, Pb, Cu, Zn and Co were high in winter; Fe, Cr, Mn and Al were high in August and September.

2.5 ESTIMATION OF METALLIC POLLUTANTS IN SOILS

Assadian *et al*. (2003) examined metal concentrations in sediments from open canal systems charged with flow from the Rio Grande and from effluents discharged from border communities. At the surface of canal beds, sediments were collected from six canal segments. Sediments were analyzed for Cd, Co, Cr, Cu, Ni, Pb, and Zn. These metals rarely exceeded 20 mg/kg. Drainage and effluent conveyance increased the variability of metal concentrations in sediments. However, most metal concentrations were within conventional global ranges and were not at levels high enough to threaten food safety.

Stroffekova *et al*. (2006) analyzed solid and liquid samples for the determination of metals by radionuclide x-ray fluorescence. Liquid samples were treated by passing through porous membrane of chelating disks of 3M Empore. X-Ray fluorescence gave best results for elements with atomic weight less than eighteen (18). LIBS technique was applied to the determination of total contents of heavy metals in a number of reference soil samples. In order to validate the technique, LIBS data were compared with data obtained on the same soil samples by application of conventional Inductively Coupled Plasma spectroscopy. The partial agreement obtained between the two sets of data suggested the potential applicability of the LIBS technique to the measurement of heavy metals in soils.

Chapter 3

METHODOLOGY

3.1 STUDY AREA

Paharang Drain was originally excavated in the 1970s to collect excess water from the water logged areas, however, with the passage of time it has become the largest carrier of untreated industrial and municipal wastewaters in Faisalabad. The head of the Paharang Drain is at *Chak No. 27*, middle at *Chak No. 7* and tail at *Chak No. 159* (Irrigation and Power Department, 2007).

Most of the industrial wastewater and municipal sewage originating from the western part of the city discharges into the Paharang Drain which ultimately falls into River Chenab.

While the total length of the Paharang Drain is around 84 Km, only first 33 Km receive wastewater discharges from residential and industrial areas located on both sides of the drain. The rest of the drain meanders through remote agricultural lands before its final discharge into the River Chenab. Six sampling stations (S1-S6) were established along the active stretch of the drain. These stations were selected on the basis of number, type, and size of outfalls into the drain. This is why these stations are not evenly spaced from each other. Triplicate wastewater samples were collected from each sampling station of drain from July to December 2008.

A small residential cluster and a major textile finishing facility “Supreme Fabrics” are located before the sampling *Station#1* (S1). Major component of drain flow at sampling S1 is industrial.

Sampling *Station#2* (S2) is located on “Same Nullah” (the only tributary of Paharang Drain) about 30 meters prior to its outfall into the main Paharang Drain. The Same Nullah contributes textile effluent from “Rasheed Textile”, “Sadique Textile” and many other large textile industries into the Paharang Drain.

Sampling *Station#3* (S3) is located on Paharang Drain about 1 Km downstream of S2 near a village called “Bawa Chak”. A major sewage pumping station discharges its flow into Paharang Drain about 100 m downstream of S3.

Sampling *Station#4* (S4) is about 1 Km downstream of “Bawa Chak Sewage Pumping Station”. Various industrial and municipal drains fall into Paharang Drain before this point.

Sampling *Station#5* (S5) is located before the outfall of the 20 MGD Wastewater Stabilization Ponds system installed by Water and Sanitation Agency (WASA), Faisalabad and about 10 Km downstream of S4. No industrial outfall exists after this station.

Sampling *Station#6* (S6) is about 1 Km downstream of S5 and 500 meters downstream of the outfall of the “WASA Wastewater Stabilization Ponds”. Figure 3-1 shows the location of all sampling stations along with GPS coordinates.

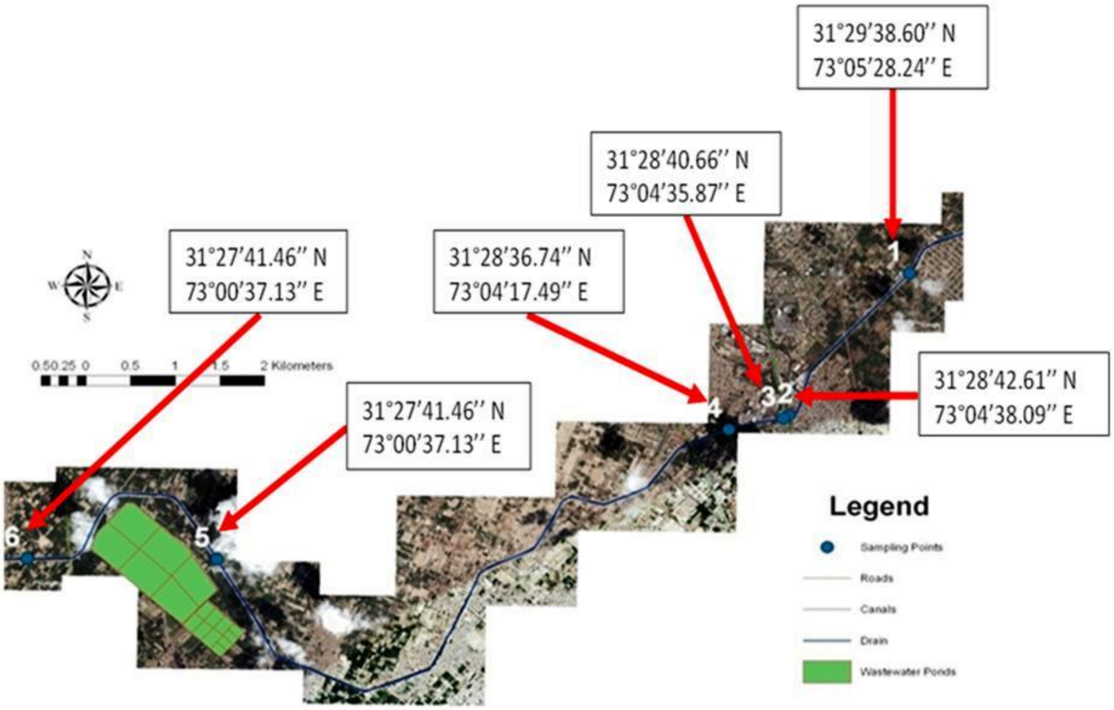


Figure 3-1: Location of six sampling stations on Paharang Drain, Faisalabad

Wastewater in the Paharang Drain is laden with organics, metals and nutrients and exerts high BOD, COD on the receiving water of River Chenab. At the same time, it introduces nutrients into the river leading to occasional algal blooms, which is evident from reduced fish population in the river. Wastewater from Paharang Drain is also diverted for irrigation of fodder crops on both sides of the drain. Toxic impacts of a few metals and other pollutants can possibly be found in those crops. This is however not within the scope of this study. Substantial concentrations of toxic elements discharged by textile industry have been found in the groundwater of the surrounding areas (Kahlon *et al*., 2006). This explains the gravity and extent of the pollution caused by Paharang Drain.

There are different types of industries located on both sides of the drain which are discharging their effluents into the drain as given in Table 3-1. The flows of these outfalls are also tabulated here.

Table 3-1: Major influents of Paharang drain (Kahlon, *et al*., 2006)

Influents	**Chemicals used**	**Discharge (m^3/hr)**
Bashir dyeing and printing factory chak no.7	Synthetic dyestuff, Cr, Cu	150
Ali Hajveri chemical factory, chak no.7	Pb, NH_3, Phosphate, Resin, Toluene, Xylene, etc.	50
Jaguar, Kay and Emms	NaOH, Hydrosulphites, Thiosulphates	150
Mumtaz Mahal dyeing unit, chak no.7	Cr, Cu, Pb, Sn, Cd	100
Sewage effluent of WASA	Detergents etc.	500
Bread factory Chak no.7	$NaHCO_3$	50
Chiniot drainage channel	Organic substances, Detergents etc.	1000
Channel no.1 Kurri road	Miscellaneous	300
Channel no.3 Chokera road	Domestic garbage etc.	800
City sewage chokera	Detergent, Organic matter	300

3.1.1 Foot Survey

The foot survey conducted by the survey team showed the agricultural area on both sides about 9 km from Chak Jhumra Road to Dry Port Road (Dhonala). Most of the outfalls were found to be dry in this area. After 9 km there was textile industrial area on right side of the drain and agricultural area on the left side up to 4 km. The *Station#*1 was selected at a point that was 13 km from Chak Jhumra Road (Starting point). The main textile industries in this area i.e. between Chak Jhumra Road and *Station#*1 were K and Ms, A.Z Apparel, F and T, New Grace, Chaudry, Jaguar, Kylash, Supreme Fabrics and Kylash Dye House. There were 79 outfalls into main Paharang Drain and 7 bridges from starting point (Chak Jhumra Road) to *Station#*1. The reason for selection of this point as *Station#*1 was to monitor the pollution load due to textile industries. After sampling *Station#*1, for about 2 km, there was agricultural area on both sides of drain. Then after 2 km from *Station#*1 the residential area starts left side of the drain about 1 km and textile industrial area on the right of the drain. Sampling *Station#*2 was selected in this area and near the Bawa Chak Bridge on Same Drain before merging into polluted Paharang Drain. The total distance between *Station#*1 & 2 was 3 km, total outfalls were 29 and total number of bridges 5. Most of the outfalls contain domestic wastewater but the Same Drain was highly polluted due to combined textile industrial and municipal effluents. Major industries discharging into Same Drain included Arif, Akram Zia, Yasir Afzal, Sitara and Rasheed Textile Mills. During each survey different color of effluents were observed from the outfalls of textile industries. The Sampling *Station#*3 was just 100 meter after mixing of Same Drain into main Paharang Drain. The total number of outfalls between *Station#*2 & 3 were 6 and only one bridge. Sampling *Station#*4 was about 1 km from *Station#*3 and there was a major, raw sewage outfall from Bawa Chak Pumping station into the Paharang Drain which was totally domestic wastewater that modified the drain water characteristics. Also there was small sewage outfall from right side of the drain due to residential area and textile industries effluents outfall from Mumtaz and Bashir Textile Mills. The total number of outfalls between *Station#*3 & 4 were 9 and there was no bridge. Then from *Station#*4 about 3 km there was agricultural area on both sides of the Paharang Drain. After that the residential area of Dar-ul Ehsan, Jinnah Colony, and Ghulam Muhammad Abad starts which is about 3 km in length. There were many small and large sewage outfalls in the main Paharang Drain in this stretch. There was only one Azam Dyeing Industry in this stretch. After this area there was WASA Pumping Station in Chakera village. The wastewater before Chakera pumping station was treated with oxidation ponds. The sampling *Station#*5 was selected prior to the treated sewage outfall at this point. The total distance between *Station#*4 & 5 was about 8 km and within this distance most of the outfalls into main Paharang Drain were found to be of wastewater from residential area. The total number of outfalls between *Station#*4 & 5 were 110 and total bridges were 8. Out of 110 outfalls, 12 were dry. The reason for selection of *Station#*5 was to monitor the quality of combined industrial effluents before the discharge of treated effluent into Paharang Drain. The sampling *Station#*6 was selected about 4 km downstream the *Station#*5 near Ghala Pind and agricultural field was found within this stretch of 4 km on both sides of Paharang Drain. The sampling *Station#*6 was selected to monitor the quality of drain wastewater after mixing of poorly treated wastewater from oxidation ponds. Total number of outfalls between sampling *Station#*5 & 6 was mere 15 and total bridges were 3. Only one was flowing and all the rest were dry. After *Station#*6 there was no major outfall into Paharang Drain and the Paharang Drain lead to River Chenab without any additional pollution. The total length of study area was 29Km and total number of outfalls into main Paharang Drain were 255 and total numbers of bridges were found to be 24. The total number of textile industries on the bank of Paharang Drain were 18, but underground textile industrial effluents are also entering into main

Paharang Drain from inside the residential area. In addition to discharging municipal and industrial effluents into the Paharang Drain, bank-side residents also use banks of the drain as their solid waste dumpsite.

Stations for the sample collection and flow measurement were established on the basis of nature, number and distance of outfalls at different locations of the drain which are given in Table 3-2.

