RISK ASSESSMENT OF LEACHATES ON SOIL AND GROUND WATER QUALITY IN INDUSTRIAL AREAS OF GUJRANWALA DIVISION

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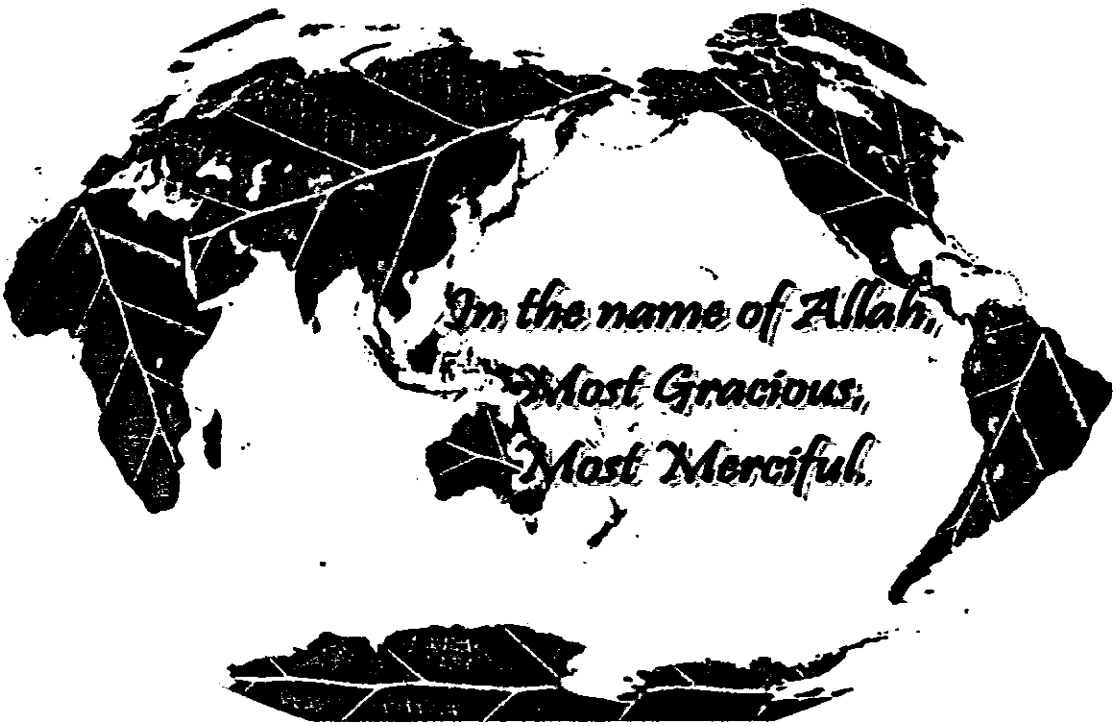
In the name of Allah,
Most Gracious,
Most Merciful.

DEDICATION

I dedicate my work to My Beloved Parents, family members

&

All those people affected by adverse effect of pollution

<u>**ACCEPTANCE BY THE VIVA VOCE COMMITTEE**</u>

Title of Thesis: Risk Assessment of *Leachates* on Soil and Ground Water Quality in Industrial Areas of Gujranwala Division

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DECLARATION

I *Mabroor Hassan* (101-FBAS/MSES/F09), student of MS in Environmental Science (session 2010-12), hereby declare that the matter printed in the thesis titled "Risk Assessment of Leachates on Soil and Ground Water Quality in Industrial Areas of Gujranwala Division" is my own work and has not been published or submitted as research work or thesis in any form in any other university or institute in Pakistan or abroad.

Dated: 11-07-2012

Signature of Deponent
Mabroor Hassan

FORWARDING SHEET BY RESEARCH SUPERVISOR

The thesis entitled "Risk Assessment of Leachates on Soil and Ground Water Quality in Industrial Areas of Gujranwala Division" submitted by Mabroor Hassan in partial fulfillment of MS degree in Environmental Science has been completed under my guidance and supervision. I am satisfied with the quality of student's research work and allow him to submit this thesis for further process to graduate with MS Degree from Department of Environmental Science, as per IIU rules & regulations.

Date: **11-07-2012**

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RISK ASSESSMENT OF LEACHATES ON SOIL AND GROUND WATER QUALITY IN INDUSTRIAL AREAS OF GUJRANWALA DIVISION

ABSTRACT

The waste generation has increased tremendously in developing countries due to lifestyle changes, population growth, pattern of consumption and consumerism. However, a large amount of different categories of waste generated is disposed off in open dump sites without segregation at source. The disposal of household organic waste continues along hazardous waste, i.e., paints, treated woods, electronic waste and batteries, that could result in making it more toxic and carcinogenic. It causes contamination through microbial byproducts present in leachates, hence, deteriorates soil and ground water quality. This study was designed to assess the effects of leachate on soil and water from aged open dump sites during pre- and post-rain season. The ground water samples were analyzed through APHA, 2005 while analysis of soil samples was carried out by ICARDA method (Rayan *et al.,* 2001). The physico-chemical characterization of soil samples collected from open dumping sites of both Sialkot and Gujranwala city confirmed the presence of macro inorganic components, high total organic carbon, and heavy metals. The heavy metal concentration present in soil was in order of: Zn>Fe>Cu>Cr>Ni>Cd>Co>Pb whereas As and Hg was not detected. As a whole, the site wise contamination order was Gujranwala-B > Gujranwala-A whereas Sialkot-A >Sialkot-B. Collectively, Gujranwala samples irrespective of water or soil were significantly contaminated as compared to Sialkot samples. The damaging environmental prospect associated with leaching of toxic chemicals from dumping sites was contamination of adjacent water

bodies and ground water. It was found that most of the pre-rain samples had pH value near to or higher than WHO/NEQS standards in both cities while TDS, EC, hardness, nitrate, sulfates, chlorides and phosphates concentrations were found to be within WHO/NEQS permissible standards. The heavy metals (Zn, Fe, Cu, Cr, Ni, Cd, Co and Pb) were detected in higher concentration than NEQS/WHO standards in most of water samples. The presence of high concentration of heavy metals, i.e., Cd, Zn, Fe, Cr, Cu, Ni was the indication of deleterious effects on ground water quality due to wate dumping sites. Moreover, people living in that area are at risk of toxic effects of heavy metals due to accumulation of metals in receipt of soils and release of concentrated leachate to the environment which further become potential source of entry into the food web.

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Those who bear the throne (of Allah) and those near to Him glorify and praise their Lord. They believe in Him and implore His forgiveness for those who believe… (Quran, 40:7).

If you be thankful, I will increase surely you (in bounty)….. (Quran surah Ibrahim 14:7)

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Mabroor Hassan

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LIST OF ABBREVIATIONS

AAS	Atomic Absorption Spectrometer
$AgNO_3$	Silver Nitrate
Al	Aluminum
APHA	American Public Health Associations
As	Arsenic
$BaCl_2$	Barium Chloride
BOD	Biochemical Oxygen Demand
Ca	Calcium
Cd	Cadmium
Cl^-	Chloride
Co	Cobalt
COD	Chemical Oxygen Demand
CPCB	Central Pollution Control Board
Cr	Chromium
Cu	Copper
DIP	Directorate of Industries Punjab
DO	Dissolved Oxygen
EBT	Eriochrome Black T
EC	Electrical Conductivity
EDTA	Ethylene-diamine-tetra-acetic Acid
E-waste	Electronics Waste
Fe	Iron
GC-MS	Gas Chromatography- Mass spectrometry
H_2SO_4	Sulfuric Acid
H_3PO_4	Orthophosphoric Acid
HCl	Hydrochloric Acid
Hg	Mercury
HNO_3	Nitric Acid
HPLC	High Performance liquid Chromatography
ICARDA	International Center for Agricultural Research in the Dry Areas
ID	Iron Deficiency
IDA	Iron-Deficiency Anemia
K	Potassium
K_2CrO_4	Potassium Chromate
KCl	Potassium Chloride
LC	Lethal Concentration
Mg	Magnesium
Mn	Manganese
MSW	Municipal Solid Wastes
N	Nitrogen
Na	Sodium
Na_2SO_4	Sodium Sulfate
NaCl	Sodium Chloride

NaOH	Sodium Hydroxide
NEQS	National Environmental Quality Standards
NH^{4+}	Ammonium
NH_4Cl	Ammonium Chloride
Ni	Nickel
NO_3^-	Nitrate
OJEC	Official Journal of the European Union
PAHs	Poly Aromatic Hydrocarbons
Pak EPA	Pakistan Environmental Protection Agency
Pb	Lead
$Pb(NO_3)_2$	Lead Nitrate
PO_4^{3-}	Phosphate
ppm	Parts per Millions
Sb	Antimony
SO_4^{2-}	Sulfate
SPSS	Statistical Package for the Social Sciences
Sr	Strontium
SS	Suspended Solids
SWM	Solid Waste Management
TCLP	Toxicity Characteristics Leaching Procedure
TDS	Total Dissolved Solids
TOC	Total Organic Carbon
TS	Total Solids
UNACCNIFPRI	United Nations Administrative Committee on Coordination on Nutrition and International Food Policy Research Institute
US EPA	United States Environmental Protection Agency
USW	Urban Solid Waste
WHO	World Health Organization
Zn	Zinc

I. INTRODUCTION

The rapid socio-economic development has interrupted physical and ecological environments due to exponential population increase and socio-economic activities, worldwide (Xie *et al.*, 2005). During the latter half of past century, waste generation has increased due to lifestyle changes and pattern of consumption and has resulted in the generation of large amount of different categories of waste (Oweis *et al.*, 2005). Waste is any material that is discarded, or produced during an operation or is disposed of after its use and expiration. Moreover, according to Basel convention[1], "Substances or objects which are disposed off or are intended to be disposed off or are required to be disposed off by the provisions of international law" are called waste (Baker *et al.*, 2004).

The exponential increase in the amount of municipal waste especially in urban centers has been observed due to the influx of human population to find employment in cities and rapid unplanned urbanization. In addition to municipal solid wastes (MSW), the manufacturing processes at industries are major sources of waste generation in both developed and developing countries (Kan, 2009). The perception of people living in the vicinity of dumping sites is limited about hazardous effects of waste on human health and environment due to lack of education (Paoli *et al.*, 2012).

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[1]Basel Convetion. (2004). The Basel Convention - Movements of Hazardous Waste and their Disposal, Kuching, Malaysia.

Although solid waste is considered as an emerging issue as it is generated depending on the affluence and has a wider range between 0.5 to 4.5 kg per person per day in different parts of world (Bakare *et al.*, 2005). Recently, the hazardous effects of waste on health and environment have ultimately increased public attention about waste management practices and contamination issues in developed world. Numerous procedures and techniques had been discussed for waste minimization through, reduce, reuse, recycle and through maximum resource recovery, as well (William, 2005).

Similarly, the waste disposal has become an important issue for societies in the developing world due to burgeoning population especially in South Asia, Africa and Eastern Europe (Papadopoulou *et al.*, 2007). The most common disposing off techniques of waste products include: by storing them on land, open burning, discharging in water bodies or disposing them off on or below the land surface such as open dumping and landfills, however it has resulted in groundwater and soil contamination over the years (Papadopoulou *et al.*, 2007; Maqbool *et al.*, 2011). Due to variation in their economies, developing countries are especially lack efficient solid waste management (SWM) plan due to inadequate financial and ill-trained human resources that has resulted in environmental health hazards reported every now and then (Calo and Parise, 2009; Mensah, 2006). In most cases, lack of basic waste management services to collect huge quantity of waste (one to two-third) go uncontrolled and even unavailable proper disposal sites to accommodate the collected waste by local authorities have already been reported (Zurbrugg, 2003). Furthermore, if sites for waste disposal are available, they are not properly designed, engineered and maintained by the municipal administration (Calo and Parise, 2009).

Landfilling has remained the most dominant municipal solid waste disposal technique in developing countries, i.e., Pakistan, due to its low cost. However, the use of ill-planned and non-engineered dumping sites which do not have proper design and operation mechanism are bad sites for final disposal of MSW and impart more adverse impacts on environment (Al Yaqout, 2003; Mangimbulude *et al.,* 2009). Such waste disposal sites could result in leaching and mobility of contaminants into water resources which is categorized as one of major environmental problem in developing world (Castaneda *et al.,* 2012).

The *leachates* are elute product of waste material that drain, filter, decompose and react and contain suspended material dissolved in water that have potential to deteriorate soil and ground water quality through infiltration and ultimately poses risks to health (Weng *et al.,* 2003). It has been reported that the biochemical degradation product of waste in the form of suspended liquid particles percolate through soil into water reservoir under-ground (Lopes de Morais and Peralta-Zamora, 2005). The leaching water either comes from surface water runoff source or through rain and once it comes into contact with waste at the dumping sites, provide required moisture to trigger degradation process (Weng *et al.,* 2003). The variability among the characteristics of leachate is very high and depends on the nature and composition of waste, hydrology and hydrogeology of landfill site, rainfall pattern of the area, age of landfill site and type of waste it contains (Vesilind *et al.,* 2002). Furthermore, disposal site engineering and its operation to deal with by products are additional factors contributing to leachate movement (Vesilind *et al.,* 2002).

Solid waste leachate are also characterized with the presence of macro inorganic components, total organic carbon and organic matter, trace elements (heavy metals) and xenobiotic organic contaminants along with toxic, carcinogenic chemicals and infectious microbial contaminants (Kjeldsen *et al.,* 2002; Matejczyk *et al.,* 2011). Such components have been reported to possess the capacity to alter microbiology of landfill and ultimately, the aquifer geochemistry (Roling *et al.,* 2001; Sastre *et al.,* 2003). Besides producing contaminated leachates, it may also results in the release of methane gas, another important environmental issue associated with landfill sites (Oygard *et al.,* 2004).

