SURFACE WATER QUALITY AND BENTHIC SOIL STUDY OF LEH NULLAH

By

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This is to certify that the

Thesis entitled

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Submitted by

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Has been accepted towards the partial fulfillment

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Faisal Hussain

APPROVAL SHEET

Certified that the contents and form of thesis entitled "Surface Water Quality and Benthic Soil study of Leh Nullah" submitted by Mr. Faisal Hussain 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.

Faisal Hussain

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LIST OF ABBREVIATIONS

AAS	Atomic absorption spectroscopy
BCF	Bio-concentration factor
BOD	Biochemical oxygen demand
COD	Chemical oxygen demand
EPA	Environmental protection agency
EPD	Environmental protection department

FAAS	Flame atomic absorption spectroscopy
I_{geo}	Geoaccumulation index
MGD	Million gallons per day
NEQS	National environmental quality standards
PCRWR	Pakistan council for research of water resources
TDS	Total dissolved solids
TOC	Total organic carbon
TP	Total Phosphorous
TSS	Total suspended solids
WASA	Water and Sanitation Agency

ABSTRACT

Heavy metals, in any stream are a damaging factor for the aquatic biota which naturally ingest the organic matter present in that stream. Also the presence of heavy metals in any stream decreases its self purification capacity. Samples from Leh Nullah, Rawalpindi/Islamabad, one of the major carriers of combined industrial and municipal effluents, were collected from six different locations between Katarian and Chaklala from September 2012 to April 2013. The objective was to study the temporal and spatial variations in the concentration of heavy metals in stream water as well as in the benthic soil of Leh Nullah. Metals selected for scrutiny were Cr, Ni, Cd, Mn, Zn, Cu, Fe, Pb, As and Hg, however preliminary results revealed that only Fe, Pb, Cd and Zn were available in both the surface water and the benthic zone. 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). Concentrations of some metals in the Leh Nullah waste water were found below or in some cases marginally exceeding Pakistan National Environmental Quality Standards (NEQS). In addition, correlation between metals concentration in the surface water, metals concentration in the benthic soil and other physicochemical parameters such as pH, total suspended solids and Electrical Conductivity etc. were investigated. Geoaccumulation indices of selected metals were also assessed for benthic soil of the nullah. Significant correlation was found between metal concentrations and Electrical Conductivity (EC) in the water environments. Metal concentrations were found to be more sensitive to temporal variations than spatial ones. Moreover, major sources of heavy metals in the nullah were identified. Mass loading of metallic pollutants running into Soan River was calculated and possible pretreatment system for industries discharging heavy metals in their effluent was proposed so that metal concentration in the nullah water could be reduced in future.

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Chapter 1

INTRODUCTION

1.1 BACKGROUND

Following the industrial development combined with rapid growth of population has inflicted ever-increasing demand on natural resources and caused adverse effects on the environments in most of the developing countries. Due to vastly practiced industrialization system, water consumption has also increased many folds.

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

Islamabad, the capital of Pakistan, is a planned city constructed in 1961 at the foot of the Margala Hills just north of the old city of Rawalpindi. Rapid growth of both Islamabad and Rawalpindi to a combined population near 1.4 million has made ever-increasing demands on natural resources and caused adverse effects on natural water stream such as Leh Nullah. In the present scenario, due to increased population and industrialization, Leh Nullah mainly carries the industrial and municipal effluents that are ultimately delivered to the Soan river.

1.2 STUDY AREA

Rawalpindi/Islamabad, with an estimated population of 1.4 million lies between longs 72°45′ and 73°30′ E. and lat. 33°30′ and 33°50′ N. Islamabad is the national capital and the hub for all governmental activities. Rawalpindi is an older and much larger city and is a center of industrial, commercial, and military activity.

The Soan and Kurang Rivers are the main water ways draining the area. Their primary tributaries are the Ling River, draining northwestward into the Soan; Gumreh Kas, draining westward into the Kurang from the area between the Kurang and Soan; and Lai Nullah, draining southward into the Soan from the mountain front and urban areas. The Kurang and Soan Rivers are dammed at Rawal and SimLy Lakes, respectively, to supply water for the urban area. Leh Nullah carries most of the liquid waste from Rawalpindi/Islamabad and contributes greatly to the pollution of the Soan River. (Iqbal, 2010). Traditionally, 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 (Revised National Environmental Quality Standards, 1999). Whilst most of the industries discharge their effluents untreated,a small fraction of industries however discharge their effluents untreated into streams or canals after retention period of some hours in stabilization pond without any secondary or tertiary treatment (Aslam *et al*., 2011).

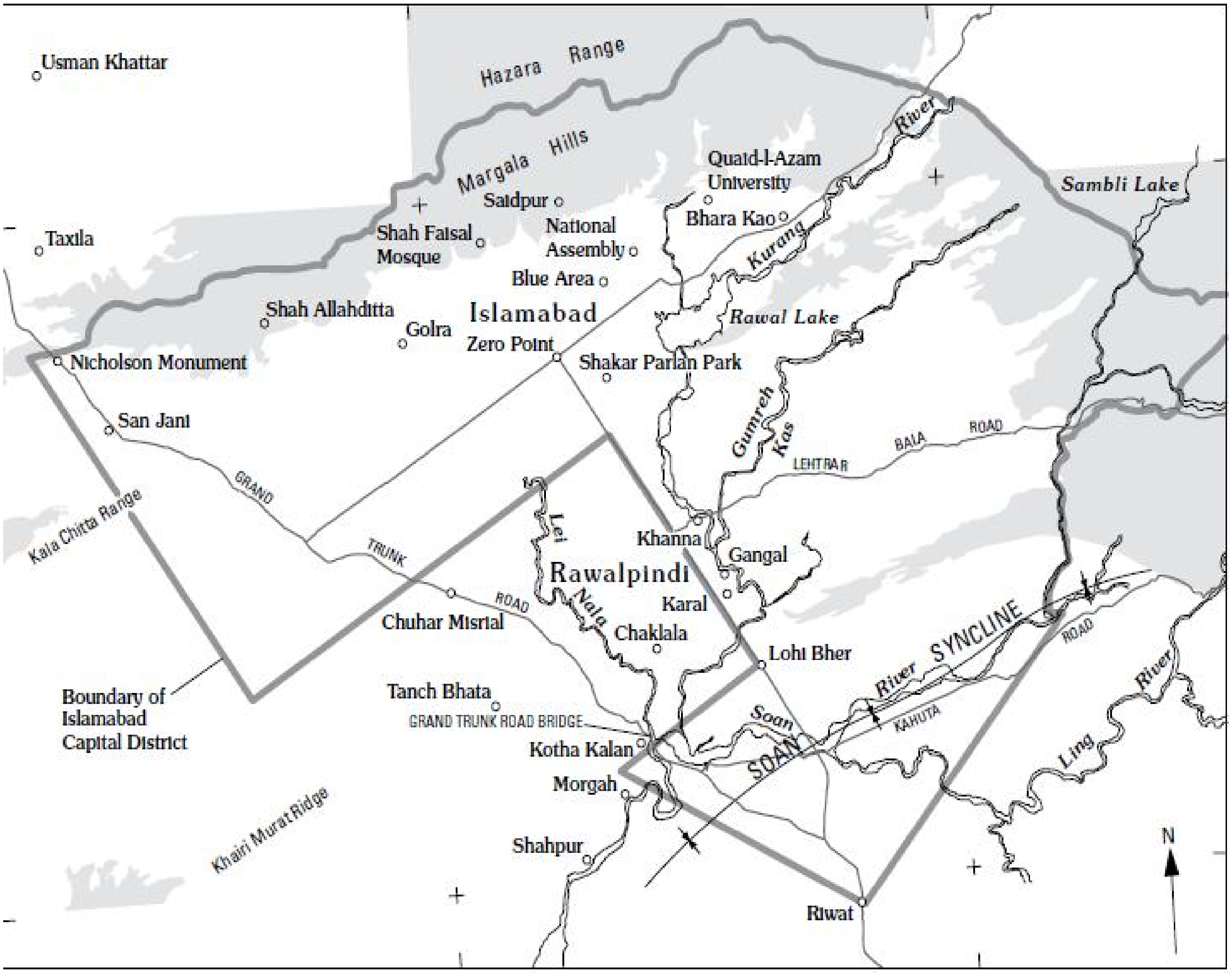


Figure 1.1: Location map for Leh Nullah Study area (Iqbal M. Sheikh, Environment Geology of Rawalpindi/Islamabad, 2010)

The sewerage system of Islamabad and Rawalpindi was laid down in early sixties is now badly damaged, blocked and undersized. Open drains passing through the Rawalpindi city are used for storm water runoff, solid waste and sewage disposal. Solid waste disposal into manholes are causing sewer blockage problems, and environmental degradation. The existing sewerage system of Rawalpindi is in extremely poor condition and needs extensive rehabilitation (Hashmi,. 2009).

1.3 THE PROBLEM

As all metals are a part of the 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 water resources and soil by these metals and uptake by some crops is a major concern because of their toxicity, persistence and non-degradable nature.

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*. (2011) high concentrations of metals in industrial 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 Water and Sanitation Agency (WASA), Rawalpindi, approximately 400 small and large industries, battery shops and car paint workshops are operating in Rawalpindi/Islamabad city on both sides of Leh including those in residential localities.

These units discharge untreated effluent containing high levels of paints, steel industries effluents, old battery shops effluents and organic material (Ashfaq *et al*., 2010) directly into municipal sewers and ultimately drain into the Leh Nullah. These effluents may also damage the aquatic life and ecosystem of the Soan River.

It has been found that a number of inhabitants living on the banks of Leh Nullah are suffering from different diseases related to digestive system (Diarrhea, Dysentery etc.) which is the indirect effect of the use of polluted ground water for drinking as well as the direct exposure to the wastewater (Mahmood and Maqbool, 2006).

The above discussion ascertains that Leh Nullah wastewater is transmitting contamination to the Soan River and causing different diseases in human population of the area. This study focused on the characterization of the Leh water and its benthic soil with focus on metallic pollutants.

1.4 OBJECTIVES OF THE STUDY

Following were the major objectives of this study:

- To investigate the spatio-temporal variations of metals in the Leh Nullah wastewater

- To develop a correlation between metals in Leh Surface water to metals in benthic zone and other physicochemical parameters
- To Identify major sources of heavy metals in Leh Nullah and propose a possible pretreatment system for industries.

1.5 APPROACH

Wastewater and soil samples were collected, preserved and analyzed using Flame Atomic Absorption Spectrometry (FAAS). A spectrophotometer was employed to measure the amount of light that a sample absorbs. The instrument operated by passing a beam of light through a sample and measuring the intensity of light reaching a detector. FAAS consisted of hollow cathode, since each element has a characteristic wavelength, the metal of the cathode lamp must be the same as present in the test sample. The atomizer-burner than converts the metal present in the sample (solution) into free atoms in Acetylene Air Flame. The light passing through the sample is dispersed in the monochromator into its component wavelengths. Slit allows the absorbed light to pass through it only and filters out others. Photocell detector then detects and amplifies the selected light and also measures the amount of light absorbed by the atomized metal atoms in the flare.

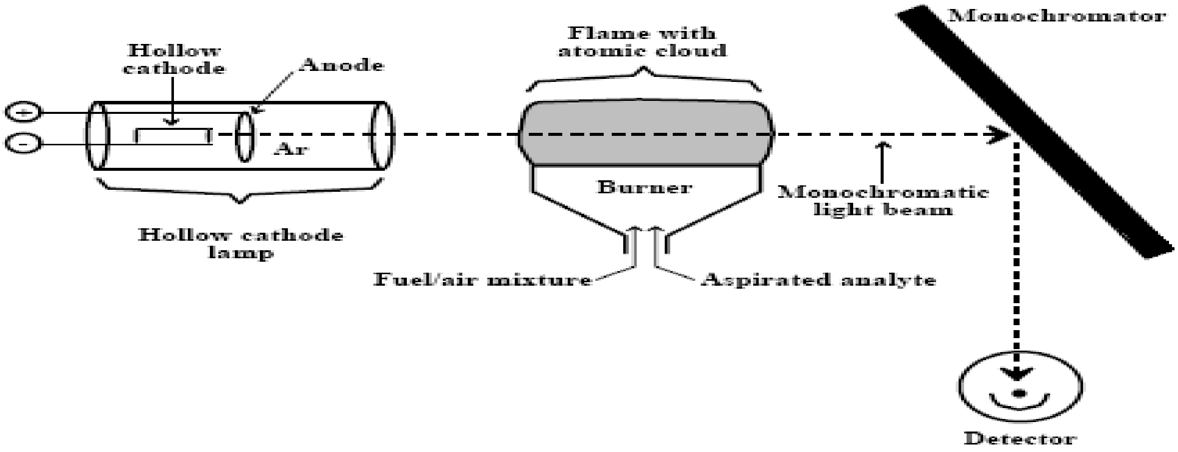


Figure 1.2: Schematic Diagram of Flame Atomic Absorption Spectrophotometer (Varian AA240, Biotech USA).

1.6 SIGNIFICANCE OF THE STUDY

- The study would provide a complete chemical profile of the nullah along with seasonal variations
- It would give a clear picture to devise a treatment terrain.
- 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.

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, 2009). 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. Fe is classified as Hard

Metal, Cu (I), Ag, Cd, Hg, Pb (II) as Soft Metals and Cr, Mn, Fe (II), Co, Ni, Cu (II), Zn, Pb (IV) are Borderline Metals (Hashmi,. 2009).

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

2.1 BASELINE DEVELOPMENT

Various national and international studies have been conducted to find out how metallic pollution is determined in streams, carrying industrial effluents.