Table 3-2: Industrial and sewage outfalls into Paharang Drain

Station Name	Approx distance between stations	Sewage outfalls between stations		Industrial outfalls between stations		Total outfalls between stations	
		Right Bank	Left Bank	Right Bank	Left Bank	Right Bank	Left Bank
S1	13 Km	40	29	9	1	49	30
S2	16 Km	9	17	3	0	12	17
S3	16.2 Km	0	3	2	1	2	4
S4	17.5 Km	5	2	2	0	7	2
S5	25 Km	68	41	1	0	69	41
S6	29 Km	5	10	0	0	5	10

3.2 METALS IN WATER

The effect of metals in water and wastewater range from beneficial through troublesome to dangerously toxic. Some metals are essential for plant and animal growth while others may adversely affect water consumers, wastewater treatment systems and receiving waters. The benefits versus toxicity of some metals depend upon their concentration in waters. So, in order to decide whether the wastewater under study is within given ranges set by Pakistan Environmental Protection Agency (Pak-EPA) or not, determination of the concentration of these metals is necessary.

3.3 SAMPLE COLLECTION AND PRESERVATION

Polyethylene containers were used for sample collection. All containers were rinsed using dilute acidic solution. Each container was tightly sealed and labeled immediately after sample collection. All sampling containers were cleaned by washing in non-ionic detergent, rinsed with tap water and later soaked in 10% HNO_3 for 24 hours and finally rinsed with de-ionized water prior to usage. Sample bottles were also rinsed with sampled water three times prior to sample collection.

Serious errors may be introduced during sampling and storage because of contamination from sampling device, failure to remove residues of previous samples from sample container and loss of metals by adsorption on and/or precipitation in sample container caused by failure to acidify the sample properly (APHA, 2005).

Triplicate samples were collected from each station of the drain at a fixed depth of 1/2 meter from the water level in the drain during each monthly visit between July 2008 and December 2008. Independent samples of domestic wastewater, industrial wastewater and River Chenab water were also collected in triplicate to develop a baseline.

3.3.1 Sample Preservation

The most practical and reliable method of preservation in the field is icing. Putting samples into ice and keeping them there, until they are deposited to the laboratory, preserves samples characteristics for most of the tests.

Standard sample preservation steps i.e., temperature control, addition of preservatives, and the observance of recommended storage time, depending on the analyte of interest as well as on the sample matrix were strictly followed (Somenath, 2003). Samples were preserved by acidifying with concentrated nitric acid (HNO_3) to pH < 2. The samples were filtered before preservation for determination of dissolved metals. The samples were not filtered for the determination of total metals. After initial acidification the samples were stored in the refrigerator at 4ºC.

3.4 SAMPLE DIGESTION

The kind of sample preparation applied depends on the sample, the matrix, and the concentration level of the analytes. In some cases, the analytes have to be released from the matrix by extraction or digestion (Zhang, 2007). All samples except river water samples were digested before analysis.

3.4.1 Digestion Procedure

100 cm^3 of each sample was transferred into a beaker and 5ml concentrated HNO_3 was added to destroy organic matrices. The beaker with all of its contents was slowly

boiled on a hot plate at 105°C and evaporated down to about 20ml. More HNO_3 was added and heating continued until the solution appeared light colored and clear which shows the completion of digestion. The beaker contents were then filtered cooled and diluted to mark. Concentration of selected metals in the wastewater samples was determined using Perkin-Elmer AAnalyst 100 Atomic Absorption Spectrometer (AAS) and GBC 932 plus Atomic Absorption Spectrometer (GBC 932+). The samples for ICP-OES analysis were also digested as per standard methods (APHA, 2005).

3.5 ANALYTICAL INSTRUMENTS AND OPERATING CONDITIONS

Following instruments were used to determine the metal concentrations in wastewater and soil samples

i. Perkin-Elmer AAnalyst 100 AAS
ii. GBC 932+ AAS
iii. Perkin-Elmer Optima 2100 DV ICP-OES
iv. X-ray Fluorescence-JSX-3202M Element Analyzer

3.5.1 Perkin-Elmer AAnalyst 100 AAS

The Perkin Elmer AAnalyst 100 system consists of a high efficiency burner system with a Universal GemTip nebulizer and an atomic absorption spectrometer. The burner system provides the thermal energy necessary to dissociate the chemical compounds, providing free analyte atoms so that atomic absorption occurs. The spectrometer measures the amount of light absorbed at a specific wavelength using a hollow cathode lamp as the primary light source, a monochromator and a detector. Table 3-3 provides details about operating conditions of Perkin-Elmer AAnalyst 100 AAS.

Table 3-3: Operating conditions of Perkin-Elmer AAnalyst 100 AAS

Metals	**Wavelength (nm)**	**Slit (nm)**	**Mode**	**Flame**	**Burner (cm)**	**Nebulizer**	**Calibration**
Fe	248.3	0.2	AA	Air-Acetylene	10	Universal	Linear
Cr	357.9	0.7	AA	Air-Acetylene	10	Universal	Linear
Ni	232	0.2	AA-BG	Air-Acetylene	10	Universal	Linear
Cd	228.8	0.7	AA-BG	Air-Acetylene	10	Universal	Non-Linear
Zn	213.9	0.7	AA-BG	Air-Acetylene	10	Universal	Non-Linear
Mn	279.5	0.2	AA	Air-Acetylene	10	Universal	Linear
Cu	324.8	0.7	AA	Air-Acetylene	10	Universal	Linear
Pb	217	0.3	AA	Air-Acetylene	10	Universal	Linear

3.5.2 GBC-932+ AAS

GBC 932+ AAS offers true uncompromised multi-element analysis, returning the highest integrity in results at a fraction of the cost of traditional means. In addition, the 932Plus offers further benefits of greatly reduced operating costs. It provides savings in source lamp costs and the high intensity D2 lamp offers unrivalled lifetime performance with enhanced operation of up to 1000 hours, even at full current. Table 3-4 provides details about operating conditions of GBC 932+ AAS.

Table 3-4: Operating conditions of GBC 932+ AAS

Metals	**Wavelength (nm)**	**Slit Width (nm)**	**Fuel Flow (L/min)**	**Oxidant Flow (L/min)**	**Flame Type**	**Calibration Mode**
Cr	357.9	0.2	2	10	Air-Acetylene	Concentration
Fe	248.3	0.2	2	10	Air-Acetylene	Concentration

Metals	**Wavelength (nm)**	**Slit Width (nm)**	**Fuel Flow (L/min)**	**Oxidant Flow (L/min)**	**Flame Type**	**Calibration Mode**
Pb	217	1	2	10	Air-Acetylene	Concentration
Cu	324.7	0.5	2	10	Air-Acetylene	Concentration
Ni	232	0.3	2	10	Air-Acetylene	Concentration
Zn	213.9	0.5	2	10	Air-Acetylene	Concentration
Cd	228.8	0.7	2	10	Air-Acetylene	Concentration
Mn	279.5	0.2	2	10	Air-Acetylene	Concentration

3.5.3 Perkin-Elmer Optima 2100 DV ICP-OES

The Optima 2100 DV ICP-OES (optical emission system) allows wavelength selection by simultaneous rotation of the prism and grating for this sequential scanning instrument. The dual monochromator system enables relatively high slits to be used with no loss of image quality, which contributes to the high optical throughput. The system automatically selects the correct slit for each analytical measurement. Table 3-5 provides information about the operating conditions.

Table 3-5: Operating conditions for Perkin-Elmer Optima 2100 DV ICP-OES

Parameter	**Setting**
RF Power	1300 W
Nebulizer Flow	0.8 L/min
Auxiliary Flow	0.2 L/min
Plasma Flow	15 L/min
Sample Flow	1.5 L/min
Source Equilibration Time	15 seconds
Read Delay	60 seconds
Replicates	2

3.6 ANALYSIS OF SOIL SAMPLES

Analysis of the metallic pollutants that accumulate at the bottom of the drain enable us to gain an integrated picture of the contamination, because the level of metals in bottom sediments is the result of prolonged sedimentation processes and do not undergo sudden changes because of altering external conditions. Additionally, by distinguishing separate layers of the bottom sediment, it is possible to evaluate the trends towards changing the metal content in terms of time, which is rather impossible at present, taking the metal contamination of water as the basis for the evaluation.

3.6.1 Soil Sample Collection and Preparation

Soil samples (0-15 cm depth) were taken by hand auger (2.5 cm diameter) from each station of the drain. Samples were dried in an oven at 25°C.

3.6.2 Soil Analysis Using XRF Technique

Pallets of the dried soil samples were formed by applying a pressure of 10-15 kgf/cm^3 using a molding press and were analyzed by X-ray fluorescence (Model: JSX-3202M Element Analyzer).

3.6.3 Soil Analysis Using FAAS

The methodology adopted for the analysis of soil samples was same as employed by Chae Jung, (2008). One gram of dried sample was taken in a 100 ml beaker and 10 mL of water was added while stirring. The beaker was heated at 95 °C on a hot plate for 15 minutes after adding 5 ml HNO_3. Another 5 mL of HNO_3 was added. When most of the bubbling has stopped, added 2 mL of HNO_3 and heating continued. Repeated the procedure with another 2 mL of HNO_3 and cooled the beaker to room temperature. Then 2 mL of HNO_3 was added into the beaker and warmed slightly. The light brown solution was filtered and diluted. The benthic soil samples were analyzed for a multi-element suite including Cd, Cu, Pb, Cr, Ni, and Zn by Flame Atomic Absorption Spectrometry (Model: GBC 932+).

3.7 STATISTICAL ANALYSIS

3.7.1 Correlation

Inter-correlation (correlation of metal concentrations with each other) and correlation with physicochemical parameters (TSS, pH and TOC) of metal concentration was studied using Statistical Package for Social Sciences (SPSS) version 13.0.

3.7.1.1 Testing of hypothesis (significance)

a) Statistical assumption

H_O: $\rho = 0$ (Metals and Physicochemical parameters are not correlated) **(Equation 3-1)**

H_1: $\rho \neq 0$ (Metals and Physicochemical parameters are correlated) (**Equation 3-2**)

Where “ρ” is the population correlation coefficient.

b) Level of significance

$\alpha = 0.05$ (95% confidence level)

$\alpha = 0.01$ (90% confidence level)

c) Test statistic

$$t = \frac{r\sqrt{n-2}}{\sqrt{1-r^2}}$$ **(Equation 3-3)**

Where,

t = Student's t- distribution

n = Sample size

r = Sample Correlation

$$r = \frac{\sum (x-\overline{x})(y-\overline{y})}{\sqrt{\sum (x-\overline{x})^2 \sum (y-\overline{y})^2}}$$ **(Equation 3-4)**

d) Critical region

$$\mathrm{P} > \alpha = \text{ Accept } \mathrm{H_O}$$ **(Equation 3-5)**

$$\mathrm{P} \leq \alpha = \text{ Reject } \mathrm{H_O}$$ **(Equation 3-6)**

3.7.2 Analysis of Variance (ANOVA)

a) Statistical assumptions

$H_O{}' : \mu_1. = \mu_2. = ... = \mu_r.$ (Station's means are equal) (**Equation 3-7)**

$H_O{}'' : \mu._1 = \mu._2 = ... = \mu._c$ (Month's means are equal) (**Equation 3-8**)

$H_1{}'$: Not all $\mu_i.$ are equal (Station's means are not equal) **(Equation 3-9)**

$H_O{}''$: Not all $\mu._j$ are equal (Month's means are not equal) **(Equation 3-10)**

b) Level of significance

α = 0.05 (95% confidence level)

α = 0.01 (90% confidence level)

c) Test statistic

Sources of Variation	Df	Sum of Squares	Mean Squares	F
Between Rows	$r-1$	$SSR = c\sum_{i=1}^{r}(\bar{X}_i - \bar{X}..)^2$	$S_1^2 = \frac{SSR}{r-1}$	$F_1 = \frac{S_1^2}{S_3^2}$
Between Columns	$c-1$	$SSC = r\sum_{j=1}^{c}(\bar{X}._j - \bar{X}..)^2$	$S_2^2 = \frac{SSC}{c-1}$	$F_2 = \frac{S_1^2}{S_3^2}$
Error (within)	$(r-1)\times(c-1)$	SSE = By subtraction	$S_3^2 = \frac{SSE}{(r-1)(c-1)}$	
Total	$rc-1$	$SST = \sum_i\sum_j(X_{ij} - \bar{X})^2$		

$$\text{Total}\, SS = \sum_{i=1}^{r}\sum_{j=1}^{c}(X_{ij} - \bar{X}..)^2 = \sum_{i=1}^{r}\sum_{j=1}^{c}X^2{}_{ij} - \frac{T^2}{rc},$$

$$SSR = c\sum_{i=1}^{r}(\bar{X}_{i.} - \bar{X})^2 = \sum_{i=1}^{r}\frac{T_i^2}{c} - \frac{T^2}{rc} \qquad \text{and}$$

$$SSC = r\sum_{j=1}^{c}(\bar{X}_{.j} - \bar{X})^2 = \sum_{j=1}^{c}\frac{T_{.j}{}^2}{r} - \frac{T^2}{rc}$$

d) Critical Region

$$F_1 \geq F_\alpha\left[(r-1),(r-1)(c-1)\right]$$ **(Equation 3-11)**

$$F_2 \geq F_\alpha\left[(c-1),(r-1)(c-1)\right]$$ **(Equation 3-12)**

Or

e) Rule of rejection

$\text{P} > \alpha =$ Accept H_O **(Equation 3-13)**

$\text{P} \leq \alpha =$ Reject H_O **(Equation 3-14)**

Chapter 4

RESULTS AND DISCUSSION

This chapter discusses spatial and temporal variations in selected metallic pollutants. Physicochemical parameters of Paharang Drain wastewater have also been discussed. The results have been compared with National Environmental Quality Standards (NEQS). A good portion of the chapter deals with the estimation and discussion of pollution level indicators.