It is evident that ground water sources in the vicinity of landfills are under the load of leachate contamination which has extensive risks to nearby population and environment, as a whole. The studies on impact of landfill leachate on both surface and groundwater quality have increased in number during recent years: due to emerging issues related to health and disease (Saarela, 2003; AbuRukah and Kofahi, 2001; Looser *et al.,* 1999; Christensen *et al.,* 1998); due to introduction of a variety of chemicals into water bodies originating from disposed products (Paxeus, 2000; Christensen *et al.,* 2001; Baun *et al.,* 2004; Oman and Junestedt, 2008); and from both industrial and household wastes through direct induction or dispersion of chemicals with municipal solid waste (Paxeus, 2000; Christensen *et al.,* 2001; Baun *et al.,* 2004; Oman and Junestedt, 2008; Tarradellas *et al.,* 1997; Eijsackers, 1998). It is evident that high concentration of heavy metal, pesticides, fertilizers, dyes and paints are found along municipal waste due to mixing of various waste (Erses *et al.*, 2005)

Heavy metals are natural components of the earth's crust and several of them are recognized as essential micro nutrients for living organisms, however, their excessive concentration leads to intoxication (Lenntech, 2004), and have been related to many ailments such as cancer, cell damage and inflammation (Seco *et al.*, 2003; Valko *et al.*, 2006). If surface and ground water contaminated with heavy metals is taken up by the plants, or is emitted into air or is distributed into soil through bonding with soil organic matter and clay particles (Krishna and Govil, 2007), it causes many environmental problems. The Official Journal of the European Union (OJEC) categorized lead (Pb), cadmium (Cd) and nickel (Ni) as precedence contaminates in leachate for ground water (OJEC, 2001). The high redox condition is favorable for increase in the metal binding potential to manganese and iron oxides which reduce the binding capacity with organic compounds, carbonates and sulfides (Flyhammar, 1998). The degradation rate along with buffer capacity of acidic components in dumping site has been significantly influenced in the upper layer of dumpsite due to the presence of sufficient moisture content and more possibility of oxygen diffusion which reduce the pH, sulfide oxidation and alkalinity and provides the most suitable condition for release of heavy metals in environment (Bozkurt *et al.*, 2000; Matensson *et al.*, 1999). It is evident that the landfill leachates contained high concentrations of cadmium, mercury, nickel, manganese, copper and lead where the toxicity of leachates depends on the concentration of such metals associated with organic matter (Olivero-Verbel *et al.*, 2008).

The untreated industrial effluents that contain dioxins, trace elements, phenols, chlorides, cyanides and furans along, percolation of pollutants from improperly disposed waste has increased the risk of environmental concerns in water resources due to insufficient initiatives for protection and conservation of environment (Flohr *et al.*, 2012; Ali and Sreekrishnan, 2001; Sisinno, 2003). The chrome tanning due to cheaper, efficient processing, colorful and stable product is widely used in leather industries (Hafeez *et al.*, 2002) but according to data 10,000 kg of skins per day resulted in 5,500 kg/day of various types of waste including by products, such as trimming, dust curing salts, shaving buffs and packing material along toxic untreated wastewater mainly contains oxidized hexa-valent chromium from leather industry of Pakistan (Barnhart, 1997; Nazir and Bareen, 2008; Syed *et al.*, 2010). In addition, some grave problems regarding phthalates, bisphenols, chlorinated solvents, petroleum hydrocarbons, adipates, poly aromatic hydrocarbons (PAHs) and resins have been reported previously in leachates of landfill sites (Moran *et al.*, 2005; Moran *et al.*, 2006; Verliefde *et al.*, 2007). In addition, the synthetic organic compounds, with diverse arrangement of their molecules, have been utilized in synthesis of medicines, industrial processes and food safety and have resulted in toxicity in both terrestrial and aquatic environment during last few decades (Schwarzenbach *et al.*, 2006; Kummerer, 2009; Lapworth *et al.*, 2012). The amount of municipal solid waste (SWM) is continuously increasing annually in developing courtiers (Kansal, 2002) which is disposed off without source segregation in open dumping sites (Pare *et al.*, 1999) that is an apparent source of soil, air and water pollution (Khajuria *et al.*, 2008).Most of MSW is discarded on land surface in more or less uncontrolled manner in Asian developing countries. Lack of adequate knowledge and responsiveness at the grassroots level of the waste producers magnify the issue of littering which results in a serious threat to public health (Khajuria *et al.*, 2010)

The environmental evaluation may be helpful to conserve, protect and rehabilitate the natural environment and health of public through analysis of various types of pollutants including metals, toxins and pesticides in food, soil, air, and water samples. The physico-chemical monitoring for identification and quantification of toxicants can be used for evaluation process, control and regulatory purposes after comparison with stipulated values for particular environmental samples (Mansour and Gad, 2010)

1.1 Problem Statement

According to various previous studies, the developing countries have around 60-90% of municipal solid waste discharged in environmentally unsafe open dumps and landfills (Khajuria *et al.*, 2010). Open dumping sites have covered 268.8 hectares land area of Pakistan till 2010 which contained many fertile pieces of land area (Khajuria *et al.*, 2010). The open dumpsite undergoes different effects due to oxygen diffusion and direct exposure to atmosphere and climatic conditions (Flyhammar, 1998). The urban and industrial waste disposal in open dumping sites along flooding and agricultural run off during monsoon season in unlined drains are some of the most alarming polluting sources of groundwater in Sialkot and Gujranwala. The industrialized areas are most important for economy of country so it is not only important to evaluate and monitor environmental situation, quality, quantity of its water resources (Rizwan Ullah *et al.*, 2009) but also soil and sediments to avoid contamination.

Previously some studies have been conducted in Gujranwala, Shekhupura, Lahore, Faisal Abad, Peshawar, Karachi, Qasur, Rawalpindi, Sialkot and Gujarat on water quality and it was concluded that ground quality is at risk due to untreated, unchecked disposal of wastewater from industries and agricultural run off having fertilizer and persistent organic pollutants (POPs) in the form of different pesticides (Bhutta *et al.*, 2002). The leachate from dumping site of waste is one of major sources of surface water, ground water and soil contamination and poses serious harmful impacts on human health and environment. The preliminary studies about health problems due to leachate contamination are not available; however, water borne diseases are common in population near to study area. This study was designed to assess the risk of leachate towards environmental hazards in and around Gujranwala and Sialkot industrial and residential areas.

1.2 Aims and Objectives

This study was designed

- To evaluate the effects of leachate on soil by collecting pre-rain and post-rain samples from open dumping sites of domestic and industrial waste in Sialkot and Gujranwala.

- To determine the effects of leachate on ground water quality by collecting pre-rain and post-rain samples from open dumping sites of domestic and industrial waste
- To detect the presence of organic pollutants in soil and water samples.
- To evaluate the ground water quality in the vicinity of dumping sites.
- To compare the contaminants concentration in pre-rain and post-rain season samples of soil and water.

1.3 Significance of Study

In order to conserve, protect and rehabilitate the environmental health, the environmental pollutants present in water, soil and air must be quantified to know their source and intensity and decisions with regards to their regulation, control and rehabilitation must be made.

The open dumping sites pose serious environmental and health effects to human population, biodiversity and ground water of that area. The leaching of toxic chemicals and persistent trace elements is consist problem in such areas moreover, illegal activities such as transfer of waste to construction sites for filling of site had magnified the problem. This study will play beneficial role in reduction of risks and adverse impacts of leachate on human health and environment from improper and inadequate dumping of waste. Furthermore, it will be helpful for researchers in identification of problems associated with peculation of chemicals into ground water.

II-REVIEW OF LITERATURE

Any used material that is disposed off or is intended to be disposed off after use, re-use or produced as a byproduct of a manufacturing process is called as waste. It is imperative that waste is properly treated before disposal in order to make it safe for environmental health. However, various types of waste, i.e., domestic garbage, wastewater from household or industry, biosolids from sewage drains, industrial effluents, waste biomass, etc. are discarded at random dumping or landfill sites in peri-urban areas without prior treatment. Current review of literature is intended to report recent work conducted in the area of municipal waste, leachates, their components and effects on water and soil.

2.1 Wastes and Leachates

The developing countries are still striving for proper disposal for their generated solid waste (World Bank Group, 2001) due to lack of organizational structure, governmental management, regulations, legislations, information, planning and financial restrictions (Tiynmaz and Demir, 2006; Vesilind *et al.,* 2002). The majority of so called landfills are just simple open dumping sites without proper lining and their construction is not in accordance with international standards and requirements. (World Bank Group, 2001). The solid waste disposed in open dump systems is a source of surface leachate runoff and gaseous emissions (Mangimbulude *et al.*, 2009; Trankler *et al.*, 2005). According to various studies, the leachates contain:

- Dissolved organic matter including, methane, volatile fatty acids, chemical oxygen demand and total organic carbon.
- Inorganic macro components such as sodium, potassium, calcium, magnesium, iron, ammonium ion, bicarbonates and chlorides.
- Heavy metals, i.e., cadmium, chromium, lead, copper, zinc and nickel etc.
- Xenobiotic organic compounds, usually coming from household or industrial chemicals that are present in relatively low concentration in the leachate (Christensen *et al.*, 1994).

Previously, it has been evaluated that the waste composition defines the hazardous or non-hazardous nature of waste and the waste composition manipulates the release mechanism of chemical components and human exposure. In order to reduce environmental threats, the decision making about risk assessment and reduction in possible impacts could be facilitated by standardized characterization leaching test through chemical speciation modeling of each constituent of leachate (van der Sloot and Kosson, 2012).

Parodi *et al.* (2011) determined that about 39% of total waste of France is still disposed off in landfills despite treatment of MSW and national recycling campaigns. It seemed necessary to integrate current techniques to new management plans and methods to meets the requirement of sustainable development and energy. For this purpose, leaching test could be introduced to assess the capacity of movement of mineral and organic compounds.

It was reported that the town of Mostar, Bosnia Herzegovinia, had many problems and difficulties in the field of environmental management after war and conflict. A number of uncontrolled dumping sites were found in the mining area where many tons of solid waste had been disposed of. Neretva River which is major source of water distribution in city was further exacerbated by the proximity of detrimental pollution and resulted in soil and ground water pollution (Calo and Parise, 2009).

Salem *et al.* (2008) designed a study to deal with the Ouled Fayet site in Algiers, which consistently received 363,000 tons/year non hazardous waste from different 34 municipalities and was operational for 5 years. The analysis elaborated that the very concentrated ratio of COD and organic matter was present on dumping site.

The current scenario of municipal solid waste management under supervision of local authorities had serious gaps and reservations in Kenya which resulted in surface and ground water contaminations due to the lack of attention and information about environment impacts and their consideration in construction of disposal sites. The illegal activities like disposal of waste on road sides and river banks along poor collection, transportations, infrastructure dumping techniques and lack of funding had potential hazards to nearby properties (Henry *et al.*, 2006).

Esakku *et al.* (2003) highlighted that the issues associated with unorganized waste disposal in India. The trace metal content in different depths of Perungudi dumping ground near Chennai was studied to analyze the leachates collected from the same sampling area. The results clearly elaborated the concentrations of nickel, zinc, lead, copper, cadmium, chromium and mercury were found exceeding the limits prescribed by Central Pollution Control Board (CPCB).

Heavy metal is a collective term, which is used for the group of metals and metalloids with atomic density greater than 4000 kg m^{-3}, or 5 times more than water (Garbarino *et al.,* 1995; Hashim *et al.,* 2011) and they are also natural components of the earth's crust. Furthermore, several of them are recognized as essential micro nutrients for living things however their excessive concentration leads to intoxication (Lenntech, 2004). The most stable oxidation states in ionic form of these metals become more toxic and preferably react with biomolecules of body and converts into extremely stable and non dissociable biotoxic compounds (Duruibe *et al.,* 2007) which have been related to many ailments such as cancer, cell damage and inflammation (Seco *et al.,* 2003; Valko *et al.,* 2006).

Osu and Okoro, (2012) characterized heavy metals content and physico-chemical characteristics of leachate from the different sites of municipal solid waste landfill dumping site in Abia State, Nigeria. The pH of all the leachate samples was slightly acidic, the electric conductivity was found to be high and a strong variation in COD level was observed in all samples. However, BOD_5 test, TSS and dissolved oxygen level were relatively low in all leachate samples. Furthermore, the metals (Zn, Cu, Mn, Cr, As, Cd, Pb and V) concentration in the leachate samples was higher than the National Nigerian standards.

The leachates were collected and analyzed from different 8 landfills for heavy metals in France, the results showed that most of metals were concentrated in <30 kDa fraction but the metals Cu, Ni, Zn, Pb developed association with larger particles. The initial speciation calculations indicated the relatively higher attraction of super-saturated heavy metals such as Cu, Zn, Ni and lead with sulphur phase rather organic matter (Claret *et al.,* 2011).

Ziyang *et al.* (2009) suggested that COD composition in leachate would vary the discarded time of waste extended. The samples of leachate having different age were collected from the largest landfill in China, Laogang Refuse Landfill of Shanghai that receives 7600 tons refuse per day for final disposal. The COD composition in leachate samples was characterized by converting size-fractioned into colloidal fractions and at the end to dissolved fractions based on the molecular weight distribution. These fractions were further classified into six more fractions based on their hydrophilic and hydrophobic nature. Moreover, results predicted that the total organic carbon decreased as disposal time increased.

Al-Muzaini, (2009) evaluated the effects of age on compositing, properties and stabilization degree of leachate from boreholes installed at ten, twenty and twenty three years old landfills situated at Qurain, Sulaibiya and Jaleeb Al Shoukh. The type of solid waste materials dumped at these sites could be attributed by presence of cobalt, arsenic, calcium, manganese, magnesium, mercury, iron, zinc, vanadium, tin, selenium, lead, nickel and sodium. Furthermore, the concentration levels of vanadium copper and nickel were high indicating the final disposal of mainly petroleum related waste at the sites.