Sr #	Brief title of study	Drain	Research Focus	Conducted by	Year	Outcome
1	Characterization of metallic pollutants in Paharang Drain, Faisalabad	Paharang drain, Faisalabad	Heavy Metals	Ghulam Mustafa	2009	Faisalabad is now facing serious environmental problems of waste water pollution which is partly as a result of industrial growth. The monthly levels of the metal concentrations and the mean metal concentration at six sampling stations showed that Cr> Fe >Cu>Pb>Zn> Cd >Ni
2	Concentration of Fe, Cu, Cr, Zn and Pb in Makera – Drain, Kaduna, Nigeria	Makera Drain, Kaduna, Nigeria	Heavy Metals	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. 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

Sr #	Brief title of study	Drain	Research Focus	Conducted by	Year	Outcome
3	Physicochemical Determination of Pollutants in Wastewater and Vegetable Samples along the Jakara Wastewater Channel.	Jakara Waste water Channel, Nigeria	Heavy Metals	Dakan *et al*.	2008	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.
4	Metal contamination in Nullah Dek water and accumulation in rice	Pindi Bhattian (Pakistan)	Heavy Metals, Residual Sodium Carbonate (RSC),and sodium adsorption ratio (SAR)	Plant Nutrition Division, Soil Salinity Research Institute	2007	The results showed that the concentration of all the metals analyzed especially Cu, Mn, Cd and Sr was within the safe limits or NEQS.
5	Spatio-temporal changes in water quality of Nullah Aik, a tributary of the Chenab River, Pakistan.	Chenab River, Pakistan	Heavy Metals	Qadir et al.	2008	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
6	Seasonal variation of pH, dissolved oxygen, trace metals (Fe, Zn, Cd, and Pb) in surface and bottom water of El Rahaway drain,River Nile	Rahaway drain River Nile,Egypt	Heavy Metals	Badar *et al*.	2006	The 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.
7	Heavy Metals in Three Lakes in West Poland	Drain in Southwest of Pozan,West Poland	Heavy Metals	Department of Ecology and Nature Protection, Wrocław University Poland	1999	Analyses of water and bottom sediments indicated that the lakes were polluted with Zn, Cd, Cu, and Pb and partly with Ni and Hg.

2.2 ESTIMATION OF METALLIC POLLUTANTS IN INDUSTRIAL WASTEWATERS

Sr #	Brief title of study	Location	Research Focus	Conducted by	Year	Outcome
1.	Analytical Methods for the Determination of Heavy Metals in the Textile Industry.	Vilnius University, Naugarduko Vilnius, Lithuania	Analytical procedures for metals in industrial effluents	Zeiner *et al*	2007	The advantages and disadvantages of various analytical techniques such as Thin Layer Chromatography (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 TLC can be applied as a fast screening method prior to ICP-OES or GFAAS measurements.
2.	Determination of heavy metals in industrial wastewaters and their influence on activated sludge biocenose	Bratislava, Slovak Republic	Metals in industrial wastewaters and studied their influence on activated sludge	Frank and Harangozo	1994	Radionuclide X-ray fluorescence method with a Si/Li semiconductor detector and pu238 exciting source was used for the determination of Cr, Fe, Ni, Cu, and Zn content in industrial wastewaters
3.	Analytical study of heavy metals of industrial effluents at Jaipur, Rajasthan (India)	Jaipur, Rajasthan (India)	Heavy metals in industrial wastewater	V, S and CP	2006	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.
4.	Characterization of textile industries effluents in Kaduna, Nigeria and pollution implications.	Kaduna, Nigeria	Heavy metals	Yusuff, R. O., and Sonibare, J. A.	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
5.	Characterization Distribution and Comparison of Selected Metals in Textile Effluents, Adjoining Soil and Groundwater.	Hattar Industrial Estate, NWFP, Pakistan	Heavy metals	Manzoor et al.	2006	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

S#	Brief title of study	Location	Research Focus	Conducted by	Year	Outcome
6.	Detection of Toxic Metals in Waste Water from Dairy Products Plant Using Laser Induced Breakdown Spectroscopy. Bull Environ Contam Toxicol, 80, 561-565.	Dharan,Saudi Arabia	Heavy Metals	Hussain, T., and Gondal, M. A	2008	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. (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.
7.	Metals Contamination through Industrial Effluent to Irrigation Water and Soil in Korangi Area of Karachi (Pakistan)	Korangi Area of Karachi, Pakistan	Heavy Metals	Saif et al.	2005	Heavy metals detected in Industrial effluentrs were Zn, Cu, Fe, Mn and Cd, Cr,Ni and Pb respectively. Out of all these metals Pb was found to exxceed NEQS by 36%,Cd by 21% and Ni by 4%.Rest all the other metals exceeded NEQS by 4%.
8.	Assessing Pollution Levels in Effluents of Industries in City Zone of Faisalabad, Pakistan.	Faisalabad, Pakistan	Physico chemical and heavy metal analysis	Hanif *et al.*	2005	Effluents from seven industries were investigated 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
9.	Quality of Effluents from Hattar Industrial Estate	Hayatabad Industrial Estate, Peshawar, Pakistan	Heavy metals and physicochemical analysis	Sial et al.	2006	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.

2.3 DETERMINATION OF METALLIC POLLUTANTS IN MUNICIPAL EFFLUENTS

S#	Brief title of study	Location	Research Focus	Conducted by	Year	Outcome
1.	Effluent analysis in analytical chemistry: an overview. Anal Bioanal Chem, 382, 978-991	University of Malaga, Spain	Effluent analysis in analytical chemistry A review	Rojas and Ojeda	2005	In this review paper Rojas and Ojeda 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.
2.	Determination of Cu, Zn, Fe, Ni and Pb in europia by ICP-AES after preconcentration by saccharomycete immobilized on silica gel	Center of Analysis and Test; Shanxi Normal University, China	Determination of Cu, Zn, Fe, Ni and Pb in europia by ICP-AES	Fan Zhefeng, Jin Xiaotao	2002	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%.
3	Determination of physicochemical parameters and trace metal contents of drinking water samples in Akure Nigeria	Akure Nigeria	physicochemical parameters and trace metal contents of drinking water	Abulude et al.	2007	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.
4	Factors affecting the distribution of heavy metals in wastewater treatment processes: role of sludge particulate.	China	Metals in municipal wastewater treatment plants as a function of several parameters including pH, COD, ionic strength and SS.	Huang and Wang	2001	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. Correlation between metal distributions (as the ratio between dissolved to total metals) and wastewater characteristics were attempted. Correlation between the parameters monitored and metal distribution was poor. Metal distribution relies almost entirely on the concentration of solids in wastewater samples.

S#	Brief title of study	Location	Research Focus	Conducted by	Year	Outcome
5	Wastewater of Gaza, chemistry and management approach. Water for Life in the Middle East,	Turkey, Antalya	Metals in domestic wastewater	Shomar et al.	2004	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

S#	Brief title of study	Location	Research Focus	Conducted by	Year	Outcome
1.	Determination of Cr, Pb and Ni in water, sludge and plants from settling ponds of a sewage treatment works	South Africa	Determination of Metals in the Waste water, plants and sludge using an inductively coupled plasma-mass spectrometer (ICP-MS)	Moodley et al.	2007	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.
2.	Determination of heavy metals at sub-ppm Levels in seawater and dialysis solutions by FAAS after Tetrakis(pyridine)-nickel(II)bis(thiocyanate) co-precipitation	Erciyes University, Kayceri, Turkey	Determination of heavy metals at sub-ppm Levels in seawater	Sahin et al	2008	The results showed that 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 <2.44 µg/L, respectively.

S#	Brief title of study	Location	Research Focus	Conducted by	Year	Outcome
3	Determination of trace metals in waters by FAAS after enrichment as Metal-HMDTC complexes using Solid Phase Extraction.	Korea	Determination of trace metals in waters by FAAS	Tokahoglu et al.	2002	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.
4	Evaluation of some heavy metals in water, sediment and fish samples from River Nile (Kafr El-Zyat city)	River Nile Kafr El-Zyat city Egypt	Evaluation of some heavy metals in water, sediment and fish samples from river	Daifullah et al	2003	They determined iron, manganese, zinc, copper, lead and cadmium in water samples collected from surface and bottom layers of River Nile using atomic absorption spectrophotometer (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.
5.	Determination of some trace metal levels in Asa River using AAS and XRF techniques.	Asa River (Nigeria)	Trace metal levels	Eletta et al.	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.

S#	Brief title of study	Location	Research Focus	Conducted by	Year	Outcome
6.	Determination of heavy metal pollution with environmental physicochemical parameters in waste water of Kocabas Stream (Biga, Canakkale, Turkey) by ICP-AES	Biga, Canakkale, Turkey	Heavy metal pollution with environmental physicochemical parameters in waste water	Yayıntas et al.	2007	The results of metal concentrations in waste water were found between 0.00001–77.69610 mg/l by the ICP-AES technique.
7	Quality of Effluents from Hattar Industrial Estate.	Haripur, Punjab, Pakistan	To compare the effects of irrigation water with 100% canal water, 50% wastewater (conjunctive) and 100% wastewater on groundwater quality	Sial et al	2005	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.
8	Evaluation of irrigation water for heavy metals of Akbarpura area of NWFP, Pakistan	Nowshera NWFP, Pakistan	Metal contents of irrigation water	Nazif et al.	2006	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.
9.	Heavy metals in water of the San Pedro River in Chihuahua, Mexico and its potential health risk.	San Pedro River in Chihuahua, Mexico	The seasonal and downstream water quality variations of the San Pedro River	Roberto et al	2008	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.
10	Heavy metals pollution profiles in streams serving the Owabi reservoir	Ghana, West Indies	Metal (Zn, Cu, Mn, Cu, Pb and As) concentrations and some physical parameters	Akoto et al	2008	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.

S#	Brief title of study	Location	Research Focus	Conducted by	Year	Outcome
11	Heavy-Metal Concentration of Sewage Contaminated Water and Its Impact on Underground Water, Soil, and Crop Plants in Alluvial Soils of Northwestern India.	Ludhiana, Punjab, India	Metal concentration in surface water, soil, and crops grown in fields near the industrial city of Ludhiana	Dheri et al.	2007	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.
12	Load of heavy metals in drainage waters in the Middle, Sudety Mountains. Annals of Warsaw University of Life Sciences	Warsaw University of Life Sciences, Poland	Load of heavy metals in drainage waters	Pulikowski et al	2007	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.
13	Distribution of heavy metals in surface water of Ranipet industrial area in Tamil Nadu, India	Tamil Nadu, India	The contamination of surface water bodies due to industrial effluents	Gowd and Govil	2008	The results revealed that the surface water in the area was highly contaminated showing very high concentrations of some of the metals.
14	Seasonal variations in dissolved heavy metals in the Keritis River, Chania, Greece	The Keritis River, Chania, Greece	Seasonal variations in dissolved heavy metals	Papafilippaki et al	2008	The relative variability followed the order: Zn>Pb>Cu>Cd>Cr.
15	The Seasonal Variation of Heavy Metals in the Suspended Particulate Material in the Iskenderun Bay	Iskenderun Bay (North-eastern Mediterranean Sea, Turkey	Seasonal Variation of Heavy Metals	Türkmen and Türkmen	2004	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

S#	Brief title of study	Location	Research Focus	Conducted by	Year	Outcome
1.	Metal Distribution in Open Canals and Drains in the Upper Rio Grande Basin.	Southwestern United States	Metal concentrations in sediments from open canal systems	Assadian et al.	2003	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.
2	Determination of heavy metals in samples of different states by radionuclide x-ray fluorescence.	Russia	Analyzed solid and liquid samples for the determination of metals by radionuclide x-ray fluorescence	Stroffekova et al	2006	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.

Above in view, it can be summarized that:

i. Atomic Absorption Spectrophotometer (AAS), Laser Induced Breakdown Spectroscopy (LIBS) system and X –ray fluorescence (XRF) are most commonly used techniques for detection of toxic metals in waste water.

ii. The concentrations of metals in various waters studied above were mostly found to be well within global conventional ranges, however there are significant implications of high concentrations of these metals on the aquatic biota and consequently on e human being who is at the end of the food chain.

iii. Metal distribution relies on the concentration of suspended solids in wate water samples, variations in pH and dissolved oxygen.

2.6 Metallic load estimation methods

The literature review shows that existing methods of river load estimation are many and varied in detail. Some methods are simplistic because even when flow and concentration data are available at low frequency of sample collection (e.g monthly) they employ, for example if frequency of sampling is high and are spaced regularly in time then the load will be calculated with little error as the sum of the products of concentration and stream flow, multiplied by the time interval and constant to account for the units used as indicated in (2.1).

$$\text{Load} = K.\Delta t \;.\; \Sigma(C_i .\, Q_i) \qquad (2.1)$$

where K is a constant
Δt is the data time interval
C_i is the concentration of sample
Q_i is the flow at sample time

If the high frequency data are spaced irregularly in time, mass load of the metallic pollutants into the receiving water body with the little error as the sum of the products of the individual time intervals, concentration and flow as indicated in (2.2).

$$\text{Load} = K.\Sigma(\Delta t_i . C_i . Q_i) \qquad (2.2)$$

where Δt_i is the short time interval over which C_i and Q_i are considered to apply

Load calculated using high – frequency flow and concentration data and (2.1) or (2.2) can be expected to be very close to the true load, however such methods can result in load estimates which are biased or imprecise (or both) to an acceptable errors. In the context of load estimation, suspended sediment is a worst-case detrimand because it typically increases in concentration with increasing flow by orders of magnitude and therefore has a high coefficient of variation. Suspended sediment is a key variable because significant amount of certain metals be transported with the sediment as an adsorbed phase.

2.7 Computational framework for accessing load estimation methods

The problem to compute true metallic loads for different streams can be circumvented by a prototype program for Simulations and Methods Investigation of Load Estimates for Rivers through flowing streams (SMILER) has been introduced. The rationale behind SMILER that it uses any available continuous data with at least 30 numbers of samples for flow and concentrations in water sample from any flowing stream. Work undertaken for the department of the Environment by the Water Research Centre (Harrison et al, 2003) computed heavy metals load estimation for the Thames at Kingston by manual 'routine' grab sampling at the interval of 4 days along with the stream flow readings from an automatic flow proportional sampling system linked to an ultrasonic guaging station. Samples were taken at regular intervals (daily, weekly, monthly). SMILER use transfer function model as computational technique for mass loading calculation.