4.1 ESTIMATION OF PHYSICOCHEMICAL PARAMETERS

Wastewater of the Paharang Drain was analyzed for several physicochemical parameters at each station of the drain as listed in Table 4-1. The reason for adopting this strategy was to assess the level of contamination and establish a correlation between these pollutants and the concentration of metals.

As evident from Table 4-1, concentrations of BOD_5, COD and TOC increased gradually up to *Station#4* indicating a continuous influx of industrial and municipal wastewaters. Fractional changes in the mentioned parameters at *Station#4* indicated that no major out fall existed in this area. It was highly likely that, the self purification phenomenon of the drain would have improved the drain water quality but might not reach to NEQS level.

Table 4-1: Concentration* of physicochemical parameters at six selected stations

Parameters	Stations						NEQS
	S1	**S2**	**S3**	**S4**	**S5**	**S6**	600
Sulphates (mg/L)	481.66	422.5	422.5	452	419.17	440.83	1000
Chloride (mg/L)	1223.1	957.1	968.33	977.69	826.76	834.87	
DO (mg/L)	0.48	0.61	0.50	0.58	0.61	0.52	
TOC (mg/L)	88.13	169.65	159.03	146.4	106.98	109.22	
TDS (mg/L)	2838.33	2735.83	2734.33	2793.67	2593.00	2634.00	3500
TSS (mg/L)	108.00	319.66	388.17	348.67	244.5	271.33	150
COD (mg/L)	467.29	604.24	561.68	488.29	446.93	457.95	150
Flow rate (MGD)	6.00	18.01	30.47	44.41	97.70	105.51	
Temp. (°C)	30.16	34.3	34.22	33.07	30.33	30.28	40
EC (mS/cm)	5.11	5.28	5.24	5.49	5.06	5.16	
pH	8.65	8.96	9.11	9.26	8.42	8.49	6-10
Turbidity (NTU)	40.68	188.92	214.44	151.38	84.07	88.05	
BOD (mg/L)	182.14	303.88	298.49	257.68	242.48	252.60	80
TN (mg/L)	19.21	75.13	67.60	69.00	50.58	50.60	
TP (mg/L)	17.03	22.7	21.13	18.72	15.67	17.27	
Oil and Grease (mg/L)	32.70	43.92	65.68	54.25	39.1	53.63	10

*Means of six measurements

The value of DO was found to be very low from *Station#1-6* due to high pollution load of industrial and municipals effluents.

Concentration of Total Solids (TS) and Total Dissolved Solids (TDS) decreased down the stream, whereas total suspended solids concentration, increased gradually. Similarly, values of TSS and TN were found to be higher in concentration from *Station#1* to *Station#4* due to high pollution inputs from industrial and domestic outfalls. Total Phosphorous concentration at *Station#2, 4 & 6* was a clear evidence of large inflow of untreated sewage.

4.2 SPATIAL ANALYSIS OF METALS

Since Paharang Drain receives wastewater from both industrial as well as municipal sources, the distribution of metals in separate industrial and municipal effluent drains was studied by analyzing 4 hour composite samples from a few industrial and a few residential streams. The objective was to establish a baseline and to determine the general concentration range of each metal in both independent streams. Results of these investigations are shown in Figure 4-1.

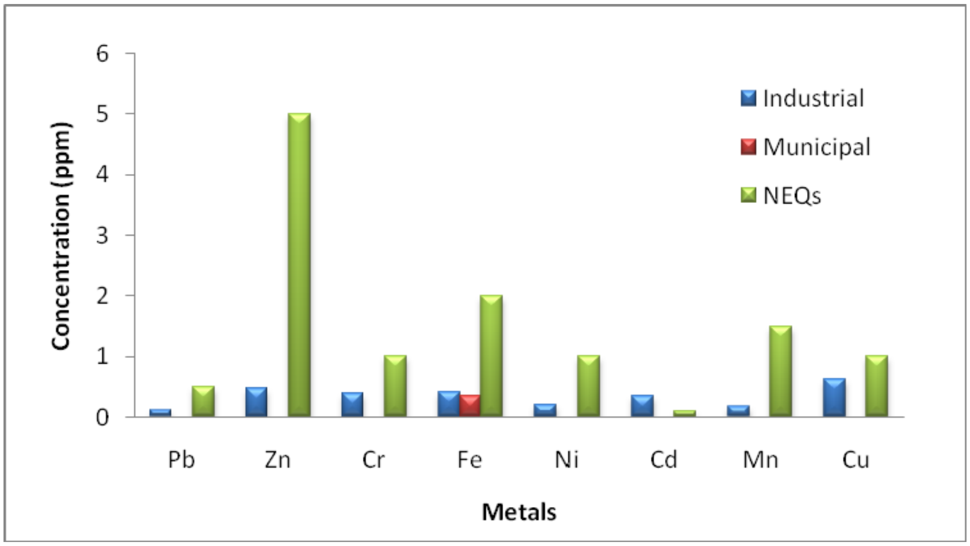
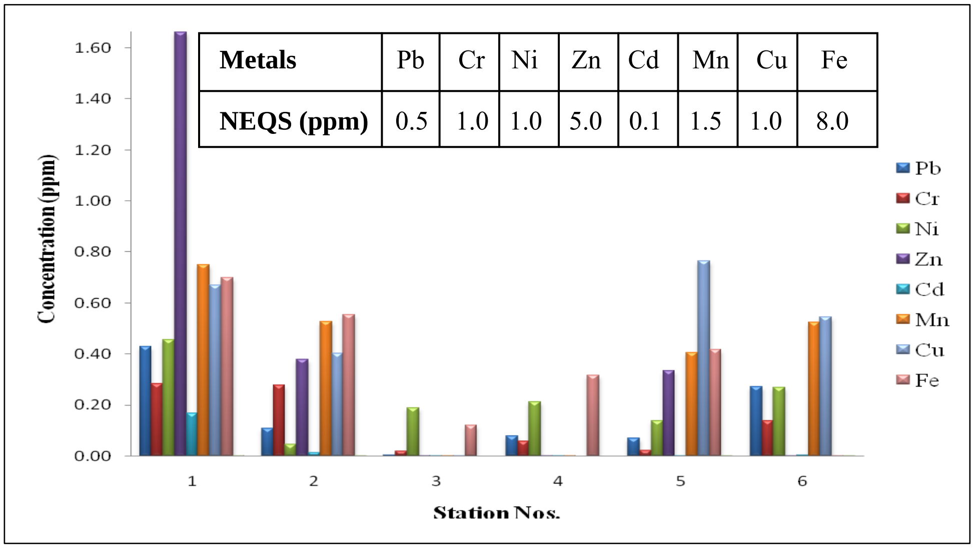


Figure 4-1: Metals concentration in separate industrial and municipal streams

Figure 4-1 shows that the concentration range of metals in the industrial stream varies between 0.111 and 0.002 ppm and all metal concentrations except Cadmium are within NEQS. This can be attributed to the fact that enormous quantities of water are used and abused by these industries and mixing between various polluted and an unpolluted streams within the industry dilutes the effluent. None of the metals except Fe was detected in the municipal stream which shows that the major fraction of metals in the wastewater of the Paharang Drain stems from the industrial activities. Total concentration of metals at each sampling station of the drain is given in Table 4-2.

Spatial distribution of metals between *Station#1* and *Station#6* are illustrated by Figure 4-2. NEQS values are also shown for reference. Metal concentrations are high at *Station#1, 2, 5* and *6*, and are relatively low at *Station#3* and *4*.



Metals	Pb	Cr	Ni	Zn	Cd	Mn	Cu	Fe
NEQS (ppm)	0.5	1.0	1.0	5.0	0.1	1.5	1.0	8.0

Figure 4-2: Mean concentration of metals at six selected stations

According to Huang and Wang (2001) physicochemical factors as well as surface characteristics of particulate matter in wastewater are two major components controlling the distribution of metals. The mean concentration of the metals at each station of the drain is shown in Table 4-3.

Table 4-2: Total concentration of selected metals

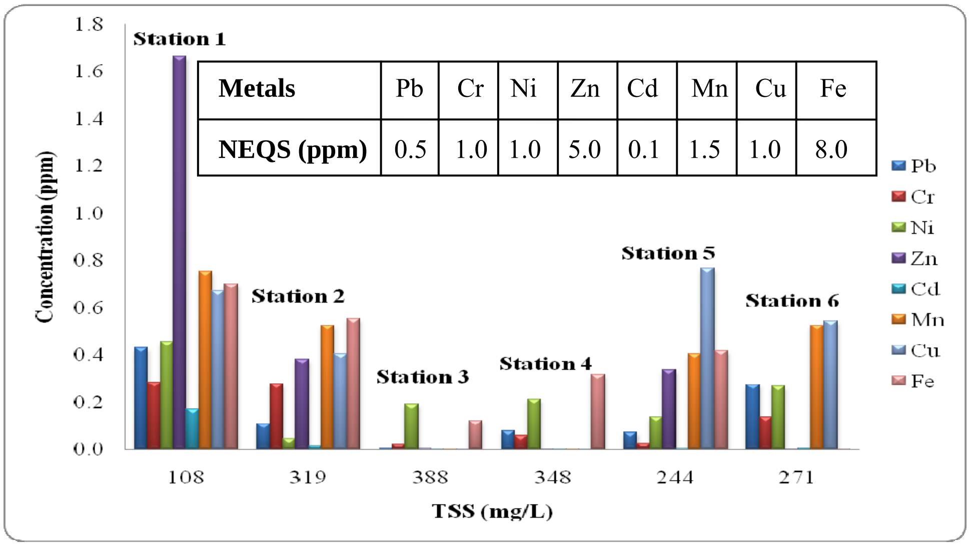
Stations	Concentration of metals (mg/L)							
	Pb	**Cr**	**Ni**	**Zn**	**Cd**	**Mn**	**Cu**	**Fe**
1	1.59	1.09	1.72	5.15	0.488	2.6	2.043	2.619
2	0.39	1.05	0.16	1.292	0.04	1.631	1.2039	1.899
3	0.02	0.07	0.70	0.008	0.007	0.003	0.0032	0.427
4	0.24	0.22	0.75	0.002	0.004	0.002	0.0005	1.052
5	0.21	0.09	0.51	1.145	0.007	1.423	2.5508	1.56
6	1.12	0.44	0.99	0.005	0.013	1.802	1.7544	0.01

Table 4-3: Concentration* of metals at each sampling station

Station	Concentration of metals (mg/L)							
	Pb	**Cr**	**Ni**	**Zn**	**Cd**	**Mn**	**Cu**	**Fe**
1	0.429	0.283	0.456	1.661	0.169	0.752	0.670	0.700
2	0.110	0.277	0.045	0.380	0.014	0.526	0.404	0.555
3	0.005	0.021	0.189	0.003	0.003	0.001	0.001	0.121
4	0.079	0.059	0.212	0.001	0.002	0.001	0.001	0.318
5	0.071	0.024	0.138	0.336	0.003	0.406	0.766	0.416
6	0.273	0.139	0.268	0.002	0.005	0.526	0.545	0.003

*Mean concentration of six samples

As COD is a measure of dissolved organic matter in wastewater, the dissolved metal concentration is expected to increase with increasing COD due to the formation of non-adsorbable metal complexes (Tien and Huang, 1991; Rudd *et al*., 1984) but COD in this study is not following any trend so it is difficult to establish a relationship between concentrations of metals and COD. Other wastewater quality variables such as EC and TDS are also not playing any noticeable role in the distribution of metals as these are not varying much from station to station. Particulate matter controls the concentration of metals (Harrison and Mora, 1996). Metal concentration is decreasing due to the increased uptake by the solid particles as illustrated in Figure 4-3. Very low concentration of metals can be observed at *Station#3* (Figure 4-3) although it has very low TSS. It is because there are very few (only 3) industrial outfalls which are the main source of metals, before *Station#3*.