Ogundiran and Afolabi, (2008) made physicochemical characterization and heavy metal analysis of solid waste dumping sites at Landfill, Lagos, Nigeria. Zn was the most abundant metal in the area mean while Cd was present in lowest concentration. A significant correlation of Cu and Cr was observed with TS and SS which were also dominant metals in dormant site and were attached to the solids. The landfill leachate analysis indicated that it was more alkaline, with high level of chemical oxygen demand.

The levels of Pb, Cr, Cd, Fe and Hg in the leachates from different four sanitary landfills in Western Norway containing deposited waste were assessed through simulation of mass balance during one year. The observed deposition per day of chromium, cadmium, iron, lead and mercury was less than 1%, 0.06%, 18%, 0.01% and 0.02% respectively and iron was found to be most mobile metal under the prevailing conditions (Oygard *et al.*, 2004).

2.2 Leachates and Soil Contamination

It has been reported that trace elements such as heavy metals are most toxic pollutants among numerous types of contaminants present in landfill leachate due to their persistent nature than organic pesticides and petroleum by products (Adriano, 2001; Santona *et al.,* 2006). These metals have capability of transfer into biotic and abiotic components of surrounding ecosystem which poses serious health effects via water supply and food chain (Mico *et al.,* 2006). The aged, mixed industrial and urban solid waste dumping sites had adversely contributed in contamination of soil and ecosystem of peri-urban areas through physical medium, mobility due to affinity and attractive flow forces that facilitate the contacts with organic pollutants, salinity and toxic heavy metals (Pastor and Hernandez, 2012).

The direct or indirect consistent release of heavy metals into terrestrial environment with high population growth rate and unplanned urbanization and industrial development has polluted the soil (Lee *et al.,* 2006; Abdul-Qadir *et al.,* 2008). The fate of heavy metals in the environment depends on sediment and soil characteristics including chemical and biological processes along with soil organic matter, mineral composition loading rate, metal source, redox potential and pH of soil (Leleyter *et al.,* 2012; Santona *et al.,* 2006). The active landfill leachates with high concentrations of the COD, volatile suspended solids, total TS, total organic carbon TOC, electrical conductivity and had high contents of Fe, Cr and Ni have been found in China (Huan-jung et al., 2006; Pivato and Gaspari, 2006).

Pastor and Hernandez, (2012) determined the soil pollution level in landfill site in Spain and evaluated the impacts of those urban solid waste (USW) landfills, were continuously assessed that were capped with a coating of soil twenty year ago. The salts (Cl^-, SO_4^{2-} and NO_3^-) and organic compounds along nickel zinc, chromium and copper were assessed in surface water and soil samples collected from landfill region. Several aliphatic and aromatic organic compounds, which used as insecticide such as lindane were detected relatively in higher concentration in soil.

Vedrenne *et al.* (2012) characterized a mature landfill site during dry season. The major pollutants were characterized in leachate samples collected during dry season from the territory of Tetlama, Morelos, Mexico landfill. Substantial value of total carbon and ammonium ion were found, furthermore, high concentrations of mercury, lead and As along with nickel, manganese, zinc, cobalt and cadmium concentration at trace levels was detected in all samples. Furthermore, the LC_{50} of the leachate among different components was demonstrated as an antagonistic interaction on Brine Shrimp Assay.

Al-Wabel *et al.* (2011) reported the liquid and bio-solids (landfill sediments) product from landfills had many toxic substances, which may negatively affect on the environmental health. The analysis of landfill leachates concluded that the concentration of COD, EC, TSS, soluble ions of sodium, calcium, potassium, magnesium, chloride, bicarbonate, sulphate and heavy metals (Fe, Mn, As, Ni, Cr, Zn and Cu) was relatively higher than permissible limits. While in the bio-solids (landfill sediments) the average content of vanadium, nickel, molybdenum, cadmium, manganese, iron, copper, and chromium concentrations was also detected. The pH value of samples was slightly acidic. The relatively higher variations between the upper and lower limits of the studied parameters had led to conclude that in order to obtain representative data of landfill sediments long term monitoring programmes are essential.

Regadío *et al.* (2012) recommended that the geological barrier beneath landfills can play an effective role soil protection. The observations were made in waste deposited landfills for twelve years in Spain. The major physico-chemical characteristics i.e., EC, NH^{4+}, Na^+ water-soluble organic carbon and exchangeable Na^+ and NH^{4+} were measured. According to the results, geological parameters like cationic exchange capacities, surface area and mineralogy were found as a function of depth.

Bareen and Tahira, (2011) described that the lands contaminated by tannery effluent had been lost its fertility because of continuous percolation and logging of effluents from Depalpur road, Kasur, Pakistan. The different twelve plant species including *Suaeda fruticosa, Calatropis procera* and *Salvadora oleoides* were planted under same condition in study area which were found to be the most common and high biomass producing plants along with very high capabilities for metal extraction. According to the results, a variable uptake of heavy metals released from tannery, i.e., Cr, Cu and Ni was reported.

To estimate the presence of heavy metals in municipal solid waste (MSW), Cu and Zn were estimated with extensive distribution in most types of municipal solid waste in China and an overall 55.1% to 99.5% of ash, paper, plastic and kitchen waste was observed (Long *et al.,* 2011). Furthermore, the contribution of zinc and copper level in all characteristics was calculated between 76.3- 82.3% whereas heavy metals concentration in municipal solid was at variable degrees, was found beyond the permissible limits of "environmental quality standards of China for soil" (Long *et al.*, 2011). Similarly, Yidong *et al.* (2011) explored the heavy metal content in the rural waste samples collected from one classical dumping site in Ningbo and evaluate the contamination potential. The experimental results narrated the average heavy metal content in the rural waste was in the sequence of zinc> copper> chromium> lead>cadmium and their corresponding concentration levels were 692.0±900.9, 402.6±452.4, 196.3±299.6, 167.3±124.5 and 3.9±4.5 mg/kg, respectively.

In terms of determining the levels of various heavy metals present in the soil and leachate of the Addis Ababa, Africa, solid waste dumping site and its possible ecological and public health risk were determined by examination of total six soil and six leachate samples from December 15, 2009 to January 10, 2010. The concentration of heavy metals such as Zn, Al, Cr, Co, Pb and Ni of the dumping site and nearby open land soil samples were found comparatively higher than the internationally acceptable limit for the soil (Beyene and Banerjee, 2011).

Palma and Mecozzi, (2010) observed the percolation of contaminants, yet the presence of specific pollutants in low concentrations could stimulate a strong adaptation in soil physical and chemical properties because of change of soil matrix and aqueous phase equilibrium. The concentrations of nickel, iron and manganese were selected to evaluate the modification in characteristics of soil. Results indicated a greater release of those parameters under acidic conditions, a positive effect was observed in the addition of an oxidant and negative redox potentials facilitated a great Mn mobilization.

Malik *et al.* (2010) studied concentrations of some metals particularly sodium, potassium, calcium, cadmium, chromium, cobalt, lead, zinc, nickel, magnesium, iron and copper in soil surface of Sialkot, an internationally well known for surgical, pharmaceutical industry and tanneries. The spatial distribution map exhibited that the heavy metal concentrations were comparatively higher in streams and traffic routs of city. The results demonstrated that the lead, cadmium, zinc, chromium and nickel values exceeded the stipulated values for urban soil and required a detailed study to assess gravity of problem.

In a similar study, Nawaz *et al.* (2006) observed the possible effects of heavy metals on rice straw, paddy yield and soil from polluted water. The goals of study were achieved by growing three fine varieties of rice at bank of Nallah Daik at three different locations in Sheikhupura. Copper and cadmium contraction in rice crop was increased after harvesting because of metal accumulation in crop while in soil was within safe limits.

It has been reported that China and Nigeria have become prime destinations for the world's e-waste disposal regions, leading to serious environmental contamination during last couple of decades. A comparative study was carried out to assess the level of contamination using soils and plants from e-waste dumping and processing sites in both countries. Poly brominated diphenyls ethers, poly chlorinated biphenyls, and poly aromatic hydrocarbons concentration levels whereas heavy metals were also detected. The results clearly revealed that the soil samples from China and plant samples from Nigeria were amongst the contaminated samples of e-waste (Alabi *et al.*, 2012).

Perez-Leblic *et al.* (2012) pinned down the effects of polychlorinated biphenyls (PCBs), hydrocarbons, and polycyclic aromatic hydrocarbons (PAHs) on microbial diversity and activity in a municipal solid waste landfill in Torrejon de Ardoz and also regard the landfills as the recipients of environmentally degrading aliphatic as well aromatic hydrocarbons contaminants. Various areas were selected for soil sampling in which the concentration of PAHs, PCBs and total hydrocarbons, were measured. The samples showed high level of total hydrocarbon among 4 samples, while due to benzo-a-pyrene presence in some samples, a low microbial diversity was exhibited. In another similar study, Matejczyk *et al.* (2011) evaluated and characterized the chemical and microbiological parameter in leachates of landfill sites situated in Southern Poland and results confirmed the presence of only poly aromatic hydrocarbons, pentachlorobenzene, Cd, mercury and hexachlorobutadiene along different types of infectious bacteria and filamentous fungi and bacteria which was the indication of epidemiological hazard.

An integrated risk assessment study was reported in the territory within five kilometers from a landfill that received non-hazardous waste. The maximum exposure of contaminated soil, food, air and water to both children and adults at chronic level was measured through risk assessment and carcinogenic effects of PAHs, vinyl chloride monomer, dioxins and furans, produced by burning of waste. The risk assessment for both carcinogenic and non-carcinogenic pollutants showed that the hazard index was relatively below the accepted values prescribed by national legislation and international agencies such as World Health Organization (Davoli *et al.*, 2010).

Municipal solid waste samples were taken for screening and analysis of hazardous organic contaminants from Channai, Kodungaiyur, and Perungudi. Toxicity Characteristics Leaching Procedure (TCLP) and solvent extraction methods were used while GC MS was used for organic extract analysis. Toxic phenolics, phthalates were found in higher concentration while other hazardous compounds like di-butyl, mono butyl, *p*-cresol and di-ethyl phthalates were detected in the range of > 200 mg/ Kg (Swati *et al.*, 2008)

2.3 Leachates and Water (Surface and Ground Water) Contamination

Although 70% of planet earth is covered with water, fresh water supply constitute only 0.73 % of total water available to living organisms to survive in the form of rivers, lakes, underground water supply and aquifers. According to World Water Assessment Program (WWAP), a drastic decline in per person available water to 30% in future within next two decades would result in 2.7 billon people falling under acute water stress (Harvey *et al.*, 2002). The availability of safe, clean and nearby-available drinking water has remained a dream for almost one sixth inhabitants of this universe (Smedley and Kinniburgh, 2002). It has been implicated that lifestyle change, i.e., living in bigger houses with lawns and furthermore, household consumption pattern due to high water-required gadgets installed in houses, has increased the consumption of water manifold especially in developed world (Mroczek, 2005). Moreover, contamination of available fresh water continues unabated due to perpetual release of domestic waste water and industrial effluents, non-availability of waste water treatment on-site, and neglect on governmental regulatory agencies, especially in developing world. Landfill and dumping sites are additional burden on water resource due to leaching of numerous chemicals to underground water beside contaminating soil, as well, due to run off and percolation. Once this underground water becomes a water supply to the adjoining population, the detrimental nature of chemicals cause acute and chronic diseases in the population, especially in developing country like Pakistan.

Due to non-existence of Clean water and Soil Act in Pakistan, or regulatory procedure through Federal or provincial governments, municipalities and industry have continued to pollute water reservoirs and distribution network. Numerous studies have suggested water pollution caused by industrial effluents and waste material goes unaccounted due to improper management and regulations. Although, some industries have followed treatment techniques before disposal, most of the industries are still lacking this requirement due to the negligence of civic authorities.

It had been depicted that the usual and the most neglected cause of water pollution are uncontrolled dumping of Municipal Solid Waste. The water present in waste accompanied with water generated by biodegradation and infiltration of water by rainfall cause the leachate to leave the dumping ground laterally or vertically and define its final destination into the groundwater thereby causing contamination (Castaneda *et al.*, 2012). The ground water samples collected during the rainy season were analyzed for various physical and chemical properties. During the study, it was observed that total dissolved solids were ranged between 546 mg/L to 907 mg/L and compared with permissible limits (Bundela *et al.,* 2012). While the contamination of ground and surface water was assessed by the analysis of landfill leachate in metro Manila, Philippines, the higher levels of calcium, sodium, potassium, chloride and tritium were detected in the leachate. The tritium and leachate ions were significantly higher in surface water rather than in non-impacted water having distance from leachate source due to leachate transportation along affected surface water (Castaneda *et al.*, 2012).

Hayder *et al.* (2011) studied the deteriorating effects of Mahmood Booti dumping site near Lahore in Pakistan and ground water quality was observed. Various tube wells providing water to human and agriculture were selected for sampling including one from Mahmood Booti and one from Mall road, Lahore, a distant source as a control to compare results. The seasonal and climatic effects were also recorded and samples were analyzed before and after monsoon season for physicochemical and bacteriological parameters i.e. turbidity, TDS, pH, hardness and fecal coliform. It was reported that *fecal coliform* percentage had increased after monsoon season. Similarly, the pre-monsoon and post-monsoon leachate samples were collected from solid waste dumping site of metropolitan city of Pune, India to assess its impacts on nearer basaltic aquifer and physico-chemical parameters by seasonal variation in ground water and leaching pollution index. A high heavy metals content including zinc, copper, aluminum, lead, cadmium, manganese, nickel, chromium, cobalt and iron was present in leachate while it do not had significant effect on aquifers in close proximity of landfill probably due to redox reaction (Kale *et al.*, 2010).