2.7.1 TRANSFER FUNCTIONS MODEL

The transfer function model is employed because it doesnot take into account a unique or one to one relationship between flow and concentrationi.e there is no need to mesure the flow every time the samples are taken for measuring the concentration and suspended solids in stream. There are several ways of expressing a transfer function model. The notation adopted here is consistent with that employed later in the report when describing a computer program for investigating errors in loads. The general form of a transfer function for relating concentration and flow is given by (2.3).

$$C_t = \frac{B(z^{-1})}{A(z^{-1})} \cdot Q_{t-b} \tag{2.3}$$

where C_t is concentration at time t
Q_{t-b} is flow at time t-b
b is pure time delay
z^{-1} is the backward shift operator
i.e. $z^{-1}x_t = x_{t-1}$

and $B(z^{-1})$ and $A(z^{-1})$ are polynomials in z^{-1} given by (2.4) and (2.5) respectively

$$B(z^{-1}) = b_o + b_1z^{-1} + \ldots + b_nz^{-n} \tag{2.4}$$

$$A(z^{-1}) = 1 + a_1z^{-1} + a_2z^{-2} + \ldots + a_mz^{-m} \tag{2.5}$$

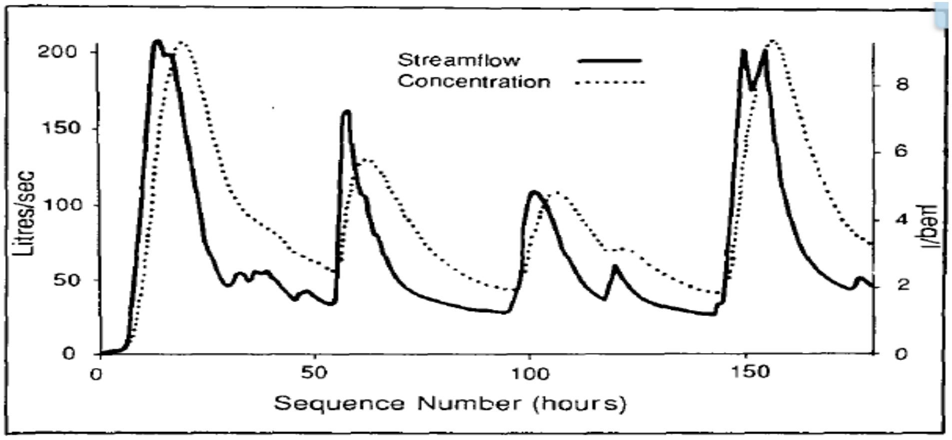
$$C_t = \frac{b_o}{1 + a_1z^{-1}} \cdot Q_t \tag{2.6}$$

which may be re-written as

$$C_t = b_oQ_t - a_1C_{t-1} \tag{2.7}$$

Equation (2.6) states simply that the concentration at time t is given by b_o times the flow at time t, plus al times the concentration at time t-1.

Figure 2.1: ***Concentration and Flow Data using SMILER***



Chapter 3

METHODOLOGY

3.1 STUDY AREA

Leh Nullah was originally a clean water channel and home of fish, turtles and variety of other aquatic species. However, with the passage of time it has become the largest carrier of untreated industrial and municipal wastewaters from twin cities of Rawalpindi and Islamabad. It starts from Margalla hills in Federal Capital City Islamabad at the Northwestern edge until Soan River at the South-eastern edge in District Rawalpindi of the Punjab (Water and Sanitation Agency Rawalpindi, 2012).

Most of the industrial wastewater and municipal sewage originating from the industrial and residential area of Islamabad and Rawalpindi discharges into the Leh Nullah which ultimately falls into Soan River.

While the total length of the Leh Nullah is around 30 Km. Throughout its length it receives wastewater discharges from residential and industrial area of Islamabad and Rawalpindi. There are total twelve bridges on Leh Nullah, however we selected six important bridges from Katarian to Chaklala for surface as well as benthic zone soil sampling. Six sampling stations (S1-S6) were established along the selected stretch of the Leh Nullah. 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 September 2012 to April 2013.

Police line Nullah from residential area of I-9/4 carrying untreated sewage of I-9/I-10 sectors of Islamabad and another Carriage Factory Nullah carrying waste water of several Steel

Industries auto painting workshops and Paint Industry warehouses including storm water runoff join Leh Nullah before the sampling *Station#1* (S1-Katarian). Sketch of Leh Nullah showing major outfalls and bridges is shown in **Figure 3.0.** It is evident from the **Figure 3.0** that Sampling Staion # 5 (Gawalmandi) receives effluents from car paint workshops and old battery shops along with municipal waste water from the residential area.

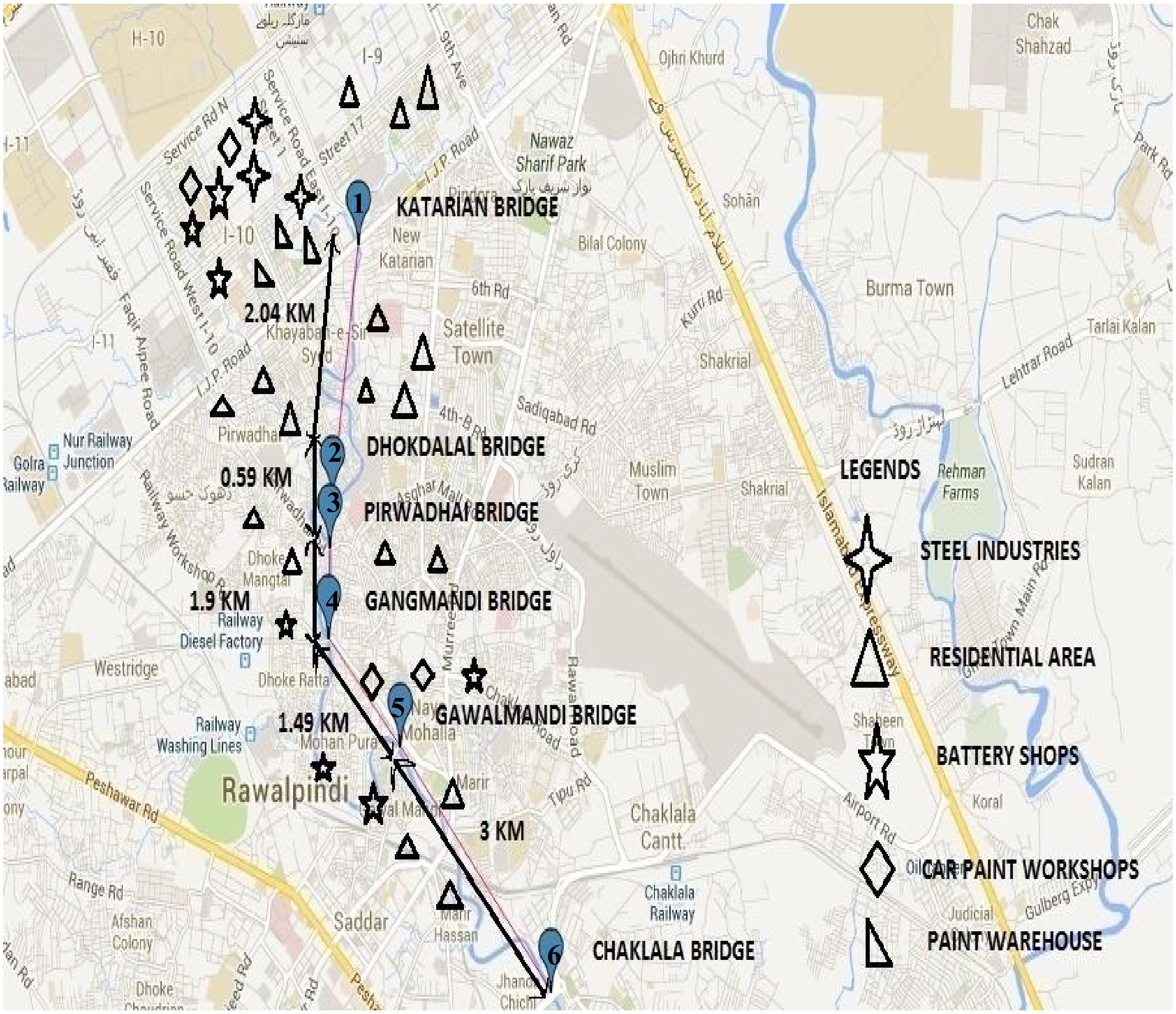


Figure 3-0: Major Outfalls in Leh Nullah

Figure 3-1: Location of six sampling stations on Leh Nullah

Wastewater in the Leh Nullah is laden with organics, metals and nutrients and exerts high BOD, COD on the receiving water of Soan River. At the same time, it introduces nutrients into the river leading to occasional algal blooms, which is evident from reduced fish population in the Soan River. Water from Soan River is then used for irrigation purpose. Toxic impacts of a few metals and other pollutants can possibly be found in those crops. This is however beyond the scope of this study. Table 3-1 shows the type of activities around Leh Nullah.

Table 3-1: Major influents of Leh Nullah (Source: EPA Survey, 2010)

Influents	Location	Materials Used
M/s Pothar Steel Ltd	Industrial Area of Sector I-9/I-10 Islamabad	poor quality of scrap bundled(shredded containers of edible oils, paints, lubricants and even rubber other type of scrapused as fuel)
M/s Mumtaz Steel & F.S.L Group Ltd.		
M/s R. K Steel Ltd.		
M/s Itihad Foundry		
M/s Zia Steel Mills Ltd.		
M/s Pak Iron & Steel Casting		
Car Paint Workshops		
Used Battries and Paint Shops	Gawalmandi (Rawalpindi)	Repairing of Old Battery and Car Paint workshops effluent going to Leh.
Car Paint Workshops		

3.2 METALS IN LEH 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 wastewater treatment systems and receiving waters. The benefits versus toxicity of some metals depend upon their concentration in waters. In order to decide whether the wastewater under study is within given ranges i.e National Effluent Quality Standards set by Pakistan Environmental Protection Agency (Pak-EPA) or not, determination of the concentration of these metals was necessary.

3.2.1 SAMPLE COLLECTION AND PRESERVATION

Virgin PET Bottles were used for sample collection as suggested by (Zhang, 2007). 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 water in question three times prior to sample collection. Each container was tightly sealed and labeled immediately after sample collection

Triplicate water samples were collected from each station at a fixed depth of 1/2 meter from the water level at the same time of the day each month, between September 2012 and April 2013.

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 followed0 (Somenath, 2003). Each sample was splitted into two parts, one part of the sample was filtered before preservation for determination of dissolved metals. Samples were preserved by acidifying with concentrated nitric acid (HNO_3) to $pH < 2$. The other part samples were not filtered for the determination of total metals. After initial acidification the samples were stored in the refrigerator at 4°C.

3.3 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).

3.3.1 Digestion Procedure

Digestion procedure adopted in this study was as suggested by (Zhang, 2007). 100 cm^3 of each sample was transferred into a beaker and 5 mL 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 20 mL. More HNO_3 was added and heating continued until the solution appeared light colored and clear which showed the completion of digestion. The beaker contents were then cooled ,filtered and diluted to mark. Concentration of selected metals in the wastewater samples was determined using Perkin-Elmer Analyst 100 Atomic Absorption Spectrometer (Varian AA240, Biotech USA).

3.4 INSTRUMENTAL ANALYSIS

Perkin-Elmer AAnalyst 100 Atomic Absorption Spectrophotometer (Varian AA240, Biotech USA) was used to determine the metal concentrations in wastewater and soil samples. This instrument 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 3-2 provides details about operating conditions of Perkin-Elmer A Analyst 100 AAS.

Table 3-2**:** Operating conditions of Perkin-Elmer Analyst 100 AAS

Metals	Wavelength (nm)	Slit (nm)	Mode	Flame	Burner (cm)	Nebulizer	Calibration
Fe	248.3	0.2	AA	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
Pb	217	0.3	AA	Air-Acetylene	10	Universal	Linear

3.4.1 Soil Sample Collection and Preparation

Soil samples were taken by soil sampler (2.3 cm diameter) from each station of the Nullah. Volume of the soil sample collected varied from point to point depending upon the bed soil characteristics. Samples were oven dried at 25°C. Inner side of the Soil Sampler was engraved to trap soil. Top end of the soil sampler was covered with a lid that opened when sampler was dropped into the water and closes when the sampler was pulled out of the water, thus avoiding any air bubbles to trap inside the soil sample. A slightly tapered weight of about 5 Kg is added to the soil sampler to take it to benthic zone of Nullah.