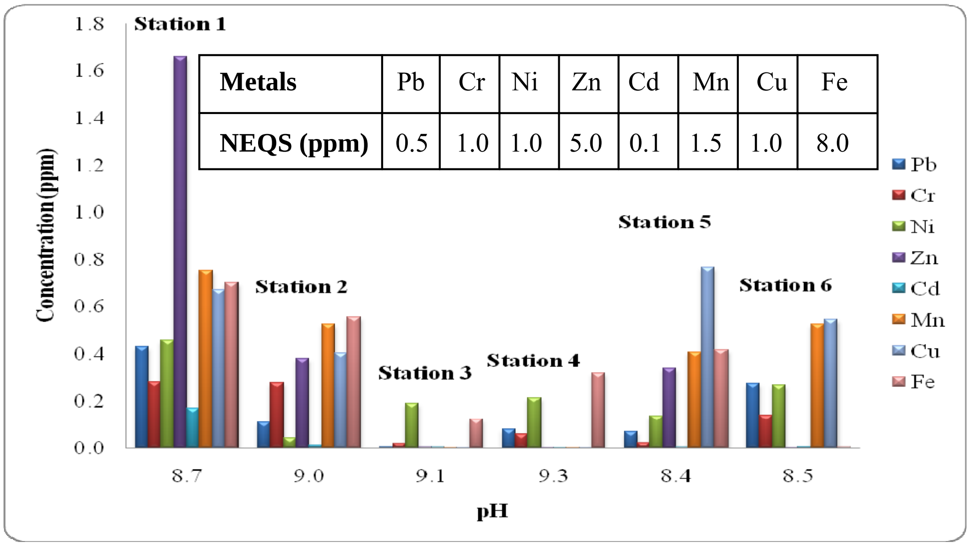


Metals	Pb	Cr	Ni	Zn	Cd	Mn	Cu	Fe
NEQS (ppm)	0.5	1.0	1.0	5.0	0.1	1.5	1.0	8.0

Figure 4-3: Variations in metals concentration with respect to TSS

Out of all the six stations, *Station#1* exhibits highest metal concentration at relatively lower pH and flow rate. This is consistent with the findings of Doilido and Best (1993) who concluded that concentration of the metals is generally high at low pH. *Station#1* is located after an outfall from a large industrial and small residential cluster. None of the other sampling station has as many industrial discharges into Paharang Drain as prior to *Station#1*. This high concentration of metals in the drain water at *Station#1* starts dampening at *Station#2* and drops to very low values until fresh industrial discharges inject more metals into the drain between S*tation#4 and* S*tation#5*. This trend indicates that metal concentration in Paharang Drain would reduce with distance if not supplemented by new discharges. Although *Station#5* and *Station#6* have pH in the same range as that of *Station#1,* but flow rate at these stations is much higher. S*tation#5* has only one major industrial outfall before it. S*tation#6* also has only one outfall before it i.e., the discharge of treated wastewater from 20 MGD Wastewater Stabilization Ponds. High metal concentrations at S*tation#5* reflect cumulative impact of all industrial discharges up to S*tation#5*. Metal concentration at *Station#6* is lower than expected as the distance between *Station#5* and *Station#6* is only 500 meter. This may be attributed to the continuous discharge and dilution from 20 MGD plant prior to *Station#6*.

pH (8) of most of the wastewater samples varies within a narrow range. In such a narrow pH range, it is rather difficult to establish any relationship between pH and metal distribution. However, as the pH has been observed above 8 for all the samples analyzed, it may be one of the controlling factors for the distribution of metals in the drain water. Also, as the acid breakpoints of most of the metals selected in this study are 5 or 7 (Levine, 2009) which are below the observed pH of the samples, so, there is a strong probability that a major amount of metals is being precipitated out in the drain as shown in Figure 4-4.



Metals	Pb	Cr	Ni	Zn	Cd	Mn	Cu	Fe
NEQS (ppm)	0.5	1.0	1.0	5.0	0.1	1.5	1.0	8.0

Figure 4-4: Variations in metals concentration with respect to pH

Variations in metal concentrations at each sampling station were determined and have been shown in Box-Whisker plots in Figure 4-5. The Box-Whisker plot compares the minimum, maximum and mean concentration of the individual metals.

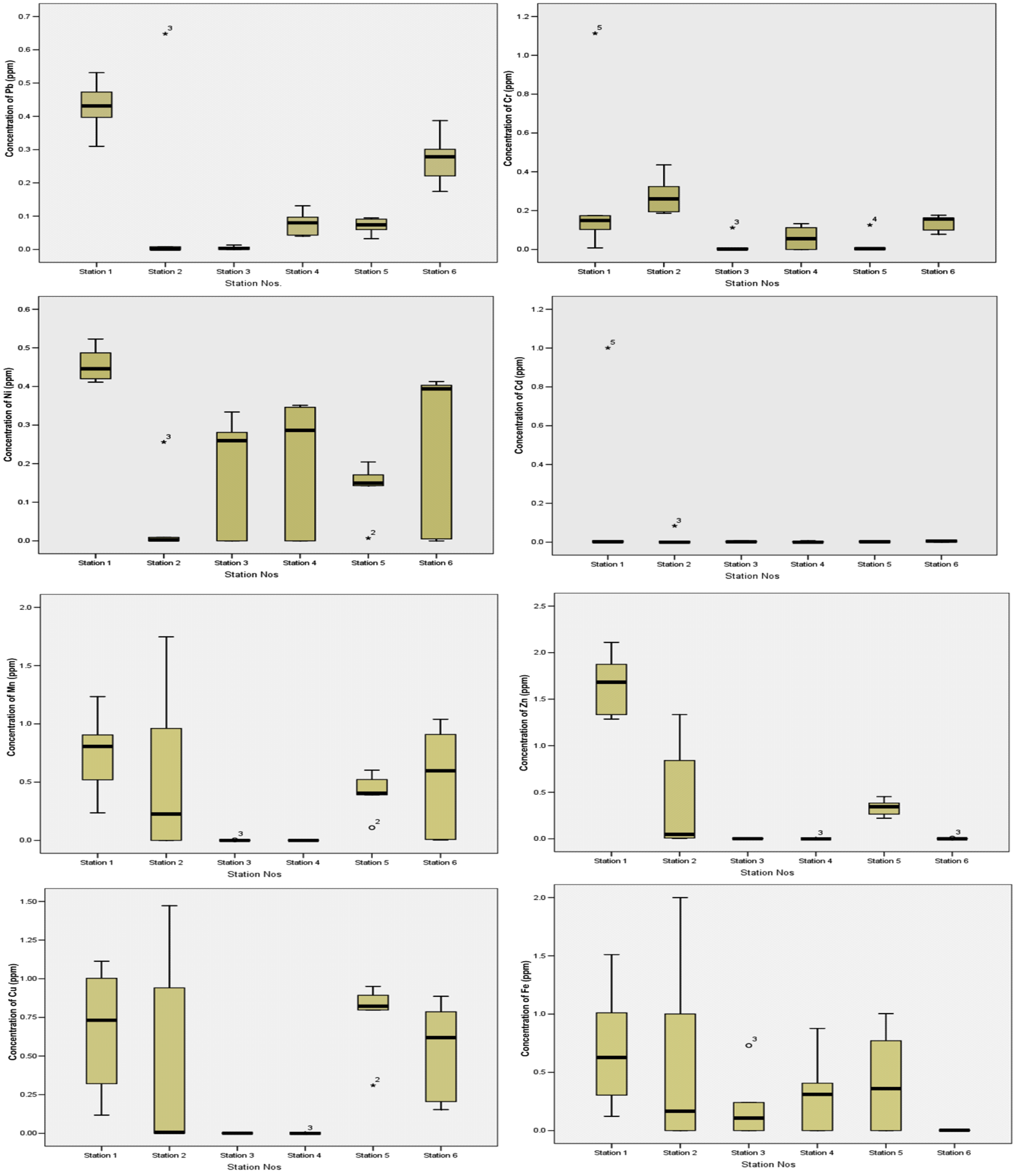


Figure 4-5: Variations in metals concentration in BOX-Whisker plot

4.2.1 Bioavailability (BA) of Selected Metals

The term 'bioavailability' is meant to denote heavy metals in a water-soluble form (i.e. dissolved form) that plant and animal communities can readily uptake and assimilate (Anilava and Das, 1999). The bioavailability of metals (expressed in percent) with respect to total metal content can be calculated as follows.

$$\%\ \text{Bioavailability} = \frac{Dissolved\ metal\ concentration\left(mg/L\right)}{Total\ metal\ concentration\left(mg/L\right)} \times 100 \quad \textbf{(Equation 4-1)}$$

Where dissolved metal concentration is determined through analysis of filtered water samples, and the total metal concentration by analysis of unfiltered water samples. As a result investigations of bioavailability tell how much a particular metal is available to the living matter (plants and animals). The higher the value of dissolved concentration of metals, higher is the bioavailability which necessitates for the estimation of metals both in filtered and unfiltered samples as is done in the present study. The percent bioavailability of selected metals at all sampling stations is given in Table 4-4.

Table 4-4: Percent bioavailability of each metal at each sampling station

Stations	**Bioavailability of metals (percent)**							
	Pb	**Cr**	**Ni**	**Zn**	**Cd**	**Mn**	**Cu**	**Fe**
1	27.03	26.04	26.53	32.26	34.6	28.9	32.787	26.74
2	28.09	26.46	28.57	29.41	35.59	32.26	33.557	29.24
3	29.24	28.57	26.95	32.05	36.1	31.06	31.153	28.41
4	32.15	27.03	28.17	29.33	37.31	30.21	32.154	30.21
5	34.48	27.4	27.03	29.33	37.59	28.49	30.03	26.67
6	24.39	31.15	26.95	31.06	36.76	29.15	31.056	26.32

It is obvious that although the concentrations of all metals vary a lot from each other but the bioavailability percentage is not much different. It is further explained in bioaccumulation factors.

4.2.2 Bioaccumulation Factors (BAFs)

The bioaccumulation of a few selected metals in different samples of the wastewater of Paharang Drain was quantified with a bioaccumulation factor (BAF), defined as the ratio of the concentration of a specific metal in the plant/ organism to the concentration of that metal in the water/wastewater (Hasan *et al.*, 2003). In the present study, the BAF of a few selected metals in various plants is tabulated in Table 4-5.

Table 4-5: Bioaccumulation factors of a few selected metals in plants

Metals	**Concentration in vegetables/crops (mg/Kg)**			**Concentration in wastewater (mg/L)**	**BAF of vegetables/crops**		
	Wheat	**Cauliflower**	**Berseem**		**Wheat**	**Cauliflower**	**Berseem**
Cd	10.3	13.6	1.8	0.169	60.95	80.47	10.65
Cr	35.3	38.3	19.1	0.283	124.73	135.34	67.49
Pb	96	133	21	0.429	223.78	310.02	48.95
Ni	139	115		0.456	304.82	252.19	0.00
Zn	108		149	1.66	65.06	0.00	89.76

In general, two mechanisms are responsible for metal uptake in aquatic systems, including;

(i) adsorption, which refers to the binding of metals onto a substrate surface, and

(ii) Absorption, which implies penetration of metals into the inner matrix of a substrate (Ramraj *et al.,* 2000).

The accumulation of a particular metal depends, to a large degree, on the presence of the metal in the water column. In this study, however, the concentration of metals in the vegetables/crops was taken from Kahlown *et al.* (2006).

The plant uptake of heavy metals depends not only on the concentration of the metals in the water column, but also on the metal species and the bio-available form of the metals (Olaniya *et al.*, 1998a).

The BAFs for different heavy metals from water to plant, or soil to plant, are a key component of human exposure to the metals via the food chain. The highest BAF value in this study is for Zn, supporting the finding that the accumulation of Ni is comparatively less, while that of Zn is more in plants (Olaniya *et al.*, 1998b).