Maqbool *et al.* (2011) determined the influence of leachate from open solid waste dumping site near Salhad stream (Abbottabad, Pakistan) to quantify the variations of water quality during August 2007 to April 2008. The samples were collected from five different sites situated along the Salhad stream and were analyzed for various physico-chemical parameters like pH, water temperature, EC, total dissolved solids, COD , BOD and dissolved oxygen. Microbiological analysis was conducted by using Membrane filtration technique. The results demonstrated the severe deleterious impact on the water quality of Salhad stream by landfill leachate. The values of pH, TDS, BOD, COD, total bacterial counts and total coliform counts was found beyond the WHO, EC and National Environmental Quality Standards. Heavy metals (Pb, Cd and Cu) were continuously released from the leachate into the Salhad stream could adversely affect the sustainability of the aquatic life.

Aderemi *et al.* (2011) analyzed physico-chemical and microbiological parameters in leachate and groundwater samples obtained at different locations adjacent to a municipal solid waste landfill in order to evaluate the impacts leachate infiltration on groundwater quality. Electrical conductivity, total dissolved solids and Na^+ had exceeded the World Health Organization (WHO) tolerance levels for drinking water in 37.5% of the groundwater samples and pH and Fe was beyond

WHO limits in 75% of the samples respectively. Significant negative correlations were observed by sodium, TDS, and EC with respect to distance from landfill. The presence of a high population of Enterobacteriaceaethe ground water samples was the indication of microbial contamination.

Biswas *et al.* (2010) evaluated environmental quality and properties discarded municipal solid waste in and around dumping site of Mathkal, Kolkata, India. The variation among cellulose (4.21 to 4.31%), organic matter (11.87 to 12.95%), hemi-cellulose (0.93 to 1.02%) and lignin (4.18 to 4.26%) had considerable effect on physico-chemical prosperities of disposed waste in the landfill. The measurement of pH and COD including heavy metals and hardness were achieved by characterization of leachate. The groundwater quality had been significantly affected due to the relatively high levels of heavy metal in groundwater than permissible values from by leachate percolation.

The leachates samples from 3 different locations, fifteen and twenty meter downstream to Al-Sahool area, Ibb, Yemen, landfill to assess ground water and leachate contamination. The ground water samples from 5 boreholes were analyzed for physico-chemical characterization. The temperature, pH, TDS, EC, DO, Cl^-, F^-, nitrates, ammonia, nitrates, Fe, Na, K, Mg, Ca, Cu, Cd, Ni, Zn, Cr, Pb, BOD_5 and COD were used as indicator of water quality but their values in four samples out of five was found above acceptable standards of Ministry on Environment and Water, Yemen (Al-Sabahi *et al.*, 2009).

Mangimbulude *et al.* (2009) pointed out that open dumping of waste is widely applied management method in Indonesia and 650- 700 tons/day of waster was discarded in Jatibrang Landfill, Java whose resulted leachate was continuously contaminated the river via collection ponds. The highest values of chemical oxygen demand, biochemical oxygen demand, organic matter, calcium, sulfates, ammonia and electrical conductivity was observed in dry season while heavy metals seriously deteriorated the river through five fold dilution in dry season and two fold dilution in rainy season.

The ground water contamination proximity of municipal landfill site in Alimosho, Lagos State, Nigeria was assessed through water quality parameters i.e. heavy metal along other physical and chemical parameters of ground water and leachate water quality parameters (Longe and Balogun, 2009). The mean concentrations of all parameters except chromium, nitrates and phosphates conform to the permissible WHO standards for potable water and the Nigerian Standard for Drinking Water Quality. The findings of this study implicated extraneous impact of waste on the landfill operations and subsequently on the groundwater resource. Ion a similar study, Laner *et al.* (2009) pointed out damages and emissions from landfills during flooding rather monitoring under normal situation of landfill operation. After investigation, it was found that 312 or 30% landfill sites out of 1064 were at risk of floods on average once in two centuries due their location in or close of flood risk zones while only 5% were well protected from flood by modern equipment and endangered 147 sites could be considered as a source leaching and erosion of soil.

Rizwan Ullah *et al.* (2009) focused on basic water testing parameters (physical and chemical) and metals (Mn, Fe, Pb, Zn, Ni, Cr, and Cu) contamination in ground water samples from different twenty five areas of Sialkot due their toxicological effects. The water of 57% of total sites was found to be highly turbid and not fit for drinking due to the presence of high levels of heavy metals including zinc, iron and lead which were beyond WHO/NEQS stipulated standards.

The major disposal site of Perungudi, Chennai city which accepts 1680 tons /day of waste, had apparent effect on ground water due leaching of pollutants from various types of waste. The results deduced severe threats to local aquifers from contaminated leachate by raising the level of hardness, pH, TDS, EC, potassium, sodium, calcium and magnesium, anions cadmium, zinc, manganese, chromium, copper and lead (Mohan and Gandhimathi, 2009).

Some traditional methods along with vertical electrical sounding and ground penetrating radar were used for identification and delineation of contaminant plume in a shallow aquifer by the open dumps used as a sanitary landfill in Mexico. The Guadalupe Victoria landfill constituted by silty and sandy soil, favoring transport and mobility of leach ate, was selected as a model study site. Geochemical and geophysical studies were also made (Reyes-Lopez *et al.*, 2008).

Abdul Qadir *et al.* (2008) reported the water quality of Chenab River tributary Nullah Aik, samples were taken from September 2004 to April 2006. Analysis was made for 24 water quality parameters. Spatiotemporal variations were calculated by employing statistical procedures. Study results indicated various factors responsible for water contamination, industrial, municipal, agriculture runoff and rock material. The study stressed on adopting managerial measures to conserve and protect water quality and aquatic system. However, the drained water of three industrial estates of Pakistan Industrial Estates of Hattar Haripur, Gujranwala and Peshawar was analyzed by use of atomic absorption as well as flame emission spectroscopy. Different toxic metals were accessed in study. The results revealed the high levels of lead and arsenic among the samples taken. The study considered the water pollution as the main source public health problems in Pakistan (Rehman *et al.* (2008).

From a municipal solid waste dumping site in Chennai, water samples were collected with a sampling frequency of three months for three years and chemical analysis was conducted. The test results indicated that standards of Bureau of Indian are violated and TDS, EC, hardness, Cl^-, nitrates, sulphates and COD values were reported higher than permissible limits. The heavy metals were also found in leachates and depicted a trend of decrease to increase in post to pre-monsoon season (Vasanthi*et al.*, 2008).

The dumping of hazardous waste without any preliminary caution in moderately vulnerable zone of Torbali River Basin, which is a most important extension of Kucuk Menderes Basin, Turkey, was measured by the analysis of leachate seepage and it was found to be slightly alkaline in nature. The concentration level of electrical conductivity along with heavy metals such as Sb, Cd, Se, As, Fe, Al, Mn and Ni the leachate samples were exceeding while copper, Zn and lead levels were below than drinking water standards. It was found that the highly productive and vulnerable zone were at the risk of leachate pollution (Simsek *et al.,* 2008).

Longe and Enekwechi, (2007) studied the role hydrogeology on the natural attenuation of contaminants in shallow aquifer originating from leachates of active Olusosun landfill, Lagos in proximity of aquifer. The outcomes of study evaluated a significant impacts leachate out flow on ground water of that area. The nitrates, chlorides and sulphates were at elevated levels in the groundwater body but copper, chromium and cadmium were found devoid of any particular attenuation at ground water down gradient of landfill location. Moreover, the leachate dispersion and migration mechanism in down gradient and away from dumping site was irregular and complicated to predict.

Hassan and Ramadan, (2005) mentioned that the total amount of solid waste generated in Alexandria normally was 2820 tons/day which increased to 3425 tons/day during summer. The sanitary landfill leachate was characterized to assess its impacts on the groundwater. The analysis of the collected data proved that leachates from the landfill were severely polluted with organics, salts, and heavy metals. The variations in concentration levels of the different parameters were attributed to aging and thickness of waste layers, status of decomposition, and re-landfilling of the concentrated constituents from the drying lagoons.

II. RESEARCH METHODOLOGY

The current study was conducted during November 2011 to April 2012 at the Department of Environmental Science, Faculty of Basic and Applied Sciences, International Islamic University Islamabad in collaboration with Integrated Environment Laboratory, Lahore, Solution Environmental and Analytical Laboratory (SEAL), Lahore and Department of Chemistry, University of Gujrat, Gujrat to assess the risk posed by the leachate to deteriorate the ground water quality and soil percolated from the open dumping sites situated in two major industrial cities Gujranwala and Sialkot.

3.1 Study Area

Gujranwala and its surrounding towns, and Sialkot, both are highly industrialized cities of Pakistan besides their burgeoning population due to availability of employment. Sialkot district is situated between $32° 24' – 32° 37'$ north latitude and $73° 59' –75° 02'$ east longitude (Abdul Qadir *et al.* 2008). It is hot and humid during summer and cold during winter with mean annual rainfall is about 1,000mm with major contribution of the rainfall during monsoon. The location of Gujranwala is between 32.16° north, 74.18° east and is 226 meters (744 ft) above sea level with a population of 2,569,090. The average rainfall in Gujranwala is 888 mm (DIP, 2009). A brief introduction of selected dumping sites has been shown in Appendix 4.

A huge amount of waste is dumped from residential and industrial sources on dumping sites inside city limits and at landfill sites in the suburban areas without any monitoring. The sampling of soil and ground water from four different dumping sites located at Gujranwala city and Sialkot (Sambrial residential and industrial zones) was focused in this study.

Two different dumping sites (Figure 3.1 and 3.2) from each city were selected for the study. Water samples from ground water sources (hand pumps) and soil samples from dumping sites were collected before (November, 2011) and after (February, 2012) rain and subjected to physic-chemical analysis of soil and water sample for pH, EC, TDS, Heavy metals, anions, cations and organic components. (Figure 3.3 and 3.4)

3.2 Material

3.2.1 Types of sample

Water Sampling: Water samples were collected in autoclaved polyethylene bottles and transported to laboratory after on-site analysis for further investigation.

Soil Sampling: Sterile plastic bags were used for soil sample collection and transported to laboratory for chemical and physical analysis.

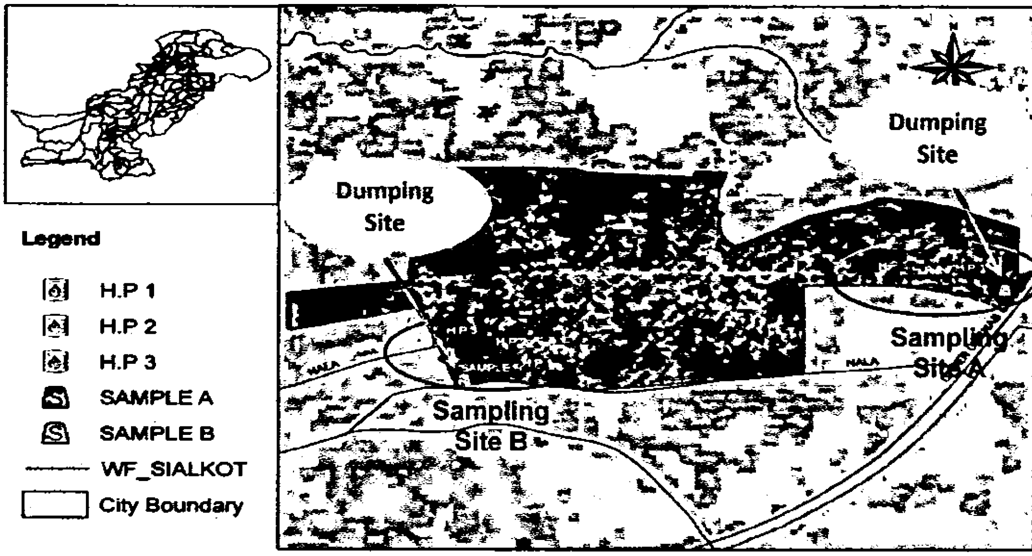

Figure 3.1 Location map of open dumping sites (Industrial and residential) in Sambrial (Sialkot)

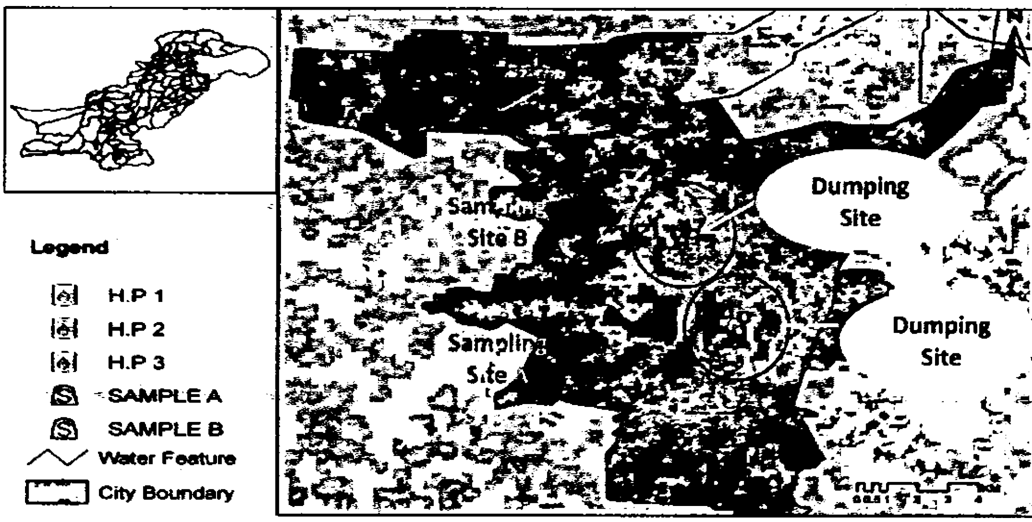

Figure 3.2 Location map of open dumping sites (Industrial and residential) in Gujranwala