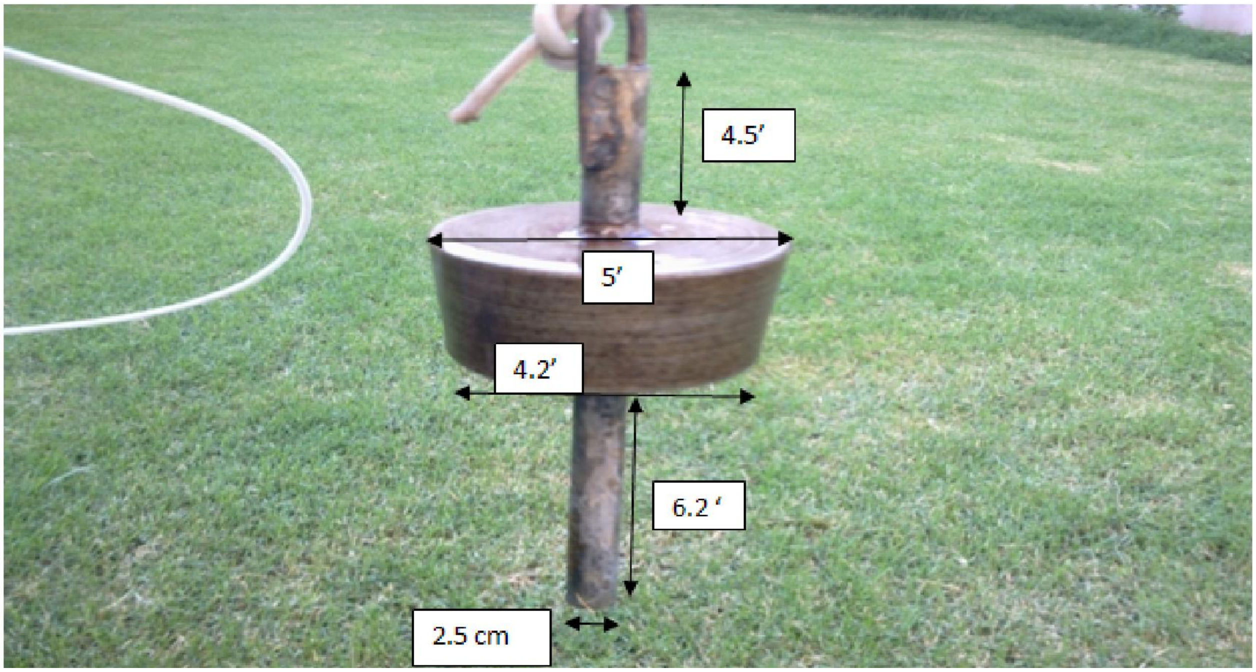


Figure 3-2: Benthic Soil Sampler

3.4.2 Benthic Soil Analysis Using FAAS

The methodology adopted for the analysis of soil samples was the 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 after adding 5 mL HNO_3 on a hot plate for 15 minutes. Another 5 mL of HNO_3 was added. After heating and stirring for 15 minutes most of the bubbling stopped, added 2 mL of HNO_3 and heating continued. Repeated the same procedure with another 2 mL of HNO_3 and cooled the beaker to room temperature. Finally, another 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 Fe, Cd, Pb, and Zn by Flame Atomic Absorption Spectrophotometer (Varian AA240, Biotech USA).

3.5 ANALYSIS OF SOIL SAMPLES

Analysis of the metallic pollutants trapped into the benthic soil of the Leh Nullah enabled us to gain an integrated picture of the contamination, because the level of metals in bottom sediments was the result of prolonged sedimentation processes and did not undergo sudden changes because of continuously varying external conditions. Additionally, by distinguishing separate layers of the bottom sediment, it was possible to evaluate the trends towards changing the metal content in terms of time, which was rather difficult at present, taking the metal contamination of water as the basis for the evaluation.

3.6 STATISTICAL ANALYSIS

3.6.1 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.

Statistical assumption

H

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

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

Where "ρ" is the population correlation coefficient.

a) **Level of significance**

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

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

b) **Test statistic**

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

Where,

t = Student's t- distribution

n = Sample size

r = Sample Correlation

$$r = \frac{\sum (x-\bar{x})(y-\bar{y})}{\sqrt{\sum (x-\bar{x})^2 \sum (y-\bar{y})^2}}$$ …………………………………………………... **3-4**

c) **Critical region**

$P > \alpha =$ Accept H_O ………………………………………. ………………….... **3-5**

$P \leq \alpha =$ Reject H_O ……………………………………………………..**3-6**

3.6.2 Analysis of Variance (ANOVA)

d) **Statistical Hypothesis**

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

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

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

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

e) Level of significance

α = 0.05 (95% confidence level) α = 0.01 (90% confidence level)

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

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	$rc-1$	$SST = \sum_i\sum_j (X_{ij} - \bar{X})^2$		

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

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

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

f) Critical Region

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

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

Or

g) Rule of rejection $P > \alpha =$ Accept H_O ……………………….. ………………….**3-13**

$P \leq \alpha =$ Reject H_O ……………………………………………. …………………**3-14**

Chapter 4

RESULTS AND DISCUSSION

This chapter discusses spatial and temporal variations in physicochemical characteristics of Leh Nullah with special emphasis on heavy metals. Last section of the chapter deals with the estimation of pollution load in the Nullah and possible treatment using lime to precipitate heavy metals before discharging of effluents into Leh Nullah.

4.1 PHYSICOCHEMICAL PARAMETERS

As mentioned earlier, Leh Nullah was divided into various stretches with one sampling station for each stretch. Several physicochemical parameters were measured at each station of the nullah as listed in Table 4.1. The objective 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 (Gangmandi Bridge)* indicating a continuous influx of municipal wastewaters. Fractional changes in the mentioned parameters at *Gangmandi* 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.

Detailed physicochemical parameters for Table 4.1 are given in **Appendix C**

Table 4.1: Concentration of physicochemical parameters at six selected stations

Parameters	Stations						NEQS
	Katarian	Dhokdalal	Pirwadai	Gangmandi	Gawalmandi	Chaklala	
DO (mg/l)	1.23	1.16	1.19	1.05	1.23	1.27	
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
Turbidity (NTU)	40.68	188.92	214.44	151.38	84.07	88.05	
Temp. (°C)	30.16	34.3	34.22	33.07	30.33	30.28	40
EC (uS/cm)	1109	807	777	760	941	799	
pH	6-8.5	6.99-8.96	7.7-9.11	8-9.26	6.85-8.42	7.9-8.49	6-10
COD (mg/l)	467.29	604.24	561.68	488.29	446.93	457.95	150
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 taken between Sept 12 & April 13

The value of DO was found to be very low from *Station#1 (Katarian Bridge) to Station#6 (Chaklala Bridge)* due to high pollution load of mainly 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(Katarian)* to *Station#4(Gangmandi)* due to high pollution inputs from domestic outfalls. Total Phosphorous concentration at *Station#3(Pirwadai), 4(Gangmandi) & Station #6(Chaklala)* was a clear evidence of large inflow of untreated sewage with noticeable fraction of detergents.

4.2 SPATIAL ANALYSIS OF METALS

Since Leh Nullah receives wastewater from industrial as well as municipal sources at station #1(Katarian) and municipal sources on other stations, the distribution of metals in separate industrial and municipal effluent drains was studied. 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.

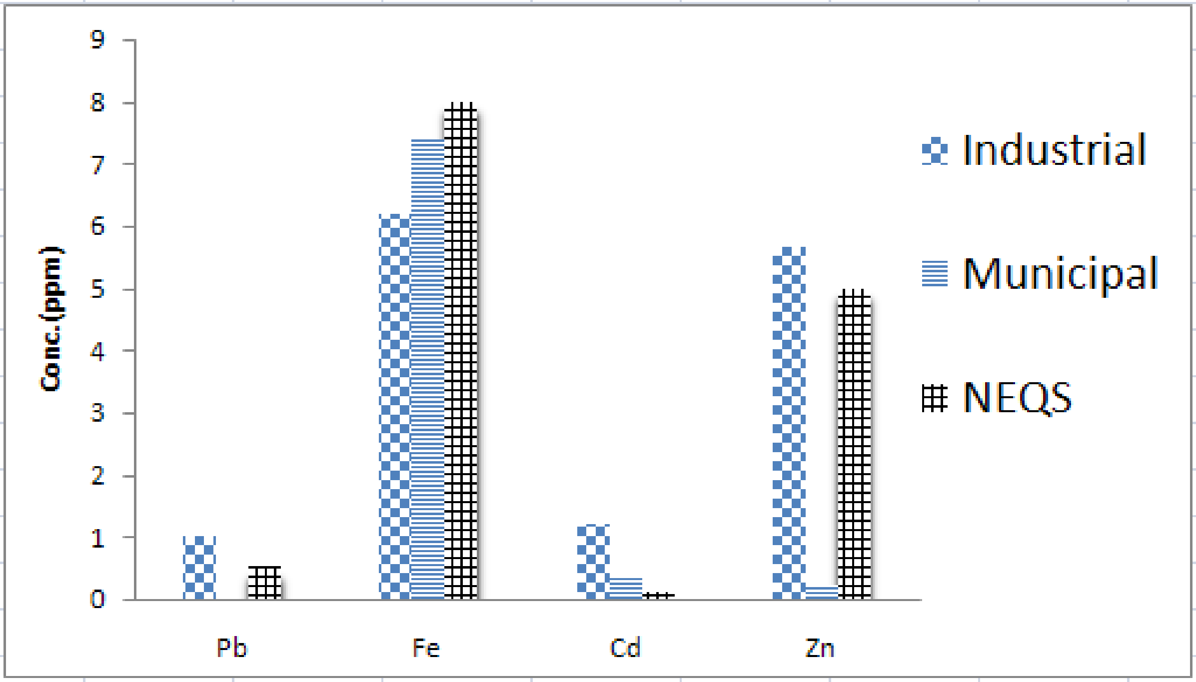


Figure 4-1: Metals concentration in separate industrial and municipal streams

Figure 4-1 shows that the concentration range of metals in the industrial stream varies between 0.111 and 7.5 ppm and Pb, Cd & Zn concentrations exceeding NEQS. This can be attributed to the fact that enormous quantities of water are used and abused by these industries,use of low quality scrap material in Steel Industries,Workshops where cars are been painted, Warehouses for paints, Metal Engineering Units and batteries shops(Source:Environmentral Survey Report of I-9 & I-10 Industrial Estate Islamabad,December 2006). None of the metals except Fe was detected in the municipal stream which may be attributed to the fact that iron content is greatest in Rawalpindi-Islamabad region soil.A laboratory analysis of the virgin soil taken from SCEE (NUST) and Gawalnmandi showed iron upto 45 ppm in the soil of Rawalpindi and Islamabad. Concentration of metals in surface water as well as in benthic zone at each sampling station of the Leh Nullah are shown in the form of error bars in figure 4.2.

Spatial distribution of metals between *Station#1* and *Station#6* are illustrated by figure 4.2. Metal concentrations are high at *Station#1(Katarian) and Station# 6(Gawalmandi)*, and are relatively low at other stations. Overall we found that the concentration of metals in benthic zone was greater as compared to surface water. Ranges of pH values were highest at Katarian and Gawalmandi stations from as compare to other sampling stations for whole study period.

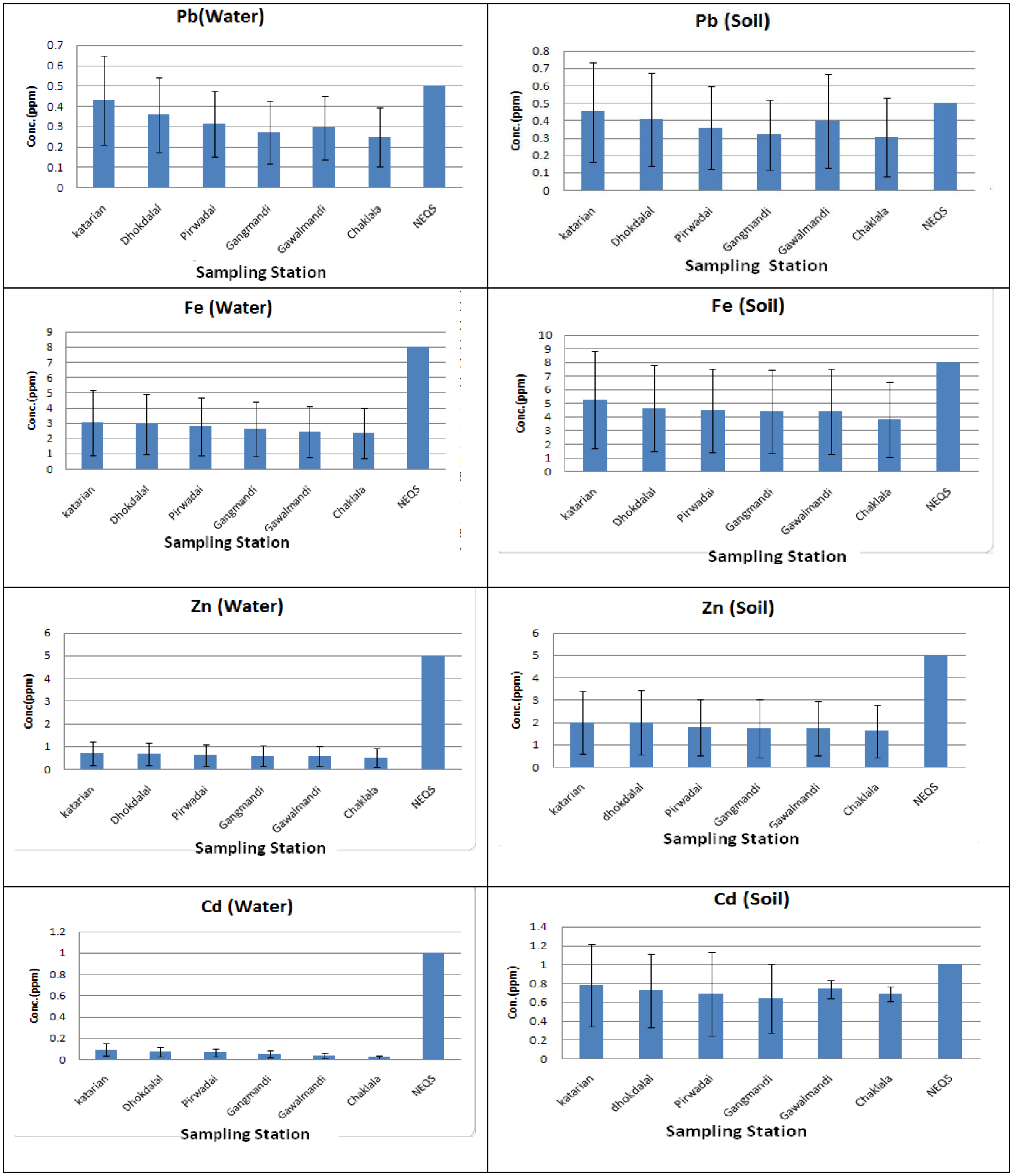


Figure 4-2: Metal concentration in Water and Soil (Spatial distribution)

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. 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, 2011; Rudd *et al*., 2009) 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 Electrical Conductivity and pH are playing noticeable role in the distribution of metals as these are 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 4.2. High electrical conductivity was observed at Station#1(Katarian) and Station #5(Gawalmandi) where the concentration of metals are highest as compared to otherstations.