4.3 TEMPORAL ANALYSIS OF METALS

The temporal variation in metals concentration is shown in Figure 4-6, which exhibits that the concentration of most of the metals is low in July and August (Monsoon season), high in September (Dry period). It starts falling smoothly from October till December (Second wet spell). The reason might be the pH which is lowest in the month of September as compared to other months. Other factors affecting metal concentrations may include variations in the magnitude of production in industry, power shortage problems in the country, variations in the processes of an industry and even the nature and types of industries near the drain.

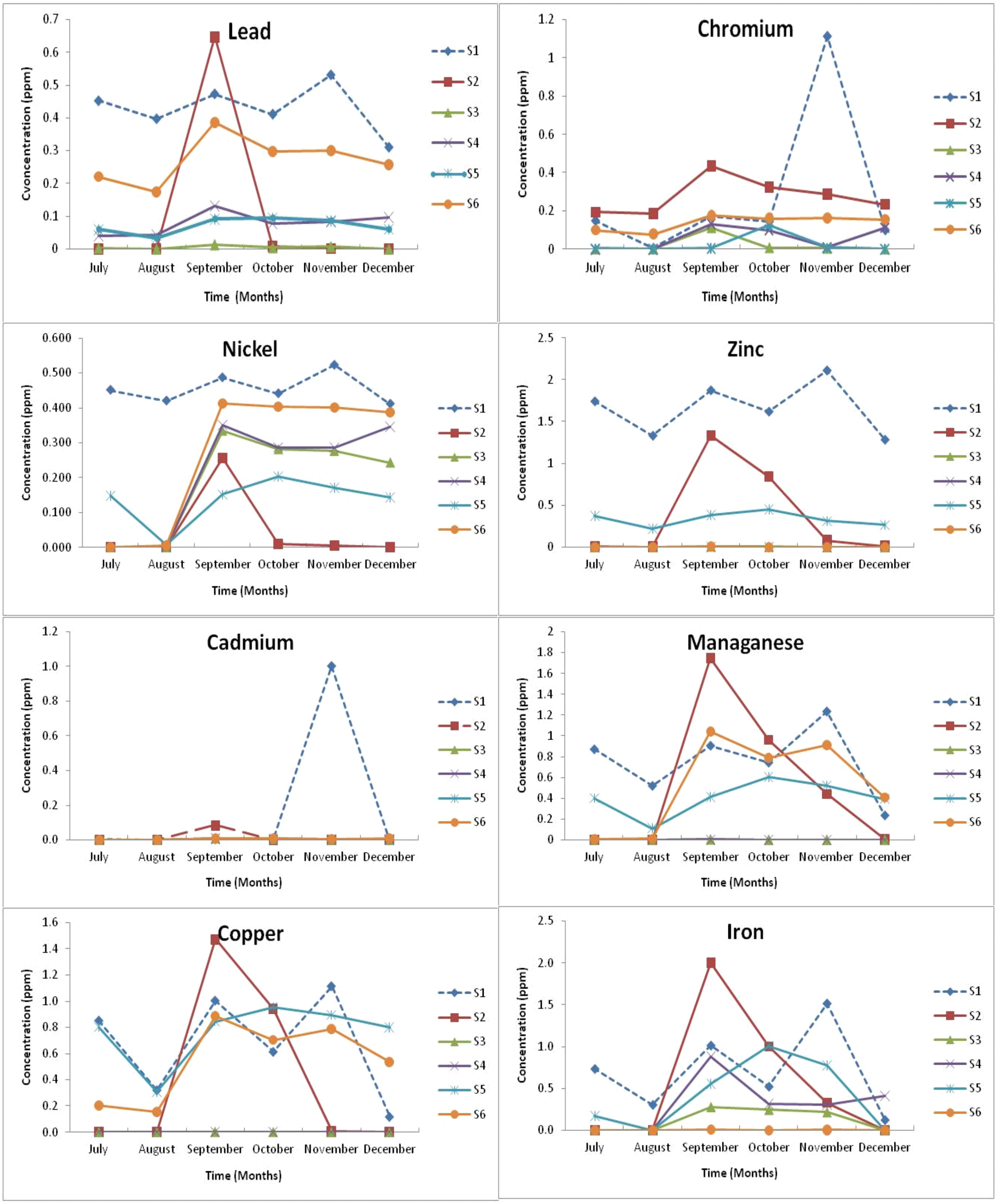


Figure 4-6: Monthly variation in the concentration of metals

There is no more industrial discharge into the Paharang Drain between *Station#6* and River Chenab so the concentration of metals keep on reducing because of natural self purification processes, uptake by benthic soils and also because of introduction of municipal effluents which act as diluting agent.

The deposition of metal precipitates into the benthic zone of the drain is highly likely because of high pH of the wastewater. This plays an important role in the reduction of metals concentration in the drain water. As shown in Figure 4-7, concentration of metals has been found in ppb range before River Chenab, which was previously in the ppm range.

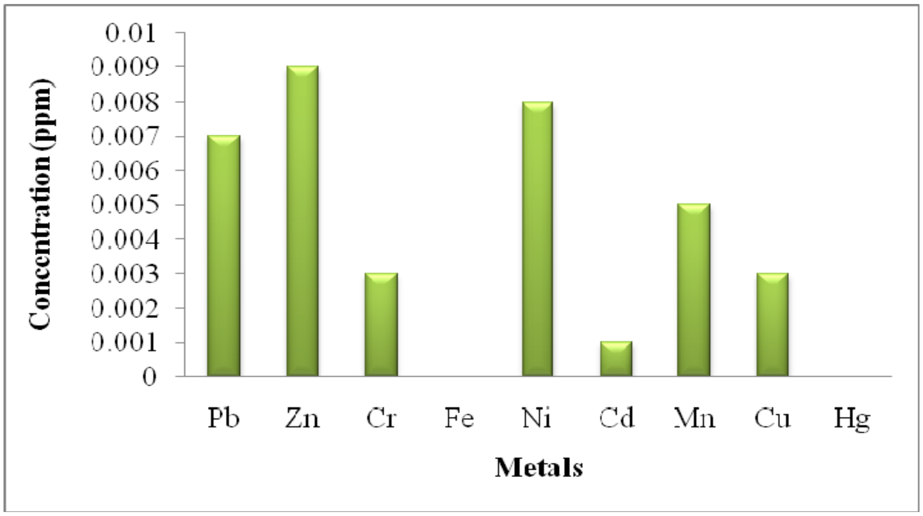


Figure 4-7: Metals concentration in the Paharang Drain just before River Chenab

4.4 MASS LOADING OF METALLIC POLLUTANTS

Concentrations of the metals analyzed in the drain wastewater are within permissible limits set by the Pak-EPA as is evident from the results shown in Table 4-3. Further, concentrations of metals in the effluent falling into River Chenab are also within permissible limits. Apparently, these findings lead us to the conclusion that there are no harmful environmental impacts on the receiving water body.

Practically, River Chenab is receiving huge amounts of these metals daily as is depicted in Figure 4-8 and Figure 4-9.

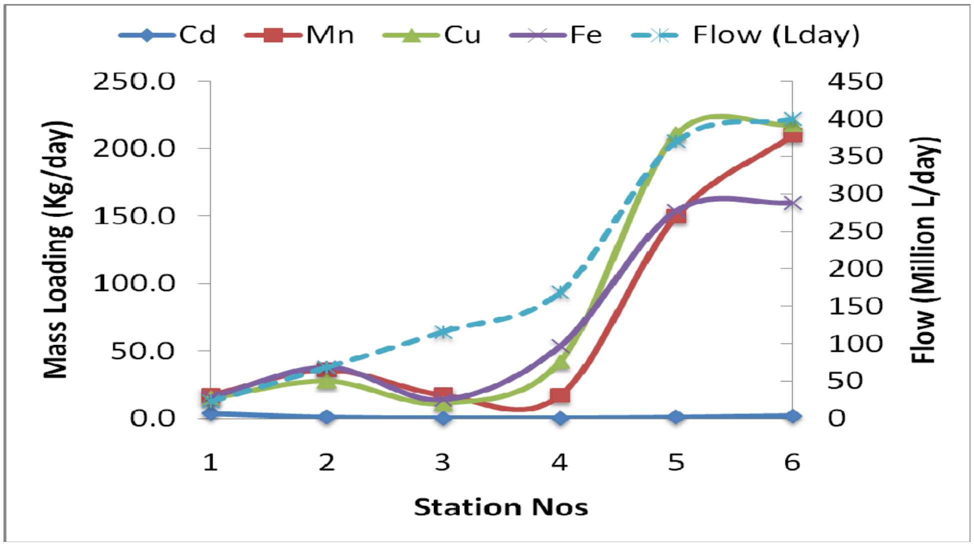


Figure 4-8: Mass loadings of Cd, Mn, Cu and Fe

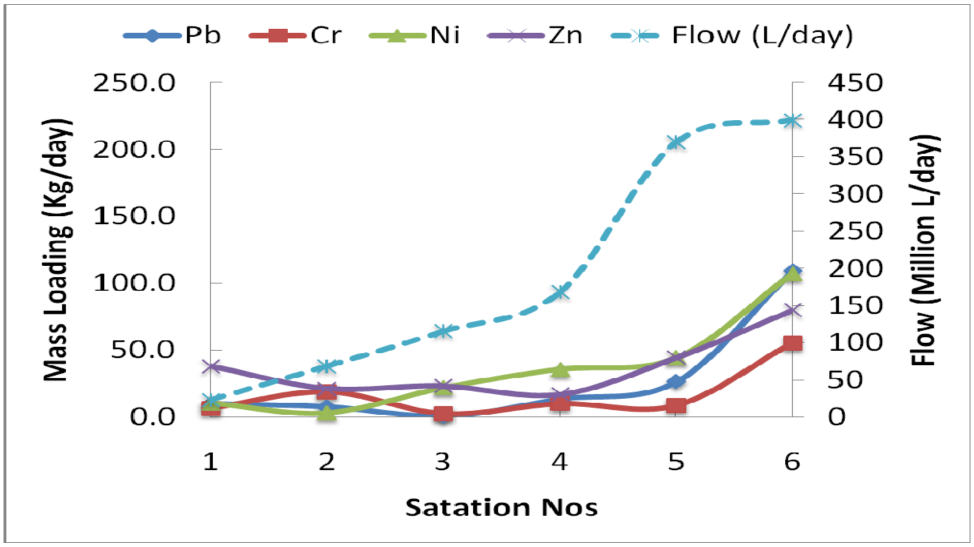


Figure 4-9: Mass loadings of Pb, Cr, Ni and Zn

This situation draws attention to an important issue i.e. efficacy of NEQS. Although concentrations of metals in the wastewater of Paharang Drain are within the permissible limits, yet the river is being contaminated. It’s not the concentration which must be considered while analyzing the quality of an effluent falling into a water body, rather the total mass load of each pollutant in an effluent should be adopted as a standard.

4.5 ESTIMATION OF METALS IN THE BENTHIC SOIL

A major environmental concern is the contamination of agricultural soil due to dispersal of industrial and urban wastes generated by human activities. The long term usage of industrial wastewater for irrigation makes heavy metals to accumulate in soil (Chaw and Reves, 2001). In order to study the metallic pollution in the benthic zone of the drain it was necessary first to determine the heavy metals in the drain water as well. Since the precipitation and dissolution of heavy metals in water is mainly affected by pH (Elzahabi and Yong, 2001; Narasimha and Prasad, 2004) and total suspended solids (Huang and Wang, 2001; Herngren *et al*., 2005), determination of heavy metals in drain water will also be helpful for investigating the extent of these factors.

The low concentration of metals at all the selected stations and occurrence of some of these metals in the crops and vegetables irrigated with this drain water, lead to the investigation of these metals in the benthic soil of the drain.

The spectrum of the metals analyzed in the soil of *Station#*3 is shown in Figure 4-10.