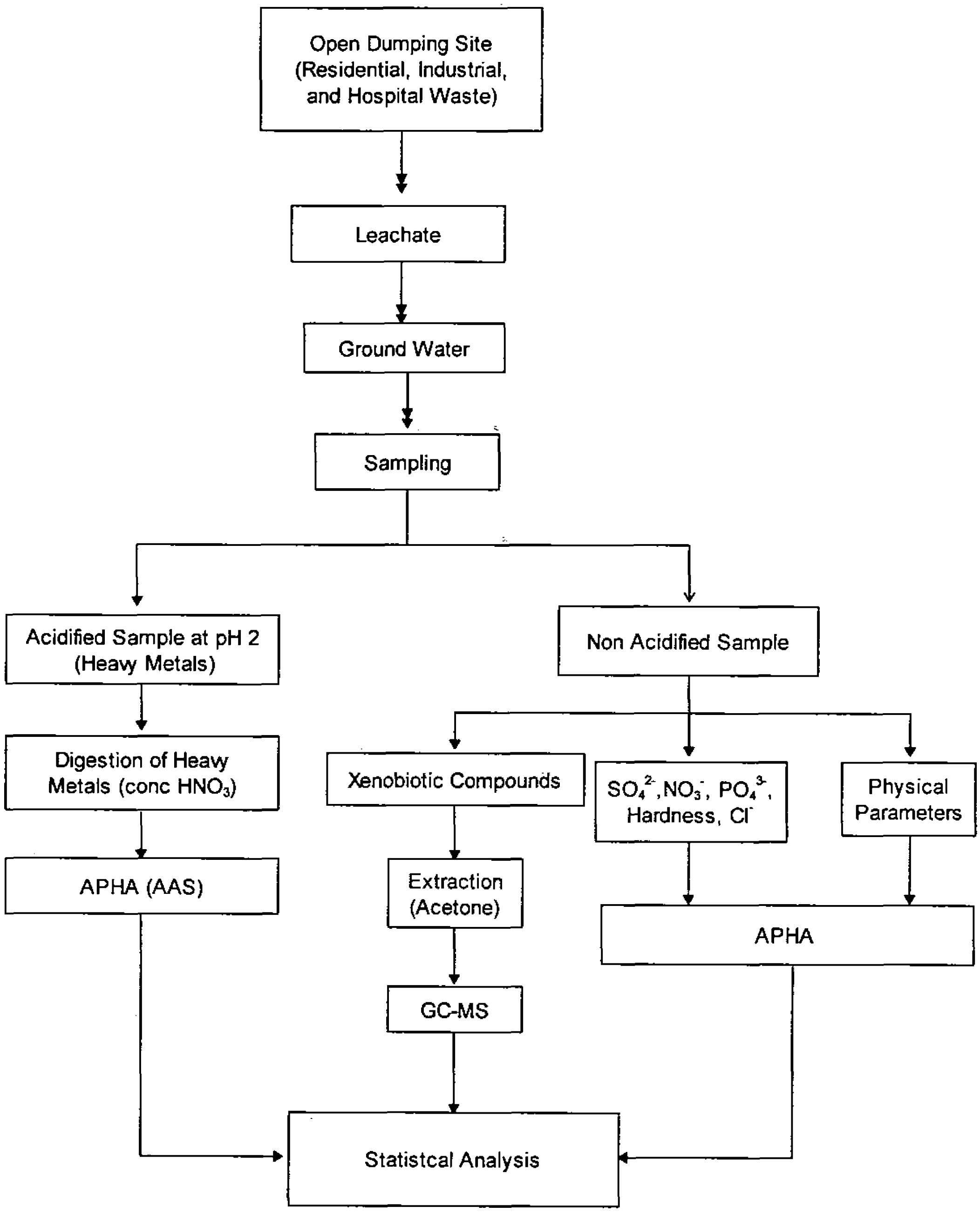

Figure 3.3 Flow chart of experimental protocols for ground water analysis

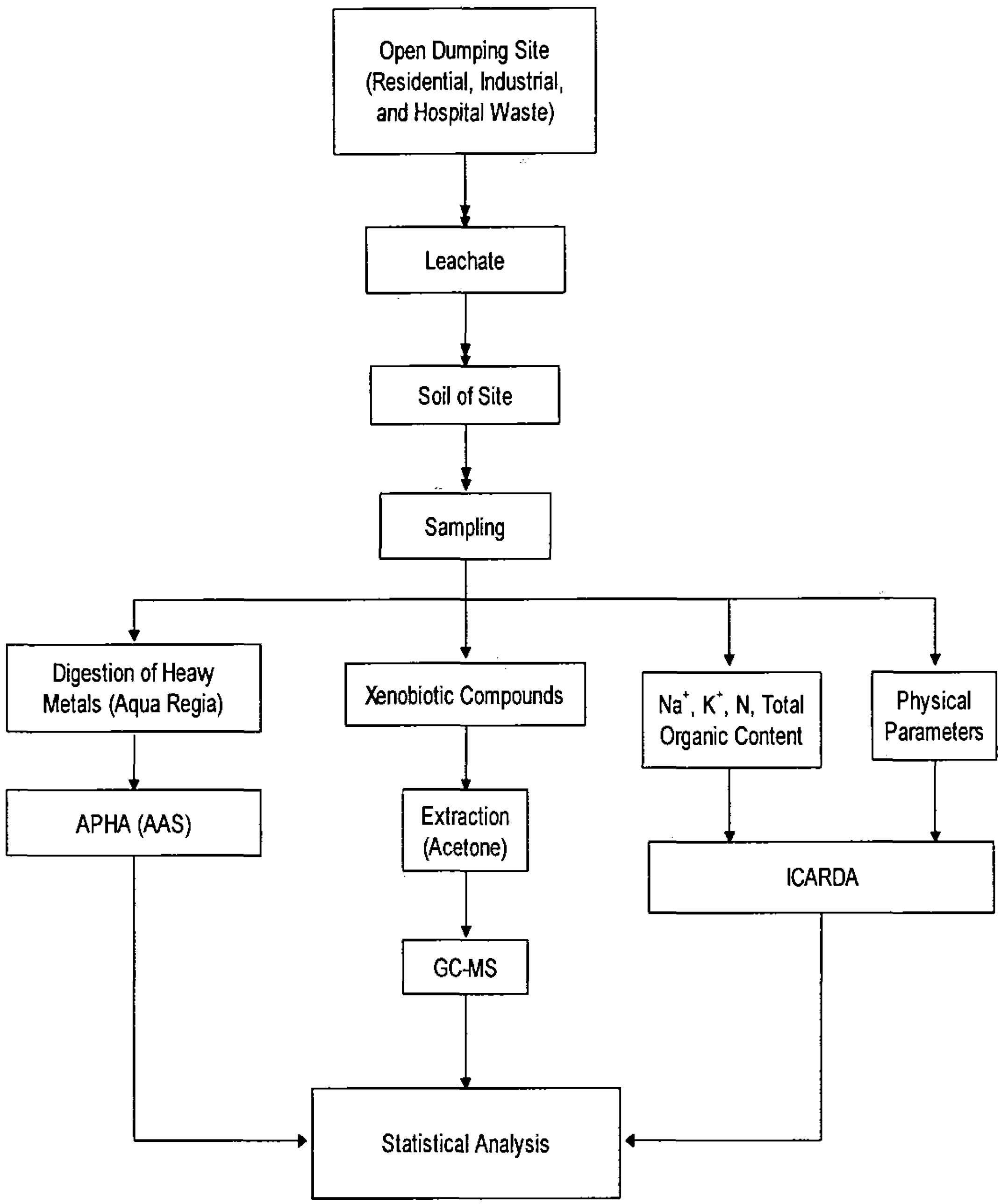

Figure 3.4 Flow chart of experimental protocols for soil analysis

3.2.2 Chemicals

The chemicals used in this study were: hydrochloric acid (HCl), nitric acid (HNO_3), barium chloride ($BaCl_2$), silver nitrate ($AgNO_3$), potassium chromate (K_2CrO_4), ammonium chloride (NH_4Cl), ethylene-diamine-tetra-acetic acid (EDTA), eriochrome black T (EBT), phosphorous powder pillow, lead nitrate ($Pb(NO_3)_2$), phenanthroline, nitrates of nickel, copper, chromium, zinc, cobalt, cadmium and mercury, sulfuric acid (H_2SO_4), orthophosphoric acid (H_3PO_4), ferrous ammonium sulfate solution, diphenylamine indicator, sodium acetate solution, ethanol, methanol, acetontrile, sodium chloride (NaCl), sodium hydroxide (NaOH), sodium sulfate (Na_2SO_4), boric acid, acetone and potassium chloride (KCl) of analytical grades procured from Merck Inc., Pakistan to conduct the study.

3.2.3 Equipments and instruments

The instruments such as sampling polyethylene bottles, weighing balance, sterilizer, freezer, hot plate, wire gauze, thermometer, spirit lamp, aluminum foils, parafilm, water bath, clips and stand, filter paper (Whatman No. 1), micropore filter paper (0.45 micrometer of HPLC grade), electric shaker, oven, rotary evaporator (RE 200A), mortar and pistle, pH meter (Walik lab TI 07-03344), arsenic kit (Merck 1.17927), TDS meter (Hanna HI 98302), turbidity meter (HannaTN100), electrical conductivity meter (Hanna HI 8733), atomic absorption spectrophotometer (AAS) (Perkin Elmer 2100), flame photometer (6410 flame photometer) and gas chromatography coupled with mass spectrometer (GC-MS) (Agilent (HP) 5972/

5890E), spectrophotometer (ANS 1640) were used to quantify the characteristics of leachate percolated into in soil and water.

3.3 Methods

3.3.1 Sample collection

There was no designated landfill site in the study area and disposal of almost all types of waste, i.e., industrial, residential and hospital waste, was found in a common aged open dumping site and it was the also found to be the most familiar practice by the local authorities. A total of ninety six (96) samples which contain seventy two (72) soil samples from the dumping sites and twenty four (24) ground water samples from hand pumps in the vicinity of dumping sites of Sialkot and Gujranwala, were collected according to experimental design.

3.3.1.1 Water sampling

There was no borehole in dumping sites to collect the water so the water samples were collected from 12 different hand pumps having different depths located at and in the vicinity of dumping sites in autoclaved poly ethylene bottles (1 liter). Three samples within 1km from each site were collected that includes 12 pre-rain water samples from all sites during November 2011 and 12 post-rain water samples during February 2012 from all sites after one week heavy rain in the study area. The samples were stored in a dark and cool place (4-5^{o}C) and analyzed on the same day.

The 500 ml water from each bottle was preserved at pH 2 by adding 2-3 drops of conc. HNO_3 (US EPA, 2009) for heavy metal analysis and remaining 500 ml sample from each bottle was used for analysis of other physico-chemical parameters.

3.3.1.2 Soil sampling

Soil samples at the distance of 100, 300 and 500 m from the dumping site corner were collected by hand digger from soil layer come after the waste layer to the depth of 30cm and 60cm respectively, overall total 72 soil samples were collected in polyethylene zippers. The three samples from each point at three depths and 9 samples from each dumping sites were collected. Furthermore, 36 pre-rain soil samples from all sites were collected during November 2011 after 4 month dry season and 36 post-rain soil samples from all sites were collected during February 2012 after one week heavy rain in the study area and transported to laboratory to assess the physico-chemical parameters (Rayan *et al.*, 2001).

3.3.2 Physico-chemical Analysis of Soil and Water Samples

3. 3.2.1 Groundwater analysis

The parameters including pH, TDS, EC, odour, colour, taste, turbidity, hardness, sulfates, nitrates, chlorides and phosphates were quantified by following Standard Methods for Examination of Water and Wastewater (APHA, 2005).

3. 3.2.1.1 Heavy metal analysis

100 ml of acid preserved water sample was transferred to a beaker and added 10 ml of conc. HNO_3 and few glass beads. Initially started the slow boiling and evaporated on hot plate to reduce the volume up to 20-40 ml, a cleared solution was the indication of the completion of digestion process. The solution was transferred into a 100mL volumetric flask, cooled down the solution, filtered by Whatman No. 42 (0.4 mm) and diluted to the mark and mixed thoroughly. The portions of this solution were taken for required metal determinations (APHA, 2005).

The amount of heavy metals (Cu, Cr, Ni, As, Zn, Pb, Co, Cd, Fe and Hg) in digested sample was analyzed following the standard methods (APHA, 2005) using atomic absorption spectrophotometer (Perkin Elmer 2100).

3. 3.2.1. 2 Determination of organic pollutants

50 ml of water sample was taken in 250 ml conical flask and added 100 ml of each acetonitrile, acetone and methonal in 1:1:1 ratio, 20 gram of sodium sulfate (Na_2SO_4) and 2.5 gram of sodium chloride (NaCl). The samples were placed on electric shaker and shaken the sample at the speed of 200 rpm for 24 hours and then the samples were filtered through micropore filter paper (0.45 micrometer of HPLC grade). After the completion of extraction the samples were concentrated in rotary evaporator (RE 200A) (US EPA, 2007, Method 3510).

The prepared samples were injected in gas chromatography (Agilent (HP) 5972/5890E) for the quantification of unknown organic compounds.

3. 3.2.2 Soil Analysis

The pH, TDS, total organic content and nitrogen in soil sample was analyzed by following the standard methods of International Center for Agricultural Research in the Dry Areas (Rayan *et al*., 2001). The sodium and potassium were determined by flame photometer following the standard methods of International Center for Agricultural Research in the Dry Areas (Rayan *et al*., 2001)

3. 3.2.2.1 Heavy metal analysis of soil

The soil samples were dried in microwave oven and then crushed in mortar and pestle and passed through 2 mm sieve to remove stones, coarse materials, and other debris. A globally suggested method (EPA, Method 3050B) was used as the acid extraction method. The 5 g of soil sample was placed in 250 ml flask for digestion of heavy metals. The soil sample was heated at 95° C with 50 ml of 50% HNO_3 and after cooling the sample; it was refluxed with further additions of 65% HNO_3 until brown fumes were not given off by the sample. Then the solution was evaporated to reduce the volume up to 25 ml and cooled down, 50 ml of 30% H_2O_2 was added slowly. The mixture was again refluxed with 50 ml of 37% HCl at 95°C for 15 minutes. The digested sample was filtered through a 0.45 µm membrane paper and diluted to 500 ml with deionized water and stored at 4° C for analyses. The total extraction procedure was completed in 180-200 min (EPA, Method 3050B; Guven and Akinci, 2011)

The amount of heavy metals (Cu, Cr, Ni, As, Zn, Pb, Co, Cd, Fe and Hg) in digested sample was analyzed following the standard method (APHA, 2005) using atomic absorption spectrophotometer (Perkin Elmer 2100).