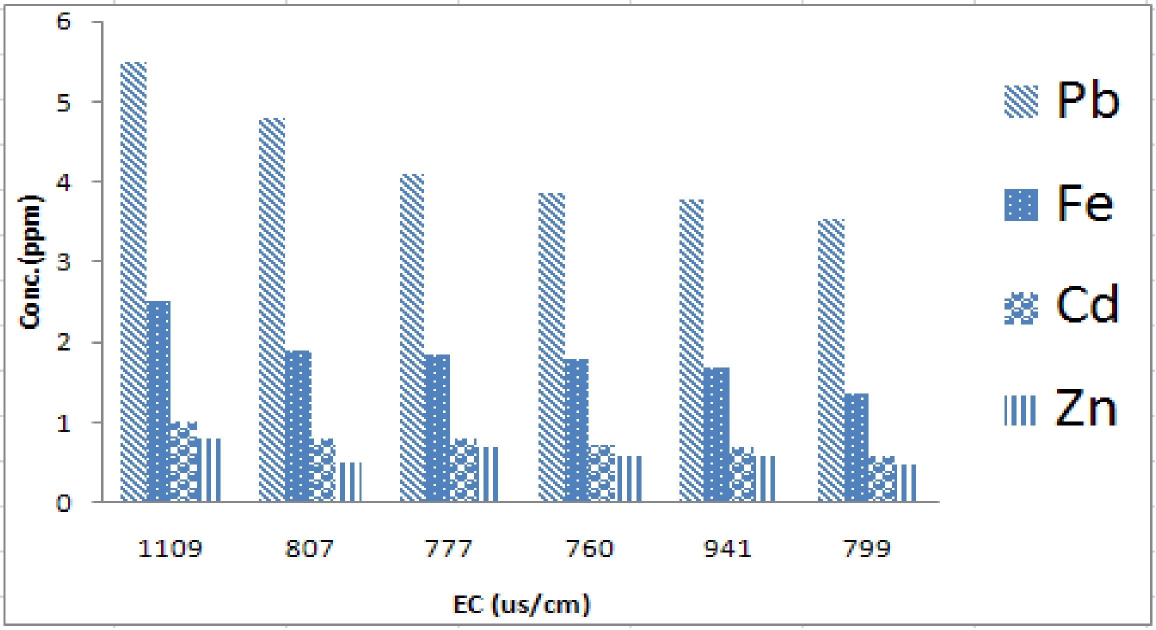


Figure 4-3: Variations in metals concentration vs Electrical Conductivity

Out of all the six stations, *Station#1(Katarian*) exhibits highest metal concentration at relatively lower pH and flow rate. This is in consistent with the findings of (Harrison, 1996) who also concluded that concentration of the metals is generally high at low pH. *Station#1* is located after an outfall from a major industrial area of I-10 and small residential area of I-9 sectors in

Islamabad. None of the other sampling station has as many industrial discharges into Leh Nullah as prior to *Station#1 (Katarian).* This high concentration of metals in the drain water at *Station#1* starts dampening at *Station#2(Dhokdalal)* and drops to very low values until fresh municipal discharges inject more metals into the nullah between Gangmandi and Gawalmandi stations. This trend indicates that metal concentration in Leh Nullah would reduce with distance if not supplemented by new discharges. Although *Station#5(Gawalmandi)* has pH in the same range as that of *Station#1,* Metal concentration at *Station#6* (Chaklala) is same as the Station#5(Gawalmandi).

No significant change in pH was observed during sampling from December, 2012 to April 2013.In such a narrow pH change (8-8.5) it is rather difficult to establish any relationship between pH and metal distribution. However, from September 16 2012 to November 2012 Wide ranges of pH was observed at Station #1 (Katarian) and Station#5 (Gawalmandi) resulted in highest concentration of metals observed during this period).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 Leh water. Also, as the acid breakpoints of most of the metals selected in this study are 5 or 7 (Levine, 2011) 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 nullah.

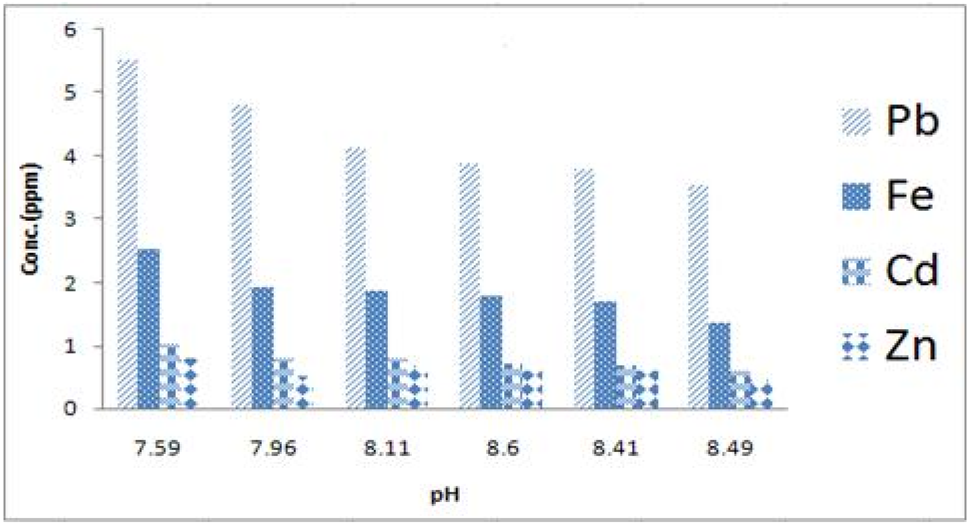


Figure 4-4: Variations in metals concentration vs pH

0.2.1 Bioconcentration Factors (BCFs)

The biconcentration of the selected metals in different samples of the wastewater of Leh Nullah was quantified with a biconcentration factor (BCF), 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 BCF of a few selected metals in various plants is tabulated in **Table 4. 2**.

BCF = Conc.of a specific metal in the plant/ Conc. of metal in the wastewater

Table 4-2: Biconcentration factors of a few selected metals in plants

Metals	Concentration in wild plants(mg/kg)		Concentration in waste water(mg/l)	BCF of wild plants	
	Chenopodiacea (Family:Grass)	Grass (Family:Pocacea)		Chenopodiacea (Family:Grass)	Grass (Family:Pocacea)
Cd	1.6	2.5	0.169	9.46	14.7
Fe	0	6.96	0.883	-	7.882
Pb	2.2	0	0.429	5.1	-
Zn	26.3	23	1.33	15.84	13.8

*the concentration of metals in the wild plants was taken from Kahlown *et al.* (2006)

In general, two mechanisms are responsible for metal uptake in aquatic systems, Kahlown *et al.* (2006).

(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.,* 2010).

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 plants was taken from Kahlown *et al.* (2006).

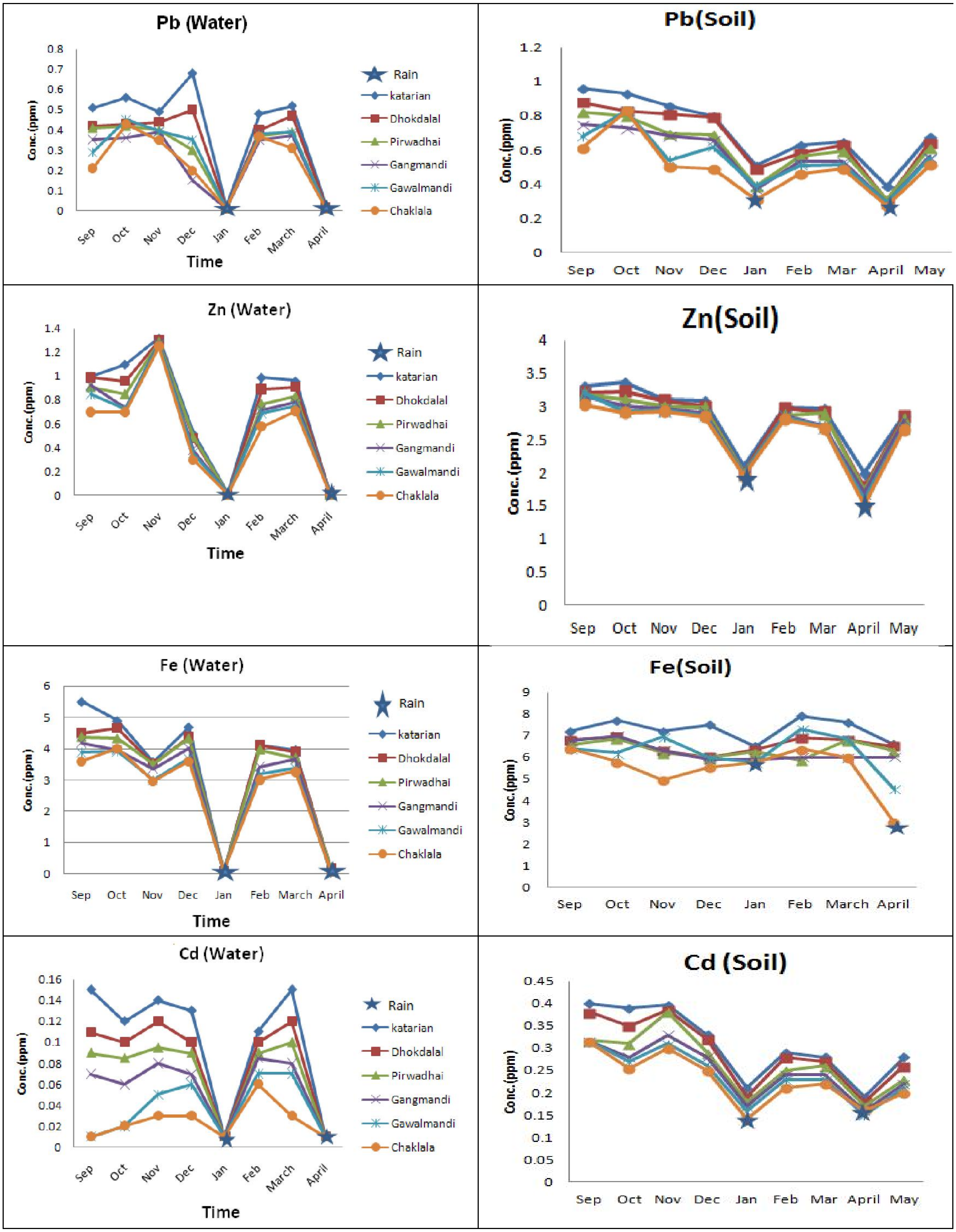
The plant uptake of heavy metals depends not only on the concentration of the metals in the water column, but also on the metal species and the bio-available form of the metals (Olaniya *et al.*, 1998a).

The BCFs 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 BCF 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).

0.3 TEMPORAL VARIATION IN METAL CONCENTRATION

The temporal variation in metals concentration is shown in **Figure 4.5**. It is clear from Figure 4.5 that the concentration of most of the metals is high in September. It starts falling smoothly from October till December. 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 Leh Nullah. Moreover during the rainy season it was found that only Fe was present in the benthic zone soil and all other metals were not detected in surface water as well in benthic zone soil of Leh Nullah. Values of metal concentration are given in **Appendices 'A and B'**

Figure 4.5: Temporal distribution of metals in water and soil



4.4 METALS IN THE BENTHIC SOIL

A major environmental concern is the contamination of agricultural soil due to these heavy metals in Sawn River. The long term usage of industrial wastewater for irrigation makes heavy metals to accumulate in soil (Chaw and Reves, 2009). In order to study the metallic pollution in the benthic zone of the Leh it was necessary to determine the heavy metals in the leh water as well. Since the precipitation and dissolution of heavy metals in water are 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 Leh benthic soil will also be helpful for investigating the extent of these factors.

4.5 GEO-ACCUMULATION INDEX

A geo-accumulation indexing (Igeo) is used to quantify the degree of anthropogenic contamination and to compare the concentration of different metals in the nullah sediments (Forstner et al 2012). 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:

$$I_{geo} = \log_2\left(\frac{C_n}{1.5 \times B_n}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots 4.1$$

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 and Igeo= Geo-Accumulation Indexing.

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 4-4

Table 4-4: 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 4-5: Geoaccumulation indices of selected metals

Metals	Metal Concentrations in benthic soil at each station (C_n-mg/kg)						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
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
Fe	409	723	1929	665	685	544	1.7	2.5	4.0	2.4	2.5	2.1

In order to determine the values of I_{geo}, geochemical background values of 76.27, 26, 0.09, 20.32,82 mg/kg were adopted from the literature (Forstner et al 2012) for Zn, Cd, Pb, and Fe. The resulting contamination intensities of metals are given in **Table 4-5**, which shows that benthic soil of all the stations (except *Station*#3) are very strongly contaminated with Cd. Cadmium 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 4-6: Contamination intensities of metals

Metals	**Contamination intensity at each station**						**Abbreviations**
	S1	**S2**	**S3**	**S4**	**S5**	**S6**	Uncontaminated to moderate (UM)
Zn	MC	MC	MC	MSC	MSC	MSC	Practically uncontaminated (PU), Strong to very strong contamination (SVSC)
Cd	VSC	VSC	UM	VSC	VSC	VSC	Moderately contaminated (MC)
Pb	PU	PU	UM	MC	SVSC	SVSC	Moderately to strongly contaminated (MSC)
Fe	MC	MSC	SC	MSC	MSC	MSC	Strongly contaminated (SC), Very strong contamination (VSC)

4.6 STATISTICAL ANALYSIS

The descriptive statistics of metal concentration in Leh Nullah wastewater is explained in Table 4-7. 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 4-7: Descriptive Statistics of metal concentrations

Statistical parameters	**Metals**			
	Pb	**Zn**	**Cd**	**Fe**
Mean	0.38	0.95	0.06	3.0
Standard Error	0.065	0.2628	0.027	0.1070
Standard Deviation	0.159	0.6437	0.067	0.2620
Sample Variance	0.025	0.4143	0.004	0.0687
Range	0.425	1.6608	0.167	0.6978

The correlation coefficients between physicochemical variables and metals under scrutiny are given in Table 4-8. In case of TSS, P-value is less than level of significance for Pb, Cd, and equal to level of significance for 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 (α = 0.05, α = 0.01) correlated with TSS. All metals are significantly correlated with EC

Table 4-8: Correlation between metals and physicochemical parameters

Parameters		Correlations			
		Pb	**Zn**	**Cd**	**Fe**
TSS	Pearson Correlation	-0.608	-0.364	-0.2875	-0.2115
pH	Pearson Correlation	-0.15	0.147	0.28	0.254
EC	Pearson Correlation	0.7351	0.514	0.37	0.445

**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 4-8** 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 4-9**. 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.