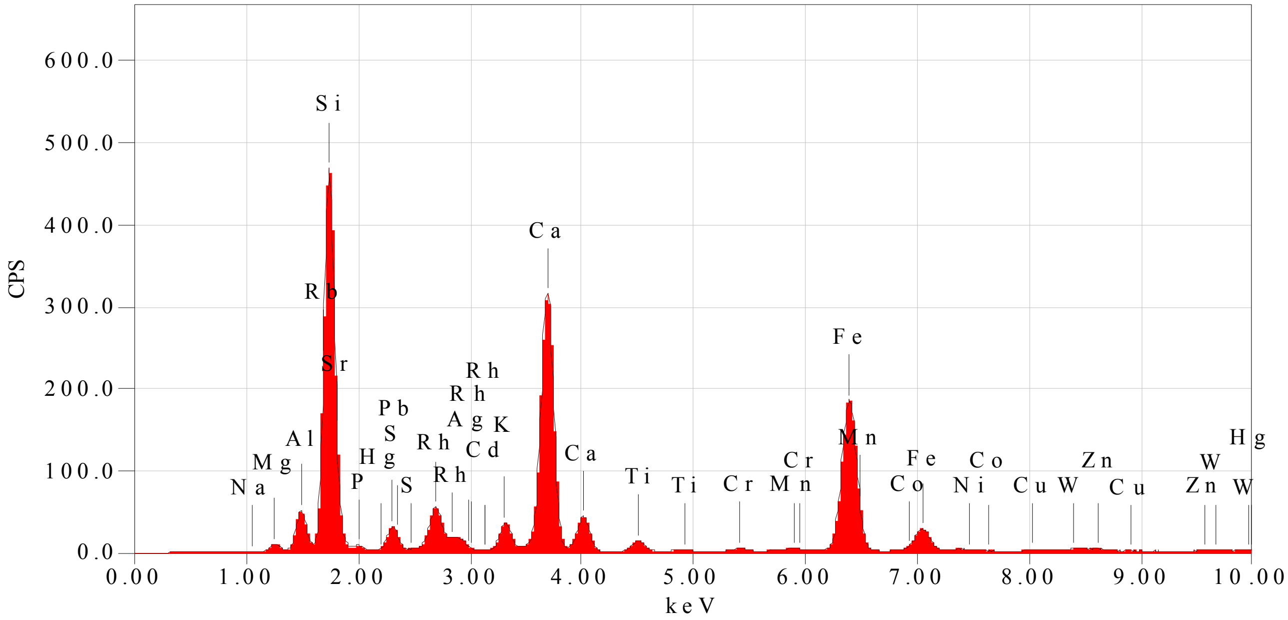


Figure 4-10: XRF spectrum of benthic soil of *Station#*3 of the Paharang Drain

The concentrations of the metals analyzed by XRF technique at all the six selected stations of the drain are shown in Table 4-6.

Table 4-6: Mean concentration* of metals in the benthic soil using XRF

Metals	**Mean Concentrations at selected stations(mg/Kg)**					
	S1	**S2**	**S3**	**S4**	**S5**	**S6**
Al	107966	85066	63600	83400	76033	85100
Pb	BDL	BDL	61	76	932	851
Cr	409	723	1929	665	685	544
Ni	194	247	134	294	608	534
Zn	370	388	425	527	867	756
Cd	6408	6557	BDL	2100	155	85
Mn	1259	845	650	976	1253	989
Cu	BDL	75	605	54	BDL	BDL
Fe	122549	83418	72727	75475	90235	82439

*Mean ± S.D of three measurements

4.6 GEO-ACCUMULATION INDEX

A geo-accumulation indexing (I_{geo}) approach was used to quantify the degree of anthropogenic contamination, and to compare the different metals in lake sediments (Müller and Suess, 1979; Förstner *et al*., 1993). This quantitative check of metal pollution in aquatic sediments was proposed in the form of an equation defined as the index of geo-accumulation, as follows:

$$I_{geo} = \log_2\left(\frac{C_n}{1.5 \times B_n}\right) \quad \textbf{(Equation 4-2)}$$

Where: C_n = measured concentration of heavy metal in soil (mg g^{-1} dry mass); B_n = background value of heavy metal (mg g^{-1} dry mass); and 1.5 = background matrix correction factor.

The background matrix correction factor of 1.5 is used to account for possible variations in the background data as a result of such lithogenic effects as the chemical leaching of bedrock, water drainage basins and run-off from banks (Upadhyay *et al*., 2006). The index of geoaccumulation consists of seven grades, for which the highest grade (6) reflects a 100-fold enrichment above background values. Forstner *et al.* (1993) identified geoaccumulation classes and the corresponding contamination intensity for different indices, as illustrated in Table 4-7.

Table 4-7: Geo-accumulation index classification (Bakan and Balkas, 1999)

Geo-accumulation index (I_{geo})	**I_{geo} Class**	**Intensity of Contamination**
<0	0	Practically uncontaminated (PU)
>0–1	1	Uncontaminated to moderate (UM)
>1–2	2	Moderately contaminated (MC)
>2–3	3	Moderately to strongly contaminated (MSC)
>3–4	4	Strongly contaminated (SC)
>4–5	5	Strong to very strong contamination (SVSC)
>5	6	Very strong contamination (VSC)

Table 4-8: Geoaccumulation indices of selected metals

Metals	**Metal Concentrations in benthic soil at each station (C_n)**						**I_{geo}**					
	S1	**S2**	**S3**	**S4**	**S5**	**S6**	**S1**	**S2**	**S3**	**S4**	**S5**	**S6**
Zn	370	388	425	527	867	756	1.7	1.8	1.9	2.2	2.9	2.7
Cu	0	75	605	54	0	0	NA	0.9	4.0	0.5	NA	NA
Cd	6408	6557	0	2100	155	85	15.5	15.6	NA	13.9	10.2	9.3
Pb	0	0	61	76	932	851	NA	NA	1.0	1.3	4.9	4.8
Cr	409	723	1929	665	685	544	1.7	2.5	4.0	2.4	2.5	2.1
Ni	194	247	134	294	608	534	2.0	2.3	1.5	2.6	3.6	3.5
Mn	1259	845	650	976	1253	989	0.5	-0.1	-0.4	0.2	0.5	0.2

In order to determine the values of I_{geo}, geochemical background values of 76.27, 26, 0.09, 20.32, 82.65, 32.39 and 585.5 mg/Kg were adopted from the literature for Zn, Cu, Cd, Pb, Cr, Ni and Mn respectively. The resulting contamination intensities of metals are given in Table 4-9, which shows that benthic soil of all the stations (except *Station#*3) are very strongly contaminated with Cd. Cd was found to be very low in wastewater samples as it was precipitating and becoming part of the benthic soil. Similarly concentrations of all those metals which were found to be very low in the wastewater samples were relatively higher in benthic soil.

Table 4-9: Contamination intensities of metals

Metals	**Contamination intensity at each station**					
	S1	**S2**	**S3**	**S4**	**S5**	**S6**
Zn	MC	MC	MC	MSC	MSC	MSC
Cu	PU	UM	SC	UM	PU	PU
Cd	VSC	VSC	UM	VSC	VSC	VSC
Pb	PU	PU	UM	MC	SVSC	SVSC
Cr	MC	MSC	SC	MSC	MSC	MSC
Ni	MC	MSC	MC	MSC	SC	SC
Mn	UM	PU	PU	UM	UM	UM

4.7 DETERMINATION OF ENRICHMENT FACTOR

To evaluate the magnitude of contaminants in the environment, the enrichment factors (EFc) were computed relative to the abundance of species in source material to that found in the Earth's crust and following equation was used to calculate the EFc as proposed by Atgin *et al.* (2000).

$$EFc = \left(\frac{\left(CM/CAl \right)_{Sample}}{\left(CM/CAl \right)_{Earth's Crust}} \right) \quad \textbf{(Equation 4-3)}$$

Where, $(CM/C_{Al})_{sample}$ is the ratio of concentration of trace metal (CM) to that of Al (C_{Al}) in the sediment sample and ($CM/C_{Al\ Earth's\ crust}$) is the same reference ratio in the

Earth's crust. The average abundance of Zn, Cu, Cd, Pb, Cr, As and Ni (70, 55, 0.2, 12.5, 100, 1.8 and 75 μg/g, respectively) in the reference Earth's crust were taken from Huheey (1983) and Al (the reference value being 7.8 %) was selected as the reference element, due to its crustal dominance and its high immobility.

Table 4-10: EF values of selected metals

Metals	**EF Values**					
	S1	**S2**	**S3**	**S4**	**S5**	**S6**
Zn	0.031	0.041	0.060	0.057	0.102	0.080
Cu	0.000	0.006	0.067	0.005	0.000	0.000
Cd	0.002	0.002	0.000	0.001	0.000	0.000
Pb	0.000	0.000	0.002	0.001	0.020	0.016
Cr	0.049	0.109	0.389	0.102	0.116	0.082
Ni	0.017	0.028	0.020	0.034	0.077	0.060

4.8 ASSESSMENT OF POLLUTION LOAD INDICES

The pollution load index (PLI) proposed by Tomlinson *et al*. (1980) to measure PLI in sediments of Tsurumi River has been used in this study. The PLI for a single site is the nth root of n number multiplying the contamination factors (CF values) together. The CF is the quotient obtained as follows:

$$CF = \left(\frac{\text{Metal concentration in the sample}}{\text{Metal concentration in background}} \right) \textbf{(Equation 4-4) and}$$

$$\text{PLI for a site} = \sqrt[nth]{CF\ 1 \times CF\ 2 \times CF\ 3 \ldots\ldots\ldots\ldots CF\ n} \textbf{ (Equation 4-5)}$$

Such site indices can be treated in exactly the same way to give a zone or area index. Therefore,

$$\text{PLI for a zone} = \sqrt[nth]{Site\ 1 \times Site\ 2 \times Site\ 3 \ldots\ldots\ldots\ldots Site\ n}$$ **(Equation 4-6)**

Where ‘n’ equals the number of contamination factors and sites, respectively

Table 4-11: Contamination factors of selected metals

Metals	**CF Values**					
	S1	**S2**	**S3**	**S4**	**S5**	**S6**
Zn	5.286	5.543	6.071	7.529	12.386	10.800
Cu	0.000	1.364	11.000	0.982	0.000	0.000
Cd	32040	32785	0	10500	775	425
Pb	0	0	4.880	6.080	74.560	68.080
Cr	4.090	7.230	19.290	6.650	6.850	5.440
Ni	2.587	3.293	1.787	3.920	8.107	7.120

Table 4-12: PLI of Paharang Drain and its stations

Stations	**PLI of each station**	**PLI of Pharang Drain**
1	658	450
2	509	
3	332	
4	310	
5	553.95	
6	437	

4.9 STATISTICAL ANALYSIS

The descriptive statistics of metal concentration in Paharang drain wastewater is explained in Table 4-13. The results show that mean concentration of the metals analyzed ranges between 0.032 to 0.398 mg/l with standard deviation ranging between 0.067 to 0.643. The confidence limits of most of the metals are also closer to the mean concentrations.

Table 4-13: Descriptive Statistics of metal concentrations

Statistical parameters	Metals							
	Pb	**Cr**	**Ni**	**Zn**	**Cd**	**Mn**	**Cu**	**Fe**
Mean	0.161	0.1336	0.218	0.3970	0.032	0.3683	0.398	0.3522
Standard Error	0.065	0.0494	0.057	0.2628	0.027	0.1249	0.135	0.1070
Standard Deviation	0.159	0.1210	0.139	0.6437	0.067	0.3060	0.331	0.2620
Sample Variance	0.025	0.0146	0.019	0.4143	0.004	0.0936	0.109	0.0687
Range	0.425	0.2622	0.411	1.6608	0.167	0.7510	0.766	0.6978
Minimum	0.005	0.0205	0.045	0.0005	0.002	0.0005	0.000	0.0025
Maximum	0.429	0.2827	0.456	1.6613	0.169	0.7515	0.766	0.7003
Confidence Level (95%)	0.167	0.1270	0.146	0.6755	0.070	0.3211	0.347	0.2750

The correlation coefficients between physicochemical variables and metals under scrutiny are given in Table 4-14. In case of TSS, P-value is less than level of significance for Pb, Zn, Cd, Mn and equal to level of significance for Cu which means we can reject H_O for these metals (Equation 3-7). Consequently we accept of H_1 (Equation 3-6) which means that concentrations of above mentioned metals are significantly ($\alpha = 0.05$, $\alpha = 0.01$) correlated with TSS. In case of pH only Cu is significantly correlated while no metal is significantly correlated with TOC.