3.3.2.2.2 Determination of organic pollutants

10 g of soil sample was transferred in 250 ml conical flask and added 100 ml of each acetonitrile, acetone and methanal in 1:1:1 ratio, 20 gram of sodium sulfate ($Na_2 SO_4$) and 2.5 gram of sodium chloride (NaCl). The samples were placed on electric shaker and shacked the sample at the speed of 200 rpm for 24 hours and then the samples were filtered through micropore filter paper (0.45 micrometer of HPLC grade). After the completion of extraction of unknown organic compounds, the samples were concentrated in rotary evaporator (RE 200 A) (US EPA, 2007, Method 3510). The prepared samples were injected into gas chromatography (GC) coupled with mass spectrometer (MS) for the further identification and quantification of unknown organic compounds.

3.4 Statistical Analysis

The data was subject to basic statistical analysis through Microsoft Excel 2007 and was statistically analyzed for ANOVA by using SPSS (Version 14)

III. RESULTS AND DISCUSSIONS

Current study was designed to evaluate the effects of leachates on underground aquifer and soil quality in Sialkot and Gujranwala. The results discussed in this chapter are divided into two sections covering analysis of soil collected from dumping sites and the water samples from underground sources around dumping sites.

4.1 Physico-Chemical Analysis of Soil Samples

4.1.1 pH of soil

Most soil type of central Punjab including Sialkot and Gujranwala is alluvial and slightly alkaline in nature that consists of fine grained fertile nutrient rich components. The pH of soil samples collected before rain (pre-rain samples) from Sialkot (All samples represented by S and dumping sites by SA & SB) was measured as alkaline with a mean maximum pH value of 8.01±0.1 and mean minimum pH of 7.8±0.06, as observed in Samples SA2 and SB2, respectively (Figure 4.1). Whereas, in post-rain samples from the same locations, the maximum pH value of 7.73±0.6 and minimum value 7.4±0.1 was observed in SA1 and SB2 respectively. The pH of soil decreased after rain due to run off, dilution and percolation of many components with rain water (Figure 4.1).

On the other hand, soil samples collected from Gujranwala (All samples represented by G and sites by GA & GB) were found alkaline in nature. A maximum pH value (8.78 ±0.3) and a minimum value (8±0.06) were recorded in GB3 and both (GA1 & GA3), respectively, in case of pre-rain samples. Whereas, in post-rain soil samples from same locations, the maximum pH value (8±0.2) and a minimum value of 7.5±0.2 was observed, as in case of GB2 and GA3 respectively.

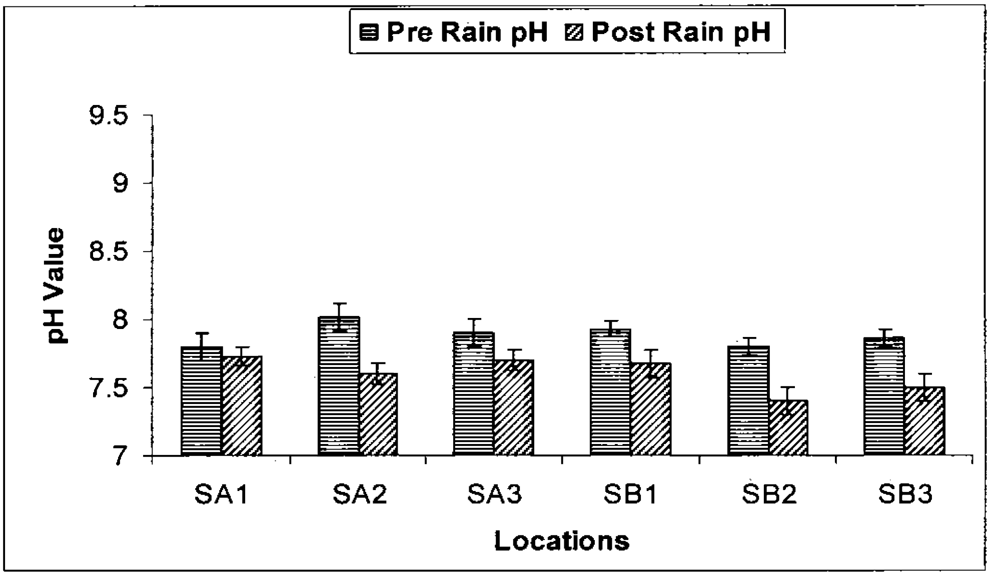

Figure 4.1 pH of soil samples collected from Sialkot dumping sites
(SA & SB = Sialkot site with locations A & B)

Similar to soil samples collected from Sialkot, the pH decreased in post-rain samples due to run off, dilution and percolation of many components with rain water (Figure 4.2). Previously, it was reported that the percolation and contact of rain water with soil reduced the pH due to base buffer reactions (Olobaniyia and Owoyemi, 2006). Based on data, the pH value was found significantly different for both cities and overall the highest value was found in pre-rain soil samples from dumping site B of Gujranwala and lowest pH was recorded in post-rain soil sample from dumping site B of Sialkot

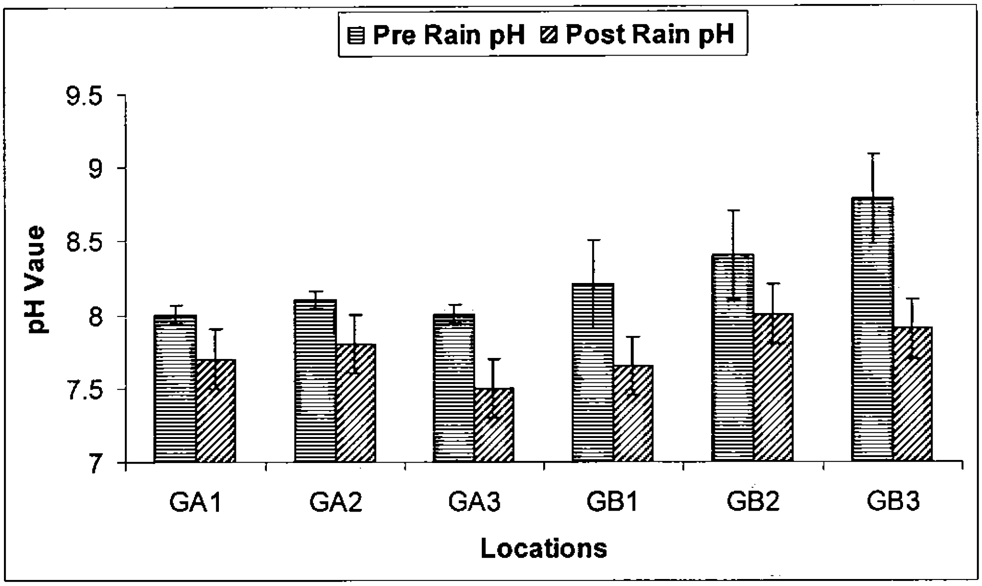

Figure 4.2 pH of soil samples collected from Gujranwala
(GA & GB = Sialkot site with locations A & B)

4.1.2 Total organic carbon (TOC) in soil

The abundance of organic carbon in the soil affects plant production, and it plays a major role as a key control of soil fertility and agricultural production has been recognized for more than a century (Jobbagy and Jackson, 2000). The organic carbon was measured in between 3%±0.4 and 1.6%±0.4 (SA1 and SB3 respectively) in case of pre-rain samples, while in post-rain samples the maximum TOC value increased significantly and was recorded between 4.01%±0.4 and 2.3%±0.2 (SA1 and SB1 respectively) in soil samples collected from dumping sites of Sialkot (Figure 4.3). Furthermore, the maximum TOC (2.9%±0.4) and minimum (1.8%±0.4) was observed in GA1 and GB3 respectively in case of pre-rain samples while the TOC variations in post-rain samples were in range of 2.5%±0.2 to 3.5%±0.4 noted in GA1 and GB3 respectively collected from dumping sites of Gujranwala (Figure 4.3). Moreover, total organic carbon was higher than normal value due to the biological degradation of huge amount of organic waste significantly comes from domestic, municipal and to some extent industrial sources. However, the evolution of the organic matter in a landfill is relatively complex and highly dependent on the environmental conditions (humidity, temperature, etc.) (Parodi *et al.*, 2011). This phenomenon showed that rain had played vital role in increase in TOC due to percolation of organic matter in soil, produced during the spell of dry season from dumping sites of both cities. TOC value was found significantly different in both cities. Thus, it undergoes various transformations which make it a relevant indicator of the different stages of degradation and stabilization of the waste (Francois *et al.*, 2006)

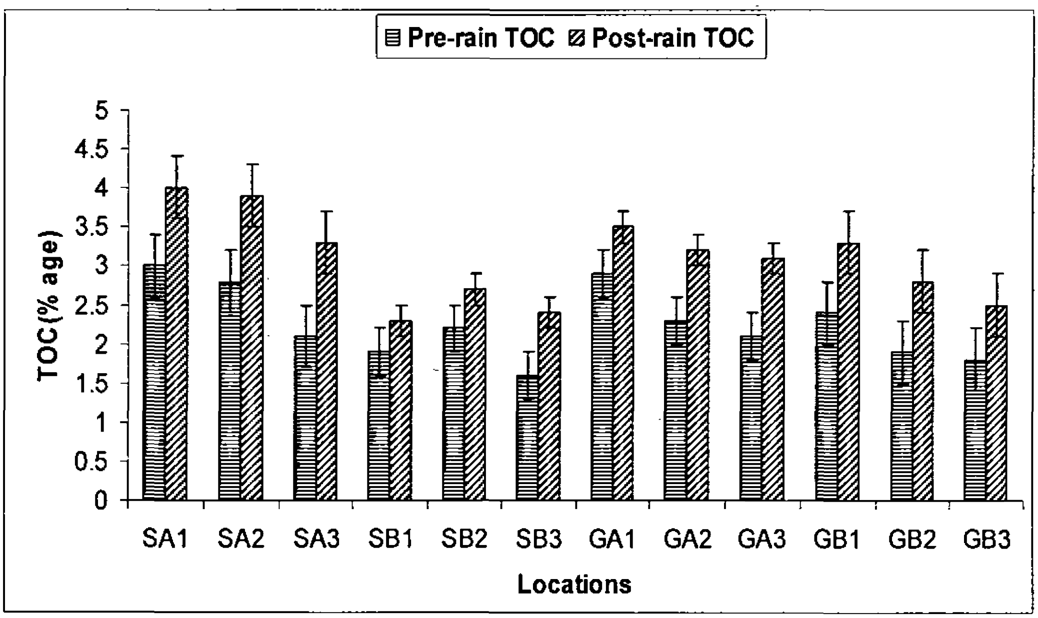

Figure 4.3 TOC in Soil samples from Gujranwala and Sialkot

4.1.3 Presence of inorganic macro components in soil

The soil macronutrients, nitrogen (N), phosphorus (P), and potassium (K), are essential elements for crop growth (Kaiser, 2001; Vadas *et al.*, 2004). The application of commercial N, P, and K fertilizers has contributed to a tremendous increase in yields of agricultural crops that feed the world's population (Kaiser, 2001; Vadas *et al.*, 2004). However, excessive use of these fertilizers had been cited as a source of contamination of surface and groundwater (Kaiser, 2001; Vadas *et al.*, 2004). In addition, sodium is considered as one of major soluble cations in soil and water (Abdul Jaleel *et al.*, 2009).

4.1.3.1 Sodium

In case of pre-rain soil samples, the amount of sodium was found in the range of 34±4 to 18±4 mg/kg in SA1 and SB2 samples, respectively. However, in case of post-rain samples the maximum value (27±3 mg/kg) and minimum value (12±3 mg/kg) of sodium was in SA1 and SB2 respectively in dumping sites of Sialkot (Figures 4.4 and 4.5). Similarly, the maximum amount (39±4 mg/kg) and minimum amount (27±4 mg/kg) of sodium was examined in GB1 and GB3 respectively in soil samples collected during pre-rain spell while in post-rain samples the maximum amount of sodium (32±3 mg/kg) and minimum amount (23±3 mg/kg) was present in GB1 and GA2 respectively in samples from Gujranwala (Figures 4.6 and 4.7).

4.1.3.2 Potassium

The maximum concentration in SB1(20±4 mg/kg) and minimum in SB3(9±2 mg/kg)of potassium was reported in pre-rain soil samples but post-rain samples from dumping sites of Sialkot showed variations in range (7±3-14±3 mg/kg)in SB3 and SB1 respectively (Figures 4.4 and 4.5). However, the results deduced potassium concentration between 19±4 mg/kg and 29±2 mg/kg (GA3 and GB1) in pre-rain samples but 15±2 mg/kg and 21±2 mg/kg (GA3 and GB1) in post-rain soil samples representing dumping sites of Gujranwala (Figures 4.6 and 4.7).