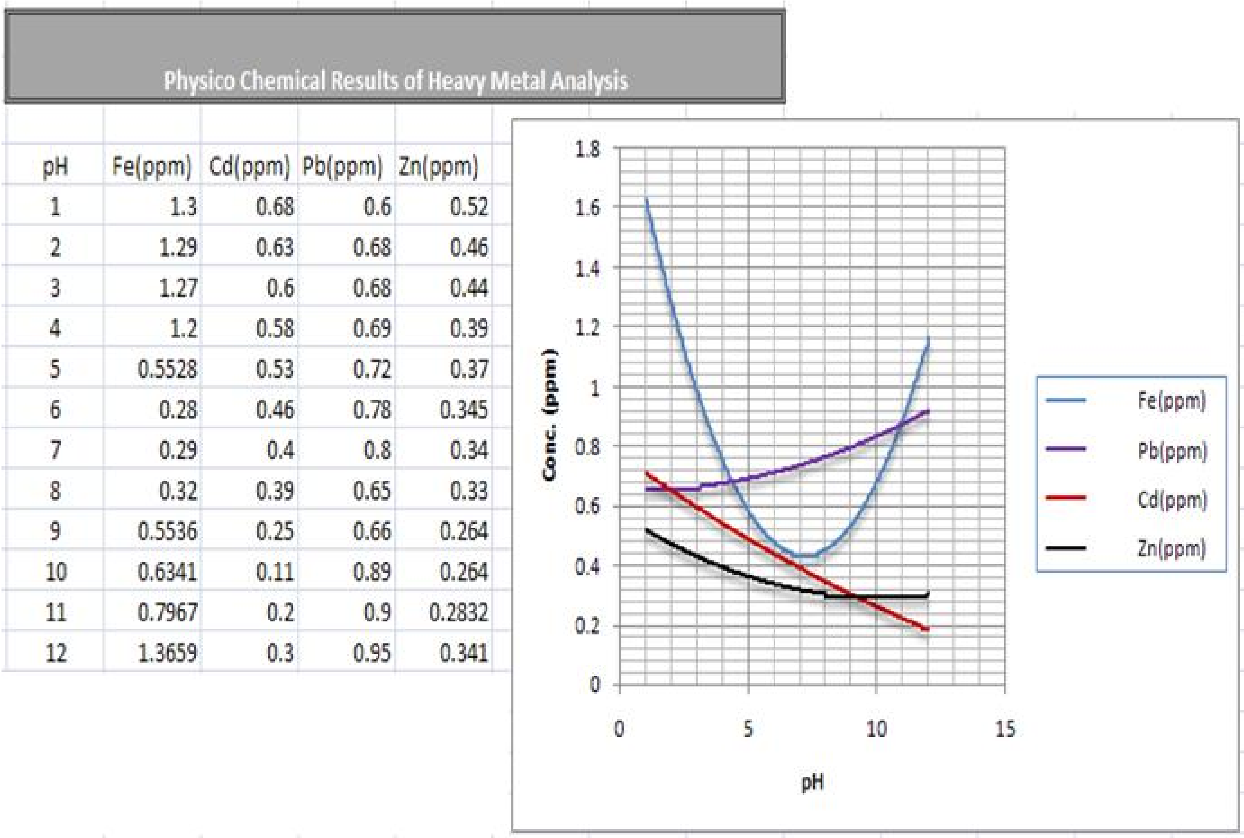
Table 4-9: Correlation of metal concentrations with each other

Metals		Correlations			
		Pb	**Cd**	**Fe**	**Zn**
Pb	Pearson Correlation	1.00	0.91	0.95*	0.89
Cd	Pearson Correlation	0.91	1.00	0.98	0.99
Fe	Pearson Correlation	0.89	0.99	1.00	0.98
Zn	Pearson Correlation	0.95	0.98	0.98	1.00

**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 (which is not changing with the time and stations. In case of months p-value is less than α for Pb, Zn, Cd 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, Cd 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. Proposed pretreatment system for industries to reduce the concentration of these metals in Nullah is given in **Figure 4-5**. The most common used method to remove soluble metal ions from solution is to precipitate the ion as a metal hydroxide. The process is readily automated and controlled by a simple pH controller. By raising the pH value of a solution with a common alkaline material such as lime, or sodium hydroxide the corresponding metallic hydroxide compounds become insoluble and precipitate from solution. **Figure 4-5** is a metal hydroxide solubility curve showing the solubility of the common heavy metal ions and their respective solubility versus pH.

Figure 4-5 Solubility Diagram for Metals



Physico Chemical Results of Heavy Metal Analysis

pH	Fe(ppm)	Cd(ppm)	Pb(ppm)	Zn(ppm)
1	1.3	0.68	0.6	0.52
2	1.29	0.63	0.68	0.46
3	1.27	0.6	0.68	0.44
4	1.2	0.58	0.69	0.39
5	0.5528	0.53	0.72	0.37
6	0.28	0.46	0.78	0.345
7	0.29	0.4	0.8	0.34
8	0.32	0.39	0.65	0.33
9	0.5536	0.25	0.66	0.264
10	0.6341	0.11	0.89	0.264
11	0.7967	0.2	0.9	0.2832
12	1.3659	0.3	0.95	0.341

These results are in consistent with Allison EmLie Lweis (2012), Review of metal sulphide precipitation. If Iron is reviewed, it was seen that at pH of 7.2 the concentration of Iron was 0.45 mg/l. Pb has a least varying curve and it occurs lowest at low pH range. Metals such as Zinc are amphoteric, being soluble at both alkaline and acidic conditions; however the Zinc is least soluble 0.32mg/l at pH 12. Certain metal ions such as cadmium readily form metallic complexes with ammonia. The ammonical metal complexes remain vary soluble at the higher pH values prohibiting the precipitation of the respective metal hydroxide. The concentration of Cadmium is lowest (0.2 mg/l) at pH of 12. The theoretical solubility usually does not exist in practice. Metallic coagulant such as ferric chloride or aluminum sulfate are generally used to accelerate the coagulation and precipitation of the heavy metals.

CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

Following conclusions were drawn from the study:

i. Concentrations of most of the metals studied in this research were within National Environmental Quality Standards (NEQS) in the wastewater of Leh Nullah except Fe. This was mainly due to the lithology of Rawalpindi/Islamabad region which comes under Murree and Kamlyal formation mainly consisting of limestones and shales and rich in Iron content. As Leh Nullah starts from the footsteps of margalla hills so due to natural erosion and weathering of rocks Iron content may be higher in the Leh Nulah Waste Water. (Sheikh, 2010)

ii. No direct relationship could be established between concentration of metal in water and benthic soil. This trend however varies from metal to metal; Lead, for example lead is high both in soil and water whereas cadmium is low in water but high in soil. Metal concentration in water decreases as we go from lead to cadmium and same in crease in case of benthic soil if we go from lead to cadmium.

iii. Most of the physico-chemical parameters of the Leh Nullah wastewater are higher than NEQS.

iv. We found a decreasing pattern in metal concentration from Station-1 to Station-5, however from station#5(Gawalmandi) to Station # 6(Chaklala) no significatnt change in metal concentration was observed in surface water samples. This may be due to the fact that average distance between other station was at least 2.5 Km while Station#5 and Station#6 are approx. 2 km apart.

v. Concentration of most of the metals is best correlated with EC.

vi. BOD/COD=0.5(means of six samples), 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 on the Leh Nullah 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 Implementation of outcomes of EPA Survey of Industrial Area Islamabad:

On the directions of Supreme Court of Pakistan a team from EPA conducted a survey at Industraial Estate of I-9/I-10 Islamabad in 2006 and shortlisted the Steel Industries, Paint Workshops and Batteries Shops who are creating more impact on the environment in terms of pollution load.the report also suggested steps to avoid recurrence in future.these reports should be given importance and culprits should be penalized.

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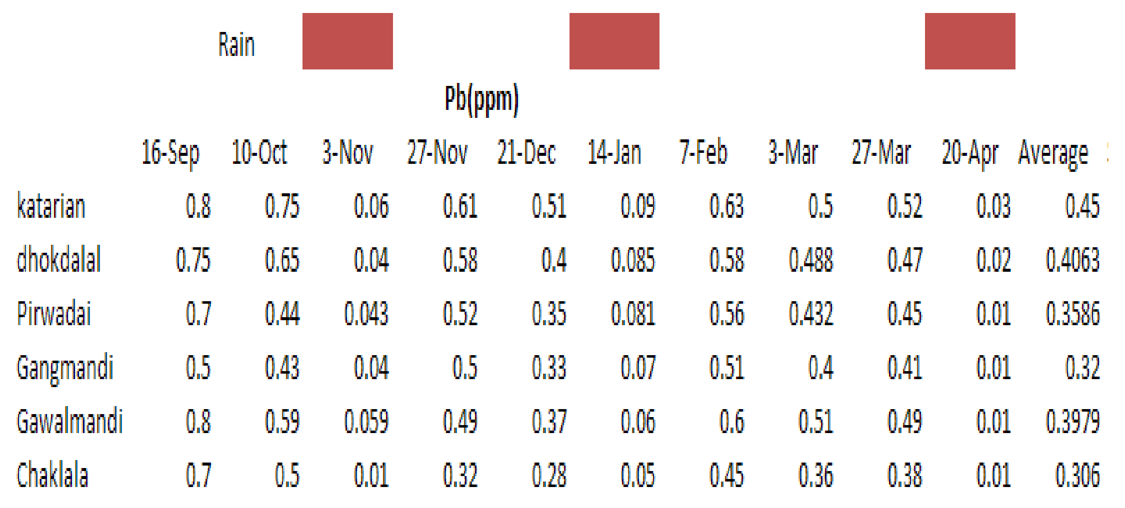
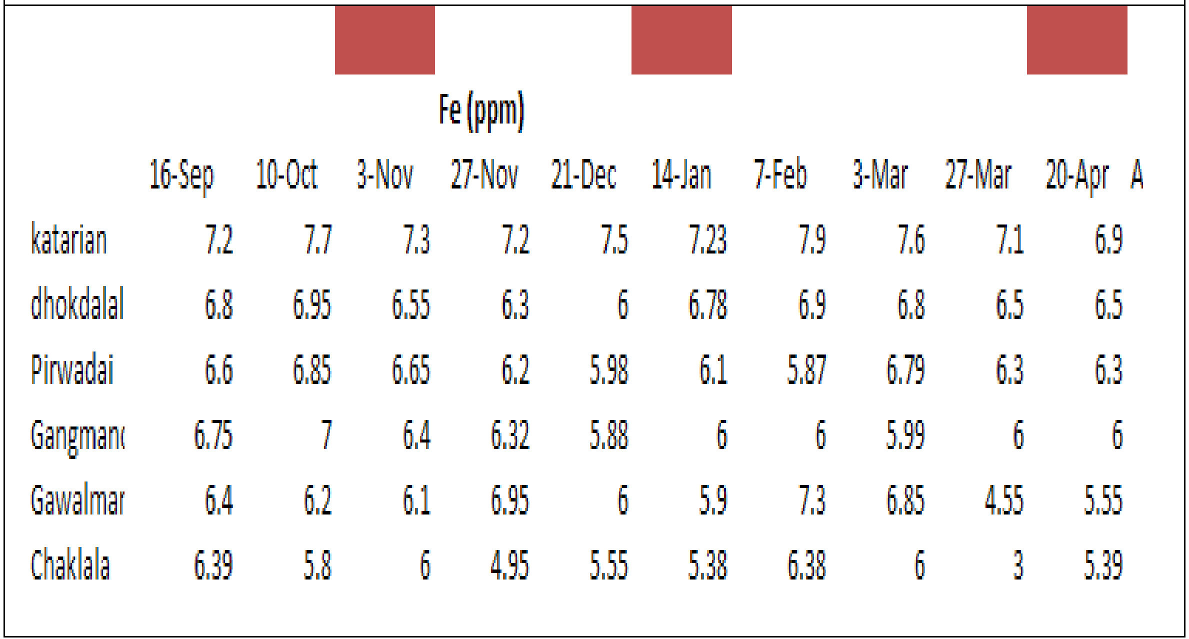
APPENDICES