Table 4-14: Correlation between metals and physicochemical parameters

Parameters		Correlations							
		Pb	**Cr**	**Ni**	**Zn**	**Cd**	**Mn**	**Cu**	**Fe**
TSS	Pearson Correlation	-0.87*	-0.56	-0.71	-0.89*	-0.85*	-0.84*	-0.80**	-0.61
	Significance (2-tailed)	0.02	0.25	0.11	0.02	0.03	0.04	0.05	0.20
pH	Pearson Correlation	-0.49	-0.13	-0.25	-0.31	-0.23	-0.71	-0.93*	-0.05
	Significance (2-tailed)	0.32	0.81	0.63	0.55	0.66	0.11	0.01	0.93
TOC	Pearson Correlation	-0.74	-0.13	-0.74	-0.59	-0.59	-0.61	-0.75	-0.19
	Significance (2-tailed)	0.09	0.80	0.09	0.22	0.21	0.20	0.09	0.22

**Correlation is significant at the 0.01 level (2-tailed), *Correlation is significant at the 0.05 level (2-tailed)

The negative values show that increase in the concentration of a physicochemical parameter will lead to the decrease of metal concentration or vice versa. So, it is evident from Table 4-14 that TSS has relatively better negative correlation with most of the metals under consideration.

Similarly correlation of metal concentrations with each other was also studied and found to be positive as given in Table 4-15. Positive correlation means increase/decrease in the concentration of one metal leads to the increase/decrease in the concentration of the other metal. Correlation between metal concentrations showed that Pb is associated with Ni, Cd and Mn, Zn is associated with Cd and Mn is associated with Cu indicating that increase/decrease in Pb, Zn and Mn will lead to the corresponding increase/decrease in the concentration of Ni, Cd and Mn. As all the correlations are positive so a direct relationship between metals exists. The reason for this fact may be attributed to the intrinsic elemental properties and to the nature of the effluent under study.

Table 4-15: Correlation of metal concentrations with each other

Metals		**Correlations**							
		Pb	**Cr**	**Ni**	**Zn**	**Cd**	**Mn**	**Cu**	**Fe**
Pb	Pearson Correlation	1.00	0.70	0.82*	0.77	0.83*	0.81	0.57	0.37
	Significance (2-tailed)		0.13	0.05	0.07	0.04	0.05	0.23	0.47
Cr	Pearson Correlation	0.70	1.00	0.28	0.68	0.66	0.79	0.38	0.64
	Significance (2-tailed)	0.13		0.59	0.14	0.16	0.06	0.46	0.17
Ni	Pearson Correlation	0.82*	0.28	1.00	0.68	0.81	0.38	0.24	0.18
	Significance (2-tailed)	0.05	0.59		0.14	0.05	0.45	0.65	0.74
Zn	Pearson Correlation	0.77	0.68	0.68	1.00	0.97*	0.72	0.54	0.80
	Significance (2-tailed)	0.07	0.14	0.14		0.001	0.11	0.27	0.06
Cd	Pearson Correlation	0.83*	0.66	0.81	0.97*	1.00	0.65	0.42	0.68
	Significance (2-tailed)	0.04	0.16	0.05	0.00		0.17	0.41	0.14

Metals		Correlations							
		Pb	**Cr**	**Ni**	**Zn**	**Cd**	**Mn**	**Cu**	**Fe**
Mn	Pearson Correlation	0.81	0.79	0.38	0.72	0.65	1.00	0.86*	0.52
	Significance (2-tailed)	0.05	0.06	0.45	0.11	0.17		0.03	0.29
Cu	Pearson Correlation	0.57	0.38	0.24	0.54	0.42	0.86*	1.00	0.40
	Significance (2-tailed)	0.23	0.46	0.65	0.27	0.41	0.03		0.43
Fe	Pearson Correlation	0.37	0.64	0.18	0.80	0.68	0.52	0.40	1.00
	Significance (2-tailed)	0.47	0.17	0.74	0.06	0.14	0.29	0.43	

**Correlation is significant at the 0.01 level (2-tailed), *Correlation is significant at the 0.05 level (2-tailed)

Analysis of variance (ANOVA) showed significant variations in metal concentration between temporal variations as compared to sampling sites for all the metals except Cd (Table 4-16), which is not changing with the time and stations. In case of months p-value is less than α for Pb, Cr, Ni, Zn, Mn, Cu and Fe which means we can reject H_O'' (Equation 3-15) which leads us to the acceptance of H_1'' (Equation 3-10) i.e. months are playing significant role in variation of concentrations of these metals. In case of stations p-value is less than α for Ni, Mn, Cu and Fe which means we can reject H_O' (Equation 3-15) which leads us to the acceptance of H_1' (Equation 3-10) i.e. stations are playing significant role in variation of concentrations of these metals. So, except Cr, Zn and Cd, all metals are changing significantly with change of both stations and months.

Table 4-16: Analysis of Variance (ANOVA) for metals

Variation Sources	Pb	Cr	Ni	Zn	Cd	Mn	Cu	Fe
Months	1.77E-06	0.033	1.7864E-06	6.33253E-11	0.462	0.002	0.0003	0.028
Stations	0.063846	0.325	0.000136271	0.182516329	0.460	0.024	0.0335	0.009

Chapter 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

Faisalabad is one of the many cities of Pakistan where industrial growth remains disorganized. In spite of this, the City is one of the most dynamic areas in the country. It is believed to be the second largest industrial city after Karachi. Till the early 80's, manufacturing growth was mainly concentrated around the center. During last ten years or so, major industrial growth has shifted outwards to areas along the main roads.

Faisalabad is now faced with serious environmental problems of wastewater pollution, which is partly a result of industrial growth. The profile indicates that several industrial sectors are hazardous and are polluting the water resources of the city. Industry is not in a position to undertake pollution control measures due to limited financial resources and technical capacity. Moreover, there is no space for combined treatment facilities in built-up areas. Residential areas for the workforce have followed the location of industry, and in consequence residential and industrial land uses are mixed with serious public health consequences.

Following conclusions can be drawn from the study:

i. Concentrations of most of the metals were within Pakistan National Environmental Quality Standards (NEQS) in the wastewater of Paharang Drain

ii. Most of the physico-chemical parameters of the Paharang Drain wastewater are higher than NEQS which makes it unfit for irrigation purposes.

iii. Wastewater quality deteriorate between sampling *Station#1* and *Station#4* and improved after *Station#4* and beyond *Station#6*

iv. Wastewater quality improves during wet season (July and August) and deteriorates during dry season.

v. Self purification of the drain increases as we move towards the River Chenab.

vi. Concentration of most of the metals is best correlated with TSS.

vii. BOD/COD=0.5, which shows the biological treatment should be preferred over physico-chemical treatment.

5.2 RECOMMENDATIONS

5.2.1 Combined Treatment plants

As Pakistan is a developing country and cannot afford to construct plant for individual industries. It would be much wiser if combined effluent treatment plants are constructed for a cluster of industries to make the solution according to the economies of the scale.

5.2.2 Cleaner Production Programme

In addition to the combined treatment plants, a cleaner production programme for textile processing should be initiated. This programme could be implemented quickly to address pollution problems of this sector. Experience in other countries suggests that 30-40 percent improvement in water consumption and pollution levels could be achieved with relatively small investment. This programme could start with a limited number of units and then gradually be extended to others with the help of trained staff.

5.2.3 Proper Planning

Environmental problems associated with industrial growth can be best addressed, on long term basis, by preparing an integrated Geographic Information System (GIS) based land use plan for different areas, including Faisalabad. The pollution potentials of different industrial sectors and the increasing volumes of industrial wastewater should be taken into consideration in the plan. This plan should include a decentralization policy that promotes a shift of industries to locations which are suitable for industrial operations (availability of road infrastructure, access to markets, etc.) but where it is possible to keep industrial activities separate from residential areas. The development of industrial zones, based on a well-considered land-use plan, could attract foreign investment from which both industrial growth and environmental management could benefit.

Based on the findings of the study following steps should be taken to avoid the adverse impacts of the drain water:

i. Feasibility for the installation of weirs may be looked at as a cheap way of treatment. The efficiency of this method should be studied.
ii. Apart from constructing a new treatment plant, the existing plant should be made more efficient or may be converted into an aerated lagoon.

iii. Industries should be supported to comply with the NEQs and new industries should be established only after installing a treatment plant.

iv. The industries should be regularly monitored

v. Government should arrange seminars/workshops etc. to create awareness among people

Chapter 6

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APPENDICES

APPENDIX A: Concentration (ppm) of metals at each station using FAAS

Stations	3/7/2008	4/8/2008	30/8/08	9/10/2008	17/11/2008	24/12/08
Pb						
S1	0.452	0.397	0.473	0.411	0.531	0.31
S2	0.001	0	0.648	0.008	0.002	0
S3	0.003	0	0.013	0.004	0.007	0
S4	0.040	0.043	0.131	0.078	0.082	0.097
S5	0.0597	0.032	0.091	0.095	0.087	0.061
S6	0.221	0.174	0.387	0.298	0.301	0.258
Cr						
S1	0.151	0.008	0.174	0.147	1.113	0.103
S2	0.194	0.187	0.435	0.324	0.287	0.235
S3	0	0	0.112	0.007	0.004	0
S4	0	0	0.133	0.101	0.009	0.112
S5	0.003	0.001	0.004	0.126	0.008	0
S6	0.100	0.078	0.176	0.160	0.162	0.155
Ni						
S1	0.451	0.420	0.487	0.441	0.523	0.411
S2	0.000	0.000	0.256	0.009	0.005	0.000
S3	0.000	0.000	0.334	0.281	0.276	0.243
S4	0.000	0.000	0.351	0.287	0.286	0.346
S5	0.148	0.007	0.152	0.204	0.171	0.143
S6	0.000	0.005	0.413	0.403	0.401	0.387
Zn						
S1	1.743	1.334	1.874	1.621	2.110	1.286
S2	0.008	0.003	1.333	0.841	0.083	0.012
S3	0.000	0.000	0.009	0.005	0.002	0.000
S4	0.000	0.000	0.003	0.000	0.000	0.000
S5	0.378	0.221	0.384	0.453	0.313	0.265
S6	0.000	0.000	0.007	0.001	0.002	0.000
Cd						
S1	0.004	0.001	0.006	0.001	1.001	0.000
S2	0.000	0.000	0.084	0.002	0.000	0.000
S3	0.000	0.000	0.008	0.005	0.002	0.000
S4	0.000	0.000	0.007	0.000	0.000	0.003
S5	0.000	0.000	0.005	0.007	0.003	0.001

Stations	3/7/2008	4/8/2008	30/8/08	9/10/2008	17/11/2008	24/12/08
S6	0.000	0.000	0.008	0.007	0.005	0.008
Mn						
S1	0.871	0.52	0.905	0.743	1.234	0.236
S2	0.000	0.000	1.746	0.961	0.441	0.009
S3	0.000	0.000	0.004	0.001	0.000	0.000
S4	0.000	0.000	0.002	0.000	0.000	0.001
S5	0.397	0.109	0.411	0.603	0.522	0.391
S6	0.003	0.008	1.040	0.787	0.909	0.406
Cu						
S1	0.851	0.321	1.003	0.613	1.113	0.118
S2	0.000	0.000	1.472	0.941	0.009	0.002
S3	0.000	0.000	0.003	0.002	0.001	0.000
S4	0.000	0.000	0.001	0.000	0.000	0.000
S5	0.801	0.310	0.843	0.951	0.893	0.798
S6	0.205	0.153	0.886	0.703	0.786	0.536
Fe						
S1	0.732	0.304	1.011	0.521	1.511	0.123
S2	0.000	0.000	2.000	1.001	0.330	0.000
S3	0.000	0.000	0.273	0.241	0.213	0.000
S4	0.000	0.000	0.877	0.317	0.306	0.407
S5	0.170	0.000	0.552	1.003	0.771	0.000
S6	0.000	0.001	0.008	0.002	0.004	0.000

APPENDIX B: Concentration (ppb) of metals at each station using ICP-OES

Stations	3/7/2008	4/8/2008	30/8/08	9/10/2008	17/11/2008	24/12/08
	Pb					
S1	542.841	436.104	588.304	380.000	480.200	298.610
S2	30.654	10.231	728.083	10.300	5.200	1.350
S3	40.591	10.887	10.334	6.100	3.410	0.000
S4	40.008	38.325	10.045	53.200	62.300	89.400
S5	78.005	34.235	120.256	75.400	71.800	55.980
S6	331.087	186.546	365.085	310.100	291.500	220.700
Cr						
S1	148.552	61.203	154.486	135.55	1201.77	119.08
S2	220.048	192.004	398.087	347.21	235.7	243.65
S3	5.001	5.021	15.025	11.3	7.08	5.04