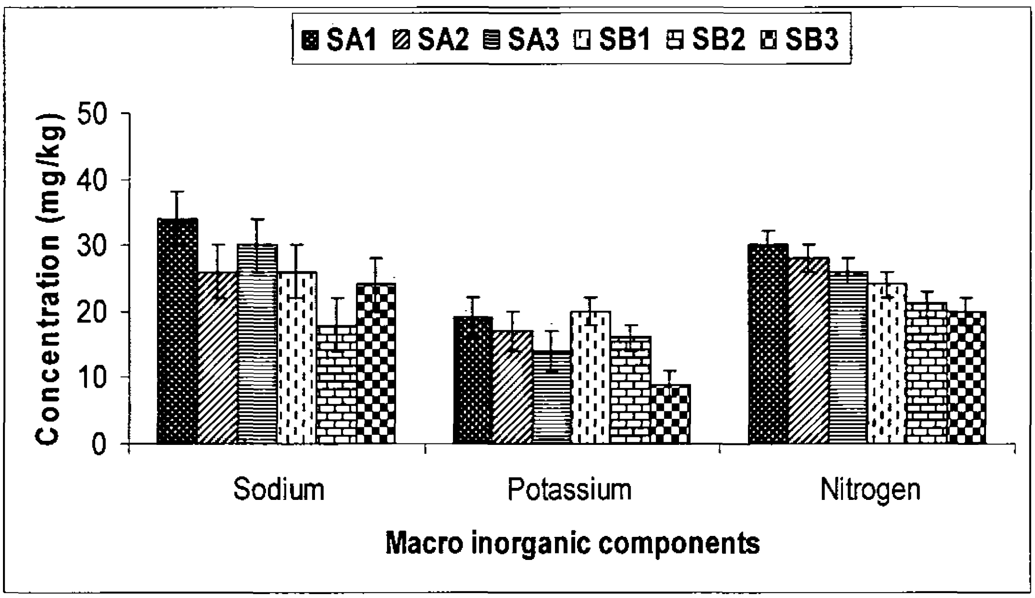

Figure 4.4 Inorganic macro components from pre-rain samples collected from Sialkot

4.1.3.3 Nitrogen

The highest nitrogen content (30±2 mg/kg) and lowest nitrogen content (20±2 mg/kg) was observed in SA1 and SB3 respectively in pre-rain soil samples while maximum nitrogen content (35±3 mg/kg) and minimum nitrogen content (24±3 mg/kg) was noted in SA1 and SB3 respectively in post-rain samples from dumping sites of Sialkot (Figures 4.4 and 4.5). Moreover, the nitrogen content in pre-rain soil samples collected from Gujranwala was (26±1 mg/kg and 34±2 mg/kg) in GB3 and GA1 respectively but results indicated the variations within (31±2-39±1 mg/kg) in (GB3 and GA1 respectively) in post-rain samples from dumping sites of Gujranwala (Figure 4.6 and 4.7)

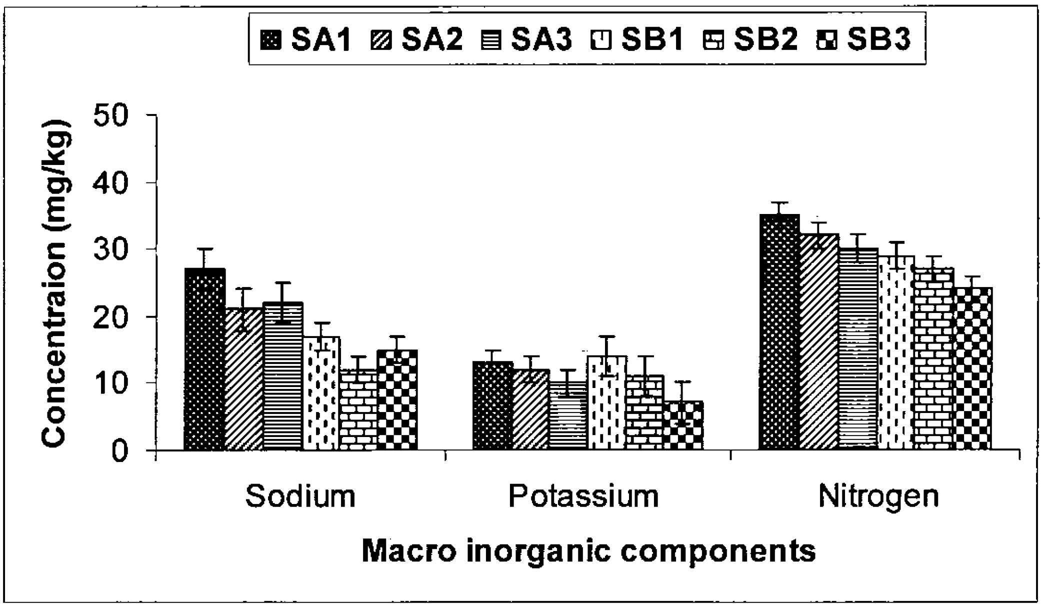

Figure 4.5 Inorganic macro components from post-rain samples collected from Sialkot

The rain had decreased the sodium and potassium concentration in soil due to the good solubility of sodium salts in water in case of both cities. Moreover, nitrogen content was increased due biodegradation and fixation of organic waste. Furthermore, the sodium and potassium was found comparatively lower than the normal fertility level but the nitrogen level was very high in soil of both cities and all values were significantly different from each dumping sites.

Overall, inorganic macro components were relatively higher in soil samples collected from Gujranwala than the Sialkot due aging, large size and amount of waste disposed off. Salt stress affects many aspects of plant metabolism and, as a result, growth and yields are reduced (Yildirim *et al.*, 2006). Potassium deficiency would result in lower osmotic pressure, lower turgor and lower water content in plant, which in turn leads to cell expansion and the damage of cell membrane unable for the development of normal metabolism (Makhdum *et al.*, 2007)

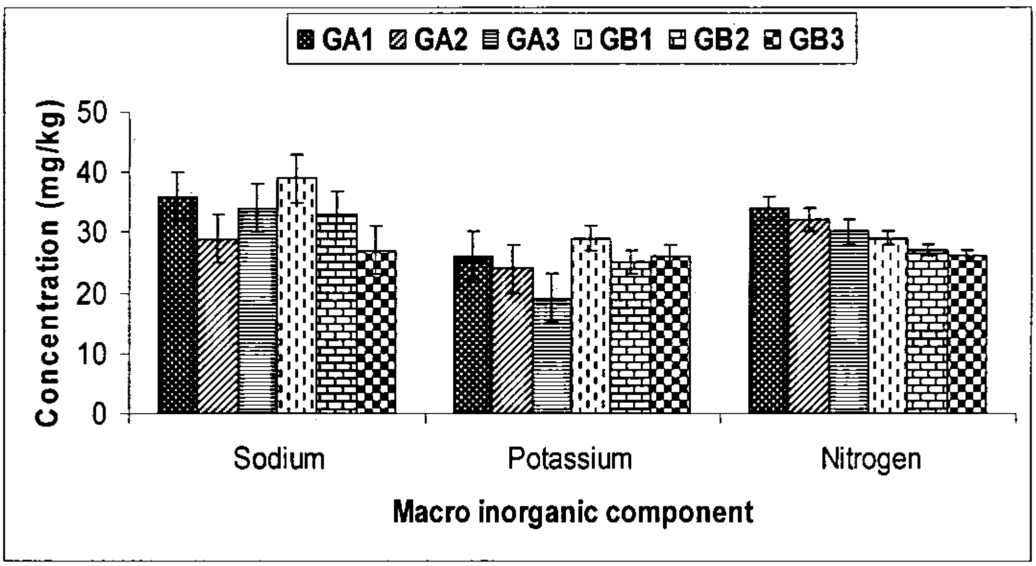

Figure 4.6 Inorganic macro components from pre-rain samples collected from Gujranwala

Moreover, high organic material and N content was present in the rural waste which could be a valuable source of nutrients and organic matter simultaneously to be compost (Yidong *et al.*, 2011).

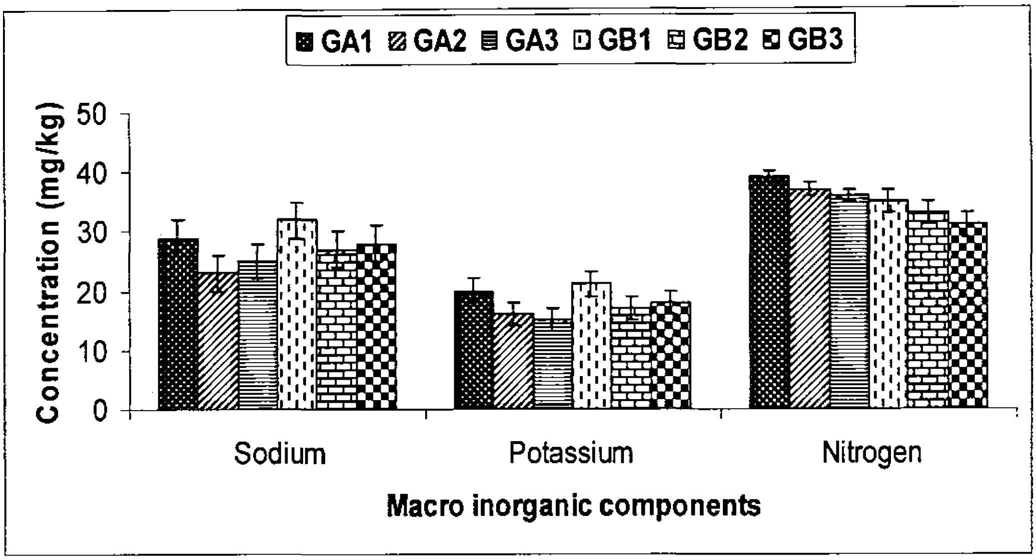

Figure 4.7 Inorganic macro components from post-rain samples collected from Gujranwala

4.1.4 Determination of heavy metals in soil

4.1.4.1 Chromium

The highest concentration of chromium detected was 3.7±0.3 mg/kg and the lowest concentration 1.1±0.6 mg/kg in SA1 and SB3 respectively in pre-rain soil samples collected from and in vicinity of dumping sites of Sialkot while the post-rain samples had highest concentration 4.5±0.3 mg/kg and lowest 1.9±0.2 mg/kg in SA1 and SB3 respectively and this values were higher than pre-rain due values due to the run off and mobility from tannery (Figures 4.8 and 4.9).

The highest concentration 2.1±0.4 mg/kg of chromium and the lowest concentration 1.5±0.4 mg/kg were observed in GB1 and GB3 respectively in pre-rain soil samples collected from and in vicinity of dumping sites of Gujranwala while the post-rain samples had highest concentration 1.6±0.1 mg/kg and lowest 1.28±0.06 mg/kg in GB1 and GA2 respectively which was comparatively lower than pre-rain (Figures 4.10 and 4.11). The overall chromium concentration was higher in Sialkot due to tanneries waste and a significant difference in chromium concentration in each site of both cities was observed during pre-rain and post-rain seasons. Heavy doses of chromium salts even though are rapidly eliminated from human body, could corrode the intestinal tract (WHO, 2004). Moreover, Cu and Cr were more likely to be attached and affinity to the solids as indicated by their significant correlation with TS and SS which was further the indications of the possibility of an immediate health risk (Ogundiran and Afolabi, 2008). Chromium concentration in current study was comparatively higher than previously reported studies on soil of Sialkot conducted by Malik *et al.* (2010) and Nawaz *et al.* (2006) due to continuous dumping of plastics, shoes, rubber, electronic waste and tannery waste (Prudent *et al.*, 1996).

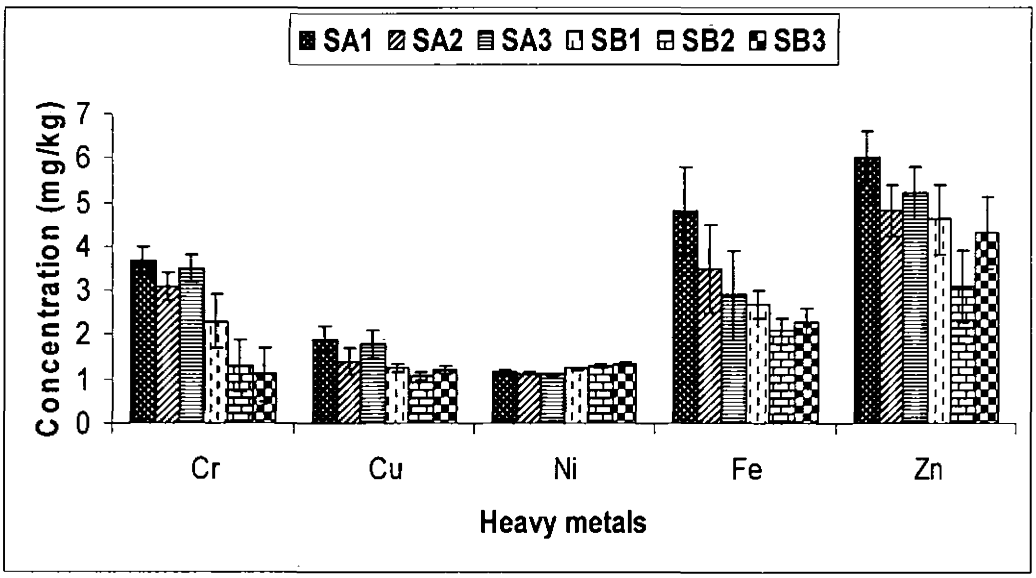

Figure 4.8 Heavy metals from pre-rain soil samples collected from Sialkot

4.1.4.2 Copper

The maximum concentration in SA1 (1.9±0.3 mg/kg) and the minimum concentration in SB2 (1.08±0.09 mg/kg) of copper was detected in pre-rain soil samples collected from and in locality of dumping sites of Sialkot while the post-rain samples had highest concentration (1.3±0.3 mg/kg) and lowest (0.8±0.3 mg/kg) in SA1 and SA2 respectively and such values were relatively lower than pre-rain (Figure 4.8 and 4.9).