APPENDIX A: Concentration (mg/l) of metals in the benthic soil



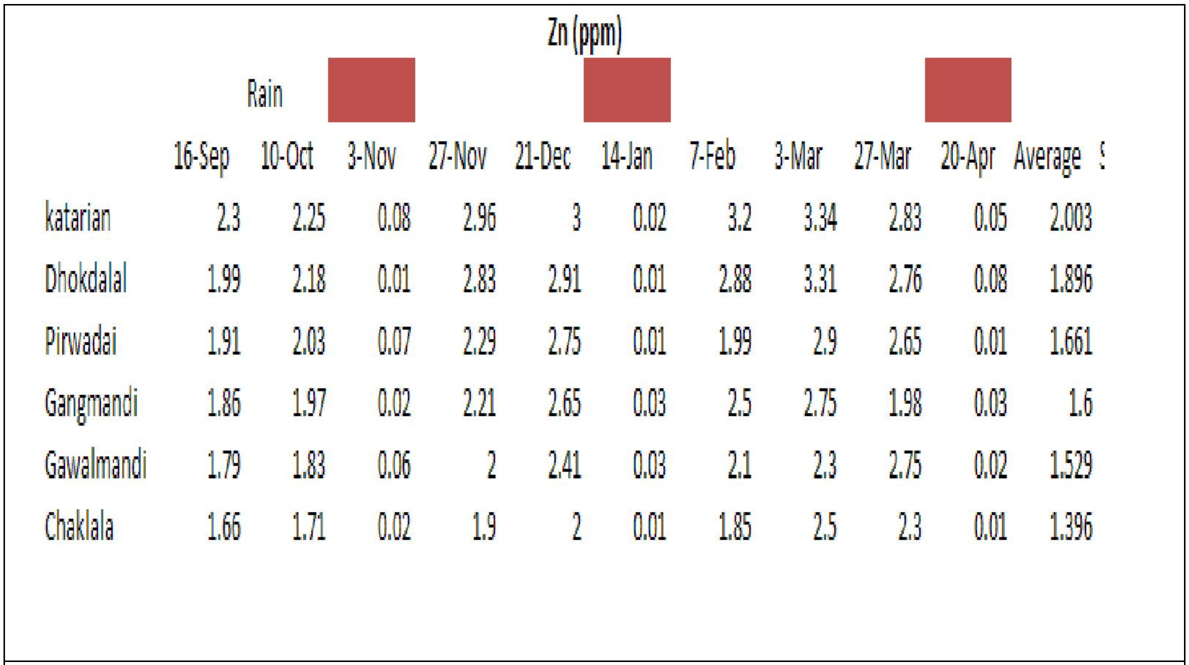
Pb(ppm)

Rain			🟥			🟥				🟥	
	16-Sep	10-Oct	3-Nov	27-Nov	21-Dec	14-Jan	7-Feb	3-Mar	27-Mar	20-Apr	Average
katarian	0.8	0.75	0.06	0.61	0.51	0.09	0.63	0.5	0.52	0.03	0.45
dhokdalal	0.75	0.65	0.04	0.58	0.4	0.085	0.58	0.488	0.47	0.02	0.4063
Pirwadai	0.7	0.44	0.043	0.52	0.35	0.081	0.56	0.432	0.45	0.01	0.3586
Gangmandi	0.5	0.43	0.04	0.5	0.33	0.07	0.51	0.4	0.41	0.01	0.32
Gawalmandi	0.8	0.59	0.059	0.49	0.37	0.06	0.6	0.51	0.49	0.01	0.3979
Chaklala	0.7	0.5	0.01	0.32	0.28	0.05	0.45	0.36	0.38	0.01	0.306



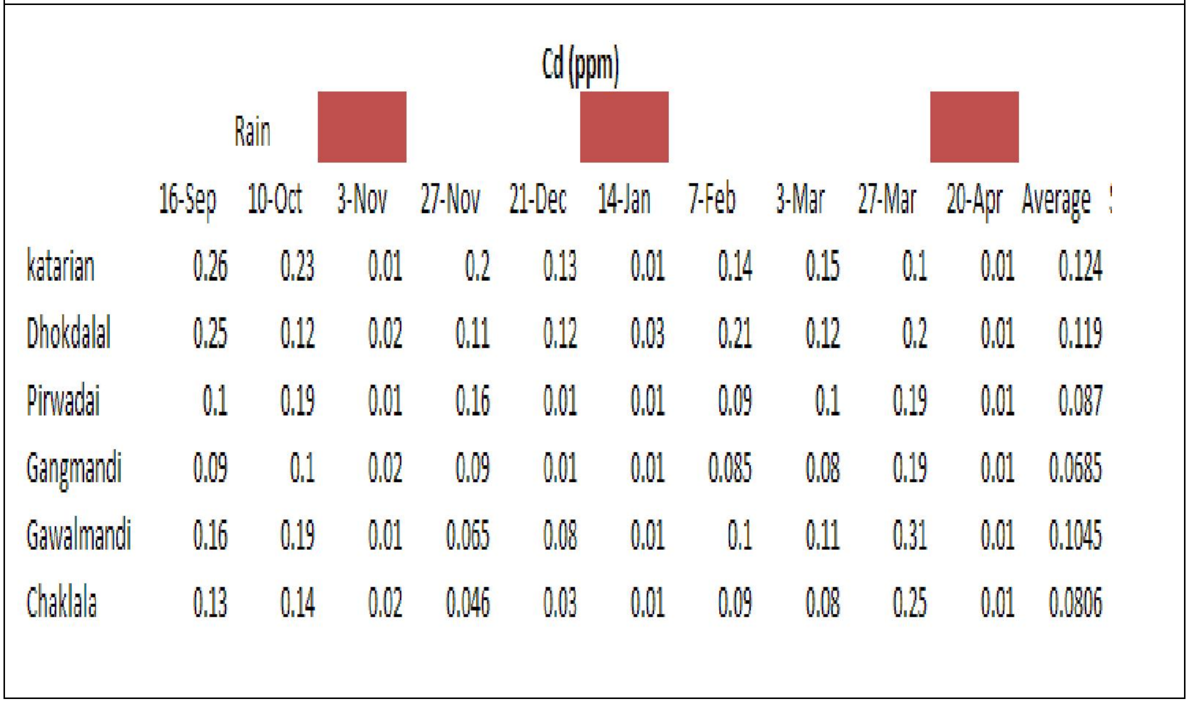
Fe (ppm)

			🟥			🟥				🟥	
	16-Sep	10-Oct	3-Nov	27-Nov	21-Dec	14-Jan	7-Feb	3-Mar	27-Mar	20-Apr	A
katarian	7.2	7.7	7.3	7.2	7.5	7.23	7.9	7.6	7.1	6.9	
dhokdalal	6.8	6.95	6.55	6.3	6	6.78	6.9	6.8	6.5	6.5	
Pirwadai	6.6	6.85	6.65	6.2	5.98	6.1	5.87	6.79	6.3	6.3	
Gangmanc	6.75	7	6.4	6.32	5.88	6	6	5.99	6	6	
Gawalmar	6.4	6.2	6.1	6.95	6	5.9	7.3	6.85	4.55	5.55	
Chaklala	6.39	5.8	6	4.95	5.55	5.38	6.38	6	3	5.39	



Zn (ppm)

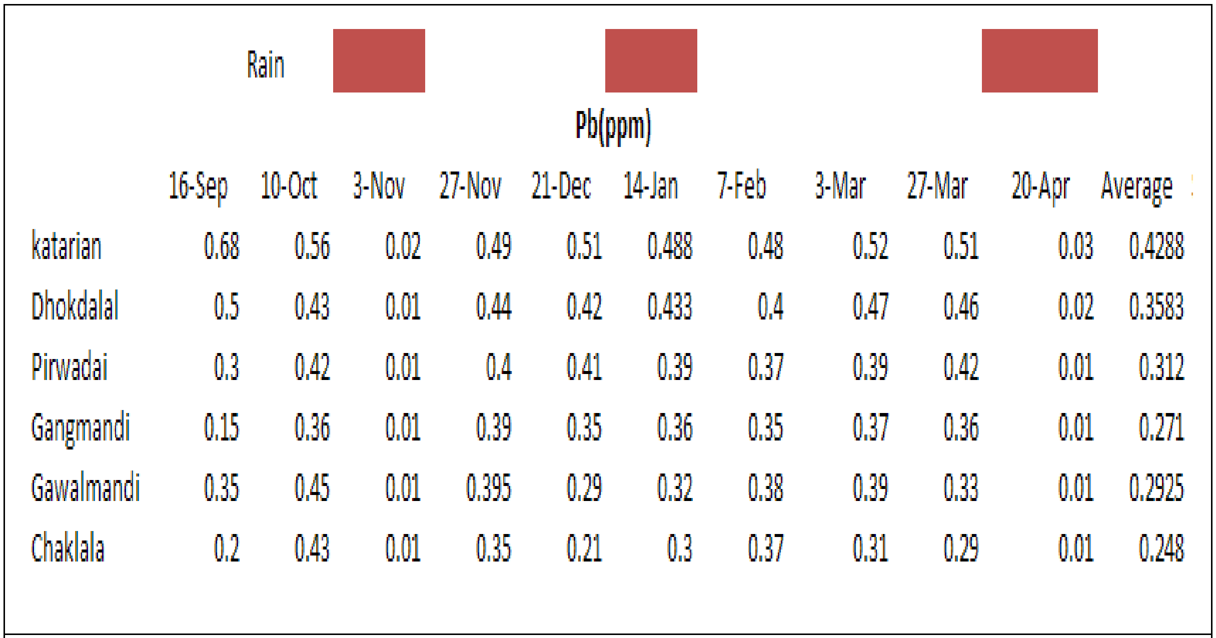
		Rain	🟥			🟥				🟥	
	16-Sep	10-Oct	3-Nov	27-Nov	21-Dec	14-Jan	7-Feb	3-Mar	27-Mar	20-Apr	Average
katarian	2.3	2.25	0.08	2.96	3	0.02	3.2	3.34	2.83	0.05	2.003
Dhokdalal	1.99	2.18	0.01	2.83	2.91	0.01	2.88	3.31	2.76	0.08	1.896
Pirwadai	1.91	2.03	0.07	2.29	2.75	0.01	1.99	2.9	2.65	0.01	1.661
Gangmandi	1.86	1.97	0.02	2.21	2.65	0.03	2.5	2.75	1.98	0.03	1.6
Gawalmandi	1.79	1.83	0.06	2	2.41	0.03	2.1	2.3	2.75	0.02	1.529
Chaklala	1.66	1.71	0.02	1.9	2	0.01	1.85	2.5	2.3	0.01	1.396



Cd (ppm)

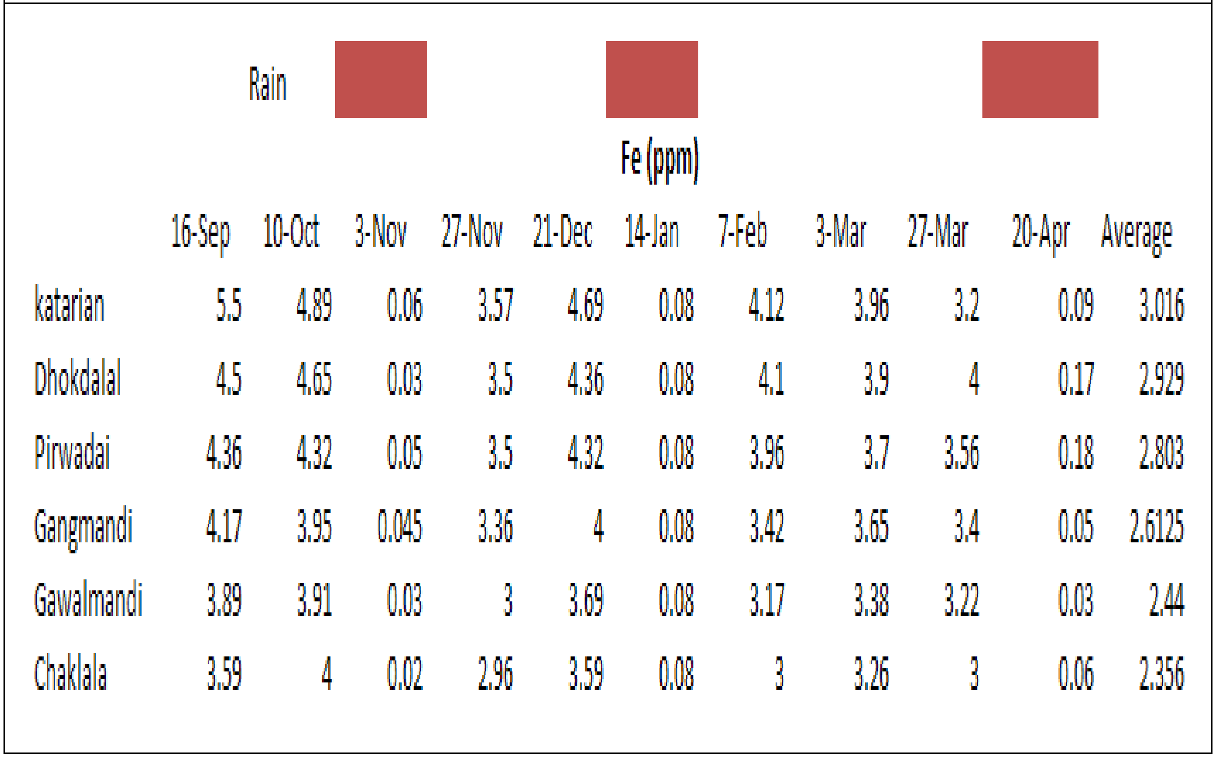
		Rain	🟥			🟥				🟥	
	16-Sep	10-Oct	3-Nov	27-Nov	21-Dec	14-Jan	7-Feb	3-Mar	27-Mar	20-Apr	Average
katarian	0.26	0.23	0.01	0.2	0.13	0.01	0.14	0.15	0.1	0.01	0.124
Dhokdalal	0.25	0.12	0.02	0.11	0.12	0.03	0.21	0.12	0.2	0.01	0.119
Pirwadai	0.1	0.19	0.01	0.16	0.01	0.01	0.09	0.1	0.19	0.01	0.087
Gangmandi	0.09	0.1	0.02	0.09	0.01	0.01	0.085	0.08	0.19	0.01	0.0685
Gawalmandi	0.16	0.19	0.01	0.065	0.08	0.01	0.1	0.11	0.31	0.01	0.1045
Chaklala	0.13	0.14	0.02	0.046	0.03	0.01	0.09	0.08	0.25	0.01	0.0806