Stations	**3/7/2008**	**4/8/2008**	**30/8/08**	**9/10/2008**	**17/11/2008**	**24/12/08**
S4	4.084	3.845	156.004	120.74	10.002	120.47
S5	5.007	13.048	48.612	170.3	7.501	3.01
S6	17.001	86.009	165.430	150.600	155.080	160.070
Ni						
S1	472.004	394.052	601.032	471.361	537.460	420.440
S2	2.543	2.001	284.065	11.040	9.040	1.050
S3	4.002	4.005	285.512	264.320	280.090	266.990
S4	2.301	2.087	312.221	301.780	290.440	330.550
S5	132.087	6.004	187.387	200.008	190.610	161.560
S6	2.898	4.387	561.068	421.350	397.480	391.360
Zn						
S1	1643.754	1446.055	2013.086	1647.087	2136.050	1305.110
S2	87.455	30.246	1275.366	871.100	78.450	18.090
S3	8.006	7.088	99.690	7.840	5.010	5.030
S4	4.056	2.575	31.088	1.360	3.066	2.047
S5	364.089	254.333	409.058	471.600	303.010	281.300
S6	4.681	6.056	8.067	5.030	5.130	1.077
Cd						
S1	6.077	11.104	8.004	3.040	1005.014	2.001
S2	2.110	1.984	89.660	4.120	5.012	1.040
S3	2.004	2.840	10.008	7.036	1.004	1.360
S4	4.031	3.008	9.086	2.087	5.012	5.007
S5	2.804	2.008	6.342	9.060	7.140	8.080
S6	2.060	3.051	9.005	10.850	8.003	3.070
Mn						
S1	901.894	584.078	1003.008	761.08	1223.45	221.06
S2	3.041	1.005	1969.088	1005.01	446.33	11.55
S3	2.004	2.407	47.707	2.710	2.010	1.340
S4	11.004	16.004	24.378	1.004	1.068	3.013
S5	400.087	118.806	409.709	611.311	536.460	401.540
S6	34.008	78.444	1045.004	758.660	921.340	411.630
Cu						
S1	801.047	341.007	1017.001	631.050	1223.410	123.001
S2	8.001	5.008	1351.002	957.080	11.030	5.320
S3	3.045	2.087	36.085	3.001	3.450	1.110
S4	2.034	4.008	11.110	1.080	1.080	1.201
S5	846.321	344.540	874.085	1010.500	905.070	809.880
S6	236.405	182.072	911.004	711.008	758.080	547.080

Stations	3/7/2008	4/8/2008	30/8/08	9/10/2008	17/11/2008	24/12/08
Fe						
S1	774.508	341.052	1087.749	533.61	1521.58	136.08
S2	4.005	3.054	209.369	1010.54	341.52	1.201
S3	6.406	5.088	301.807	262.31	223.66	1.032
S4	2.060	7.021	901.508	331.08	321.55	415.08
S5	2.004	2.853	581.085	1009.87	789.69	1.3
S6	2.064	14.002	98.063	3.041	7.302	1.804

APPENDIX C: Concentration (mg/Kg) of metals in the benthic soil

Stations	July	August	September	October	November	December
Fe						
S1	121606	126477	119564	121606	126477	119564
S2	83764	80742	85747	83764	80742	85747
S3	76383	71211	70586	76383	69961	69336
S4	76233	70890	79303	76233	70890	79303
S5	92145	88436	90123	92145	91810	93497
S6	87321	78941	81054	76172	73038	69905
Cu						
S1	BDL	BDL	BDL	BDL	BDL	BDL
S2	40	109	76	40	109	76
S3	626	601	588	626	575	562
S4	BDL	41	67	BDL	41	67
S5	BDL	BDL	BDL	BDL	BDL	BDL
S6	BDL	BDL	BDL	BDL	BDL	BDL
Mn						
S1	1179	1218	1380	1179	1218	1380
S2	831	787	916	831	787	916
S3	691	658	602	691	546	490
S4	1011	929	987	1011	929	987
S5	1476	1235	1047	1476	859	671
S6	1023	982	962	928	897.5	867
Cd						
S1	6848	4775	7601	6848	4775	7601
S2	6918	7341	5412	6918	7341	5412
S3	BDL	BDL	BDL	BDL	BDL	BDL

Stations	**July**	**August**	**September**	**October**	**November**	**December**
S4	3507	23.076	2770	3507	23.076	2770
S5	186	159	121	186	83	45
S6	101	89	65	49	31	13
Zn						
S1	375	325	411	375	325	411
S2	374	358	433	374	358	433
S3	432	402	440	432	478	516
S4	483	451	647	483	451	647
S5	862	877	861	862	845	829
S6	768	706	794	782	795	808
Ni						
S1	170	183	230	170	183	230
S2	168	359	215	168	359	215
S3	142	135	124	142	113	102
S4	249	66	567	249	66	567
S5	636	601	588	636	575	562
S6	560	534	508	482	456	430
Cr						
S1	401	415	410	401	415	410
S2	768	701	700	768	701	700
S3	1902	2010	1874	1902	1738	1602
S4	605	587	802	605	587	802
S5	701	658	697	701	736	775
S6	608	536	489	425	366	306
Pb						
S1	BDL	BDL	BDL	BDL	BDL	BDL
S2	BDL	BDL	87	BDL	BDL	87
S3	66	60	58	66	56	54
S4	146	81	3	146	81	3
S5	963	921	911	963	901	891
S6	901	851	802	752	703	653

APPENDIX D: Concentrations (mg/l) of physicochemical parameters at each station of Paharang Drain

Parameters	**3/7/2008**	**4/8/2008**	**30/08/08**	**9/10/2008**	**17/11/08**	**24/12/2008**
Station#1						
Sulphate	130	460	720	700	340	540
Chloride	2710	769.76	1520	919.72	769.76	649.4
DO	0.065	0.7	0.08	0.17	0.89	1.02
TOC	64.8	38.7	64.1	129	76.2	156
TDS	3830	2040	3240	2380	2420	3120
TSS	131	132	64	145	52	124
COD	422	608	337.9	610.88	265.0	560.0
Flow (MGD)	3.09	16.8	4.94	2.3	5.05	3.86
Temperature (^{o}C)	38.2	30.3	33.9	34.2	17.8	26.6
Conductivity(mS/cm)	5.22	3.94	6.48	4.72	4.66	5.68
pH	8.6	8.86	8.47	8.76	8.18	9.05
Turbidity (NTU)	26.9	93	21	52	12.8	38.4
BOD (mg/L)	142	74.5	80	320	119.39	357
TN (mg/L)	22.1	7.65	9.5	20	7.34	48.7
TP (mg/L)	24	3	15.2	24	12	24
Oil & Grease (mg/L)	23.4	34.5	18.3	54	42	24
Station#2						
Sulphate	440	300	430	480	460	425
Chloride	785	779.75	1200	1060	1059.67	858.2
DO	0.68	0.64	0.13	0.12	0.76	1.36
TOC	126	134.5	195.5	158	189.5	214.4
TDS	2820	2270	2760	2880	2820	2865
TSS	187	190	382	345	468	346
COD	521	625	619.52	690.56	529.4	640.0
Flow (MGD)	13.08	30.45	1 2.76	16.91	22.86	6.78
Temperature (^{o}C)	39.2	33.9	34.2	35.3	32.6	30.6
Conductivity(mS/cm)	5.36	4.32	5.53	5.75	5.34	5.42
pH	9.6	9.8	7.7	8.6	8.86	9.25
Turbidity (NTU)	125.5	400	180	125	119	184
BOD (mg/L)	309	247	252	389.76	332	293.5
TN (mg/L)	74.7	74.71	56.9	93	78.9	72.6
TP (mg/L)	11	8.6	25.6	30	25	36

Parameters	**3/7/2008**	**4/8/2008**	**30/08/08**	**9/10/2008**	**17/11/08**	**24/12/2008**
Oil & Grease (mg/L)	38.7	36.5	31.3	67	56	34
Station#3						
Sulphate	405	260	470	500	440	460
Chloride	825	639.8	1040	1280	1039.68	985.5
DO	0.6	0.55	0.26	0.16	0.6	0.78
TOC	108	95	172.4	165	190.3	223.5
TDS	2980	1872	2890	2900	2780	2984
TSS	378	414	402	367	384	384
COD	527	416	647.68	610	529.4	640.0
Flow (MGD)	19.09	68.05	21.93	22.71	34.72	16.34
Temperature (^{o}C)	38.9	31.5	35.6	35.1	31.5	32.7
Conductivity(mS/cm)	5.69	3.07	5.81	5.92	5.29	5.69
pH	9.4	9.8	8.44	8.74	8.8	9.46
Turbidity (NTU)	131.7	330.0	227.0	157.0	197.0	244.0
BOD (mg/L)	329.0	238.0	251.0	268.7	366.3	338.0
TN (mg/L)	72.5	31.1	74.6	86.0	65.8	75.6
TP (mg/L)	15.0	8.2	29.6	16.0	36.0	22.0
Oil & Grease (mg/L)	70.8	54.6	66.7	78.0	70.0	54.0
Station#4						
Sulphate	550	320	450	490	490	412
Chloride	880	819.75	860	1200	1019.69	1086.7
DO	0.53	0.6	0.17	0.14	0.97	1.04
TOC	91.7	95.5	137.5	141	196.2	216.5
TDS	3120	1934	2890	3240	2810	2768
TSS	408	430	292	338	300	324
COD	511	352	492.36	478.08	496.3	600.0
Flow (MGD)	29.8	84.75	43.3	31.75	44.4	32.46
Temperature (^{o}C)	36.4	31.3	35	35.1	30.8	29.8
Conductivity(mS/cm)	5.92	3.73	5.82	6.48	5.54	5.43
pH	9.85	9.84	8.68	9.04	9.21	8.95
Turbidity (NTU)	81.3	130	177	138	158	224
BOD (mg/L)	257	184	269	198	334.94	303.12
TN (mg/L)	80.3	49.7	69.1	57	93.6	64.3
TP (mg/L)	14.5	8.2	21.6	21	29	18
Oil & Grease (mg/L)	47.9	63.3	50.3	54	64	46
Station#5						

Parameters	**3/7/2008**	**4/8/2008**	**30/08/08**	**9/10/2008**	**17/11/08**	**24/12/2008**
Sulphate	550	320	440	390	420	395
Chloride	805	629.8	799	999.7	1079.66	647.4
DO	0.42	0.54	0.17	0.11	0.98	1.42
TOC	64.3	56.1	88.3	146	162.6	124.6
TDS	2800	1920	2720	2720	2750	2648
TSS	210	264	318	267	240	168
COD	499	352	422.4	424.96	463.2	520.0
Flow (MGD)	101.5	161.2	68.1	94.14	96.83	64.45
Temperature (^oC)	36.3	27.9	35	31.8	26.3	24.7
Conductivity(mS/cm)	5.33	3.65	5.44	5.46	5.24	5.23
pH	8.44	8.9	8.37	8.11	8.24	8.46
Turbidity (NTU)	57	127	101	75	66.4	78
BOD (mg/L)	332	220	199	175	224.69	304.2
TN (mg/L)	63	25.6	40.2	74	55.3	45.4
TP (mg/L)	14	9.6	12.4	20	22	16
Oil & Grease (mg/L)	42.3	37	47.3	46	38	24
Station#6						
Sulphate	550	290	430	550	480	345
Chloride	980	719.78	780	979.69	909.72	640
DO	0.46	0.15	0.16	0.13	0.96	1.23
TOC	78.5	70.5	100.7	130	157.2	118.4
TDS	2830	1926	2770	2800	2800	2678
TSS	288	298	338	278	242	184
COD	549	384	380.4	478.08	476.2	480.0
Flow (MGD)	105.5	179.97	70.25	99.64	106.45	71.23
Temperature (^oC)	36.5	27.7	35.3	31.6	26.3	24.3
Conductivity(mS/cm)	5.38	3.73	5.56	5.62	5.32	5.32
pH	8.76	8.93	8.21	8.34	8.3	8.42
Turbidity (NTU)	81.1	130.0	72.3	75.0	87.9	82.0
BOD (mg/L)	390.0	209.0	189.0	198.8	296.4	232.4
TN (mg/L)	68.5	35.6	39.1	64.0	53.8	42.6
TP (mg/L)	19.0	12.6	18.0	22.0	18.0	14.0
Oil & Grease (mg/L)	65.8	42.0	81.0	59.0	42.0	32.0