APPENDIX B: Concentration (ppm) of surface water metals at each station using FAAS



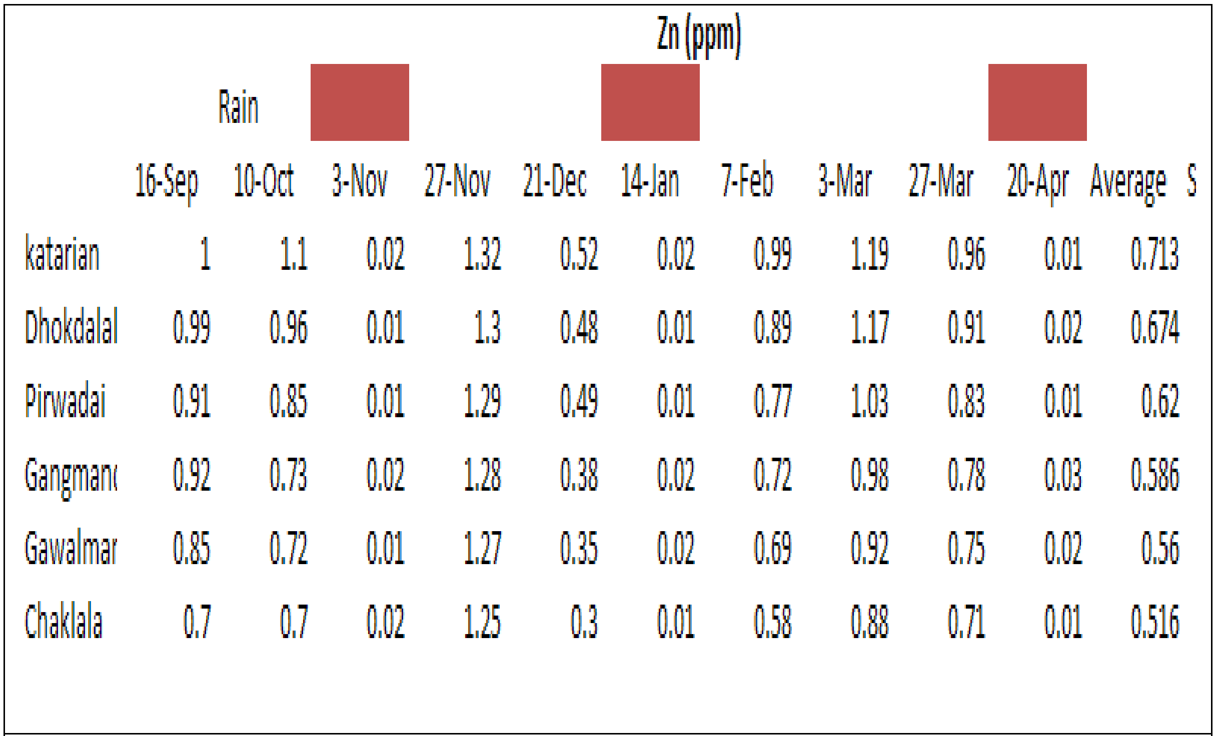
Pb(ppm)

	16-Sep	10-Oct	3-Nov	27-Nov	21-Dec	14-Jan	7-Feb	3-Mar	27-Mar	20-Apr	Average
Rain			🟥			🟥				🟥	
katarian	0.68	0.56	0.02	0.49	0.51	0.488	0.48	0.52	0.51	0.03	0.4288
Dhokdalal	0.5	0.43	0.01	0.44	0.42	0.433	0.4	0.47	0.46	0.02	0.3583
Pirwadai	0.3	0.42	0.01	0.4	0.41	0.39	0.37	0.39	0.42	0.01	0.312
Gangmandi	0.15	0.36	0.01	0.39	0.35	0.36	0.35	0.37	0.36	0.01	0.271
Gawalmandi	0.35	0.45	0.01	0.395	0.29	0.32	0.38	0.39	0.33	0.01	0.2925
Chaklala	0.2	0.43	0.01	0.35	0.21	0.3	0.37	0.31	0.29	0.01	0.248



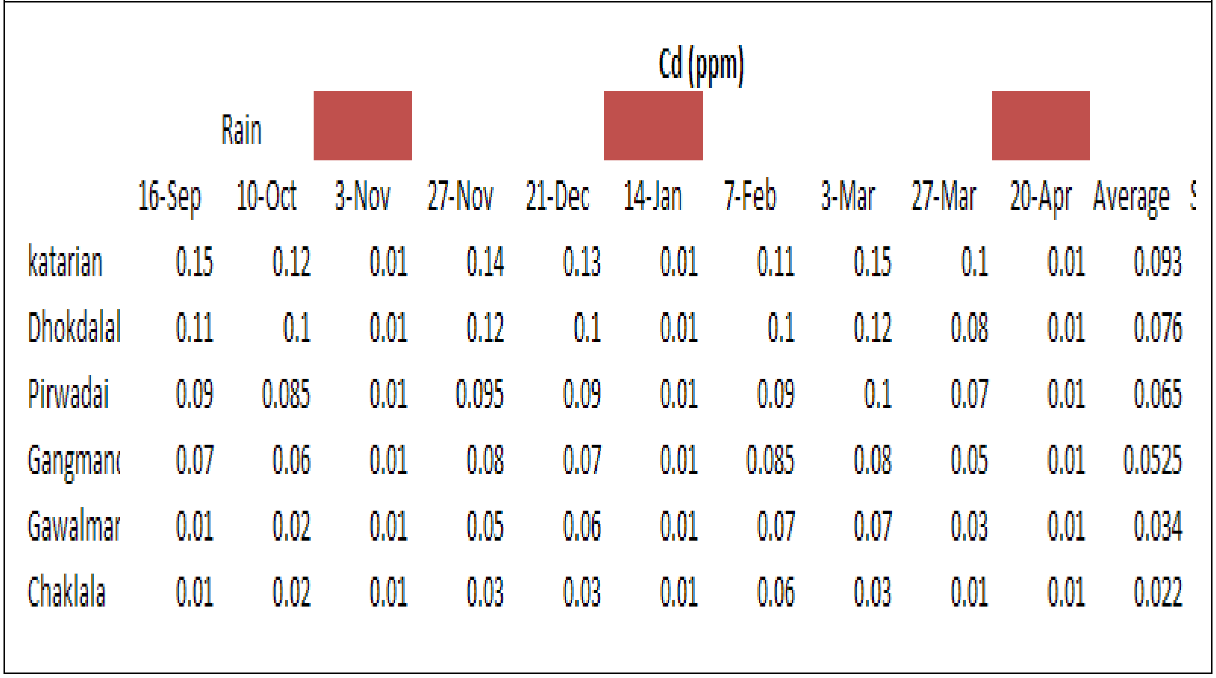
Fe (ppm)

	16-Sep	10-Oct	3-Nov	27-Nov	21-Dec	14-Jan	7-Feb	3-Mar	27-Mar	20-Apr	Average
Rain			🟥			🟥				🟥	
katarian	5.5	4.89	0.06	3.57	4.69	0.08	4.12	3.96	3.2	0.09	3.016
Dhokdalal	4.5	4.65	0.03	3.5	4.36	0.08	4.1	3.9	4	0.17	2.929
Pirwadai	4.36	4.32	0.05	3.5	4.32	0.08	3.96	3.7	3.56	0.18	2.803
Gangmandi	4.17	3.95	0.045	3.36	4	0.08	3.42	3.65	3.4	0.05	2.6125
Gawalmandi	3.89	3.91	0.03	3	3.69	0.08	3.17	3.38	3.22	0.03	2.44
Chaklala	3.59	4	0.02	2.96	3.59	0.08	3	3.26	3	0.06	2.356



Zn (ppm)

	16-Sep	10-Oct	3-Nov	27-Nov	21-Dec	14-Jan	7-Feb	3-Mar	27-Mar	20-Apr	Average	S
Rain			🟥			🟥				🟥		
katarian	1	1.1	0.02	1.32	0.52	0.02	0.99	1.19	0.96	0.01	0.713	
Dhokdalal	0.99	0.96	0.01	1.3	0.48	0.01	0.89	1.17	0.91	0.02	0.674	
Pirwadai	0.91	0.85	0.01	1.29	0.49	0.01	0.77	1.03	0.83	0.01	0.62	
Gangman	0.92	0.73	0.02	1.28	0.38	0.02	0.72	0.98	0.78	0.03	0.586	
Gawalmar	0.85	0.72	0.01	1.27	0.35	0.02	0.69	0.92	0.75	0.02	0.56	
Chaklala	0.7	0.7	0.02	1.25	0.3	0.01	0.58	0.88	0.71	0.01	0.516	



Cd (ppm)

	16-Sep	10-Oct	3-Nov	27-Nov	21-Dec	14-Jan	7-Feb	3-Mar	27-Mar	20-Apr	Average	S
Rain			🟥			🟥				🟥		
katarian	0.15	0.12	0.01	0.14	0.13	0.01	0.11	0.15	0.1	0.01	0.093	
Dhokdalal	0.11	0.1	0.01	0.12	0.1	0.01	0.1	0.12	0.08	0.01	0.076	
Pirwadai	0.09	0.085	0.01	0.095	0.09	0.01	0.09	0.1	0.07	0.01	0.065	
Gangman	0.07	0.06	0.01	0.08	0.07	0.01	0.085	0.08	0.05	0.01	0.0525	
Gawalmar	0.01	0.02	0.01	0.05	0.06	0.01	0.07	0.07	0.03	0.01	0.034	
Chaklala	0.01	0.02	0.01	0.03	0.03	0.01	0.06	0.03	0.01	0.01	0.022	

APPENDIX C: Concentrations (mg/l) of physicochemical parameters at each station

Parameters	**Stations**						**NEQS**
	Katarian	**Dhokdalal**	**Pirwadai**	**Gangmandi**	**Gawalmandi**	**Chaklala**	
DO (mg/l)	Avg: 1.23	Avg:1.16	1.19	1.05	1.23	1.27	
	Low: 0.58	Low: 0.54	Low: 0.49	Low: 0.58	Low: 0.38	Low: 0.88	
	High:1.86	High:1.66	High:1.56	High:1.36	High:1.96	High:2.06	
TDS (mg/l)	Avg: 2838.33	Avg:2735.83	Avg: 2734.33	Avg : 2793.67	Avg: 2593.00	Avg: 2634.00	3500
	Low:1575	Low:1465	Low:1830	Low:2275	Low:1975	Low:1575	
	High:3154	High:2854	High:2794	High:3254	High:3158	High:3154	
TSS (mg/l)	Avg:108.00	Avg:319.66	Avg: 388.17	Avg: 348.67	Avg: 244.5	Avg: 271.33	150
	Low: 76	Low: 250	Low: 320	Low: 320	Low: 210	Low: 250	
	High:140	High: 340	High: 400	High: 370	High: 265	High: 295	
COD (mg/l)	Avg: 467.29	Avg: 604.24	Avg: 561.68	Avg: 488.29	Avg: 446.93	Avg: 457.95	150
	Low: 440	Low: 580	Low: 520	Low: 450	Low: 430	Low: 430	
	High: 485	High: 630	High: 580	High: 510	High: 470	High: 470	
Temp. (°C)	Avg: 30.16	Avg: 34.3	Avg: 34.22	Avg: 33.07	Avg: 30.33	Avg: 30.28	40
	Low: 25	Low: 30	Low: 30	Low: 29	Low: 27	Low: 25	
	High: 34	High: 38	High: 38	High: 37	High: 33	High: 36	
EC (uS/cm)	Avg: 1109	Avg: 807	Avg: 777	Avg: 760	Avg: 941	Avg: 799	
	Low:1050	Low: 750	Low: 710	Low: 705	Low: 905	Low: 750	
	High: 1155	High: 845	High: 810	High: 805	High: 985	High: 830	
pH	6-8.5	6.99-8.96	7.7-9.11	8-9.26	6.85-8.42	7.9-8.49	6-10
Turbidity (NTU)	Avg: 40.68	Avg: 188.92	Avg: 214.44	Avg: 151.38	Avg: 84.07	Avg: 88.05	
	Low: 35	Low: 150	Low: 190	Low: 120	Low: 60	Low: 60	
	High: 45	High: 210	High: 235	High: 170	High: 105	High: 105	
BOD (mg/l)	Avg: 182.14	Avg: 303.88	Avg: 298.49	Avg: 257.68	Avg: 242.48	Avg: 252.60	80
	Low: 150	Low: 260	Low: 255	Low: 210	Low: 205	Low: 210	
	High: 210	High: 340	High: 330	High: 280	High: 280	High: 280	
TN (mg/l)	Avg: 19.21	Avg: 75.13	Avg: 67.60	Avg: 69.00	Avg: 50.58	Avg: 50.60	
	Low: 15	Low: 50	Low: 45	Low: 50	Low: 40	Low: 35	
	High: 24	High: 90	High: 80	High: 80	High: 65	High: 60	
TP (mg/l)	Avg: 17.03	Avg: 22.7	Avg: 21.13	Avg:18.72	Avg:15.67	Avg: 17.27	
	Low: 14	Low: 17	Low: 18	Low: 14	Low: 13	Low: 14	
	High: 20	High: 25	High: 25	High: 22.2	High: 18	High: 20	
Oil and Grease (mg/l)	Avg: 32.70	Avg: 43.92	Avg: 65.68	Avg: 54.25	Avg: 39.1	Avg: 53.63	10
	Low: 28	Low: 38	Low: 55	Low: 47	Low: 35	Low:49	
	High: 36	High: 47	High: 70	High: 60	High: 44	High: 59	

Means of six measurements measured between 16 Sept 2012 and 20 April 2013