The amount of copper present in pre-rain soil samples collected from Gujranwala was in the range of GA2 (2.3±0.3mg/kg) to GB1 (3.4±0.4 mg/kg) while the post-rain samples had copper concentration between GA2 (1.7±0.06 mg/kg) and GB1 (2.5±0.1 mg/kg) which was comparatively lower than pre-rain values (Figures 4.10 and 4.11).

The overall copper concentration was higher in Gujranwala due to industrial waste from electrical and electronics industry and copper concentration was significantly different in each site of both cities during pre-rain and post-rain seasons. It was earlier reported that Cu had association with organic matter, oxides of iron and manganese, silicate clays, and few other minerals. Copper is one of the least mobile heavy metals at any pH and particularly fixed or adsorbed in soils (Parth *et al.*, 2011). In human body, copper is maintained in homeostasis (Jesse and Mary, 2004). If the intake of copper exceeds the range of the human tolerance, it would cause toxic effects such as hemolysis, jaundice and even death. Most recently, the study indicates that the overload of common copper *in vivo* can induce a set of toxicological activities such as hepato-cirrhosis (Bjorn *et al.*, 2003); changes in lipid profile, oxidative stress, and renal dysfunction (Galhardi *et al.*, 2004); and stimulation of mucous membrane of alimentary canal (Galhardi *et al.*, 2004). Cu concentration in current study was found comparatively higher than the previously reported studies on soil of Sialkot (Malik *et al.*, 2010; Nawaz *et al.*, 2006). However, no proper baseline study about Gujranwala was available.

4.1.4.3 Nickel

After the analysis of soil samples through Atomic absorption spectrometer, the nickel concentration was found between SA3 (1.1±0.03 mg/kg) and SB3 (1.35±0.03 mg/kg) in pre-rain soil samples collected from and in vicinity of dumping sites of Sialkot mean while the post-rain samples showed variations in range 0.9±0.07-1.9±0.07 mg/kg (SA3 and SB3) (Figures 4.8 and 4.9).

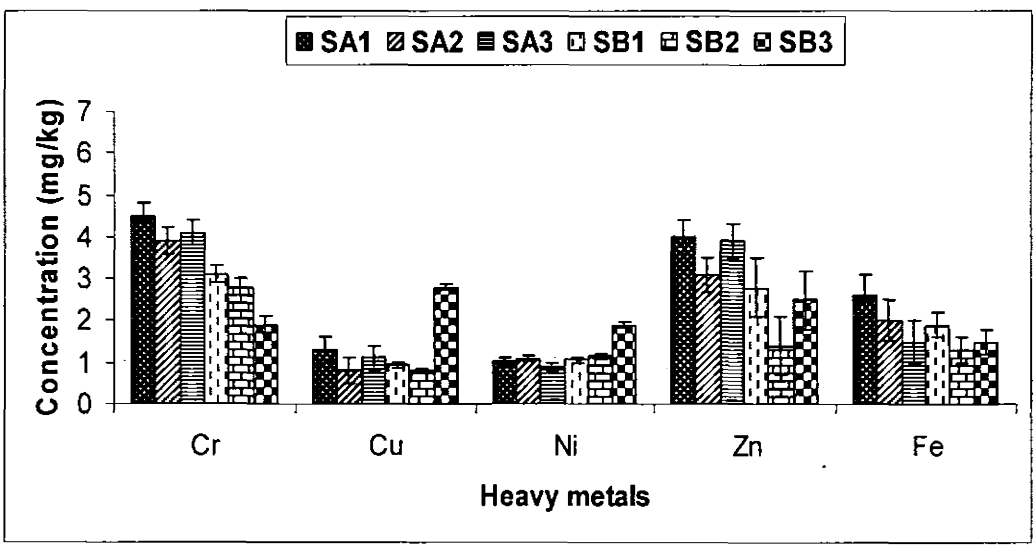

Figure 4.9 Heavy Metals from post-rain soil samples collected from Sialkot

The highest concentration of nickel was 1.6±0.3 mg/kg and the lowest concentration 1.1±0.3 mg/kg in GB1 and GB2 respectively in pre-rain soil samples collected from Gujranwala. While the post-rain samples had highest concentration 1.3±0.1 mg/kg and lowest 1.09±0.1 mg/kg in GB1 and GB3 respectively which was comparatively lower than pre-rain (Figures 4.10 and 4.11). The overall nickel concentration was higher in Gujranwala due to industrial waste from electrical and electronics industry, batteries and nickel concentration was significant in each site of both cities during pre-rain and post-rain seasons.

Soil contains nickel content in various forms such as precipitates, complex or absorbed on organic cation surfaces and inorganic exchangeable surfaces or crystalline minerals and also occurred as free ion or chelated metal complex or soluble soil solution in earth crust (Scott-Fordsmand, 1997). Nickel is an ubiquitous metal frequently responsible for allergic skin reactions and has been reported to be one of the most common causes of allergic contact dermatitis, hypersensitivity, asthma, conjunctivitis, inflammatory reactions and potent carcinogens after inhalation but also that the carcinogenic risk is limited to the conditions of occupational exposure (Haber *et al.*, 2000; Kitaura *et al.,* 2003; Cavani, 2005; Nielsen *et al.*, 1999). The proper baseline data about heavy metals in soil for Gujranwala was not available but nickel concentration in current study was comparatively higher than previously reported studies on soil of Sialkot conducted by Malik *et al.* (2010) and Nawaz *et al.* (2006).

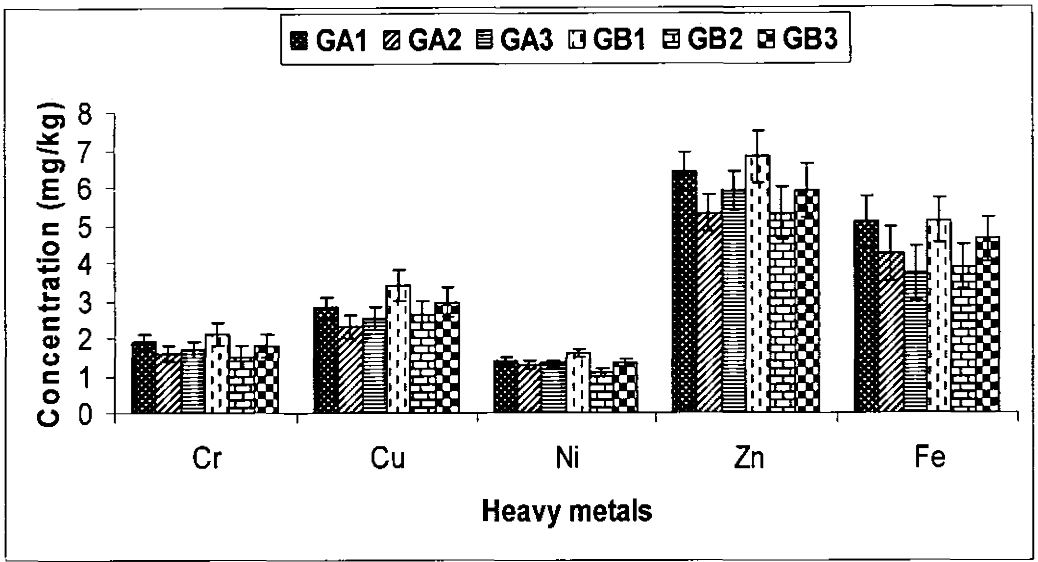

Figure 4.10 Heavy metals from pre-rain soil samples collected from Gujranwala

4.1.4.4 Iron

The highest iron content 4.8±1 mg/kg and lowest content 2.1±0.3 mg/kg was found in SA1 and SB2 respectively in pre-rain soil samples collected from and in vicinity of dumping sites of Sialkot while the post-rain samples had highest iron content 2.6±0.3 mg/kg and lowest 1.3±0.2 mg/kg in SA1 and SB2 respectively and this values were lower than pre-rain values due to the run off and percolation along with rainwater (Figures 4.8 and 4.9).

The highest concentration 5.1±0.4 mg/kg of iron and the lowest concentration 3.7±0.4 mg/kg were observed in GB1 and GA3 respectively in pre-rain soil samples collected from and in vicinity of dumping sites of Gujranwala while the post-rain samples had highest concentration 4.7±0.1 mg/kg and lowest 2.2±0.06 mg/kg in GA1 and GB2 respectively which was comparatively lower than pre-rain values (Figures 4.10 and 4.11). The overall iron concentration was higher in Gujranwala due to industrial waste from electrical and electronics industry, batteries and iron concentration was significant in each site of both cities during pre-rain and post-rain seasons. Iron is an essential nutrient for all organisms, used in a variety of enzyme systems, including those for photosynthesis, respiration, and nitrogen fixation (Morel and Price, 2003). However, iron is very insoluble under oxidizing conditions above pH 4 (Kraemer, 2004). Iron deficiency (ID) and iron-deficiency anemia (IDA) continued to be of worldwide concern. Among children in the developing world, iron is the most common single-nutrient deficiency (UNACCNIFPRI, 2000). The highly variable iron status of preterm infants, along with their risks for iron deficiency as well as toxicity, precludes determining the exact requirement, but it can be estimated to be between 2 and 4 mg/kg per day when given orally (Georgieff et al., 2005). The proper baseline data about heavy metals contamination in soil of Gujranwala was not reported however, iron concentration in current study was relatively higher than previously reported studies on soil of Sialkot conducted by Malik *et al.* (2010) and Nawaz *et al.* (2006).

4.1.4.5 Zinc

The maximum concentration in SA1 (6±0.6 mg/kg) and while the minimum concentration in SB2 (3.1±0.8 mg/kg) of zinc was detected was in pre-rain soil samples collected from Sialkot but the post-rain samples had highest concentration in

SA1 (4±0.7 mg/kg) and lowest in SB2 (3.1±0.4 mg/kg) was found similar to pre-rain samples (Figures 4.8 and 4.9).

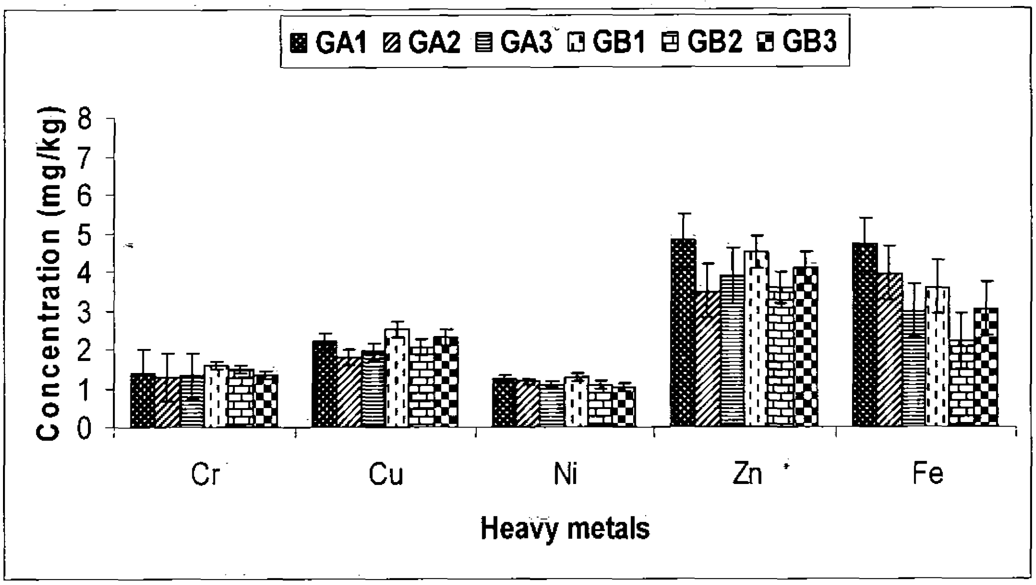

Figure 4.11 Heavy metals from post-rain soil samples collected from Gujranwala

The highest concentration of zinc was in GB1 (6.8±0.7 mg/kg) and the lowest concentration in GA2 (5.3±0.5 mg/kg) were analyzed in pre-rain soil samples collected from Gujranwala while the post-rain samples had highest concentration in GA1 (4.8±0.7 mg/kg) and lowest in GA2 (3.5±0.7 mg/kg) which was comparatively lower than pre-rain values due to percolation of zinc associated with rain water (Figures 4.10 and 4.11). The overall zinc concentration was higher in Gujranwala due to industrial waste from electrical and electronics industry, batteries and zinc concentration was significant in each site of both cities during pre-rain and post-rain seasons. The zinc was present in highest concentration among all heavy metals in dumping sites of both cities. Zn demonstrated the greatest mobility compared to other heavy metals (Xiaoli *et al.*, 2007). Zn was also found at higher concentrations than the remaining heavy metals (Esakku *et al.*, 2005). Acute, high-dose oral exposure to zinc and its compounds generally results in gastrointestinal damage, with symptoms including nausea, vomiting, abdominal cramps, and diarrhea. Exposure levels resulting in these effects generally range from 2 to 8 mg zinc/kg/day. Ingesting high levels of zinc for several months may cause anemia, pancreas damage, and decrease the level of high-density lipoprotein (HDL) cholesterol (U.S. Department of Health and Human Services, 2003). The proper preliminary data about heavy metals contamination in soil of Gujranwala was not reported however, zinc concentration in current study was relatively higher than previously reported studies on soil of Sialkot conducted by Malik *et al.* (2010) and Nawaz *et al.* (2006).

4.1.4.6 Cobalt

The amount of cobalt in pre-rain soil samples collected from and in vicinity of dumping sites of Sialkot was detected in range (0.008±0.001-0.1±0.01 mg/kg) in SA1 and SB3 respectively but the post-rain samples had highest amount in SA1 (0.06±0.02 mg/kg) and lowest in SB3 (0.0037±0.02 mg/kg) collected from Sialkot (Figures 4.12 and 4.13).

The concentration of cobalt in pre-rain soil samples collected from Gujranwala was found between GA2 (0.5±0.2 mg/kg) and GB1 (1.01±0.3mg/kg) while the post-rain samples had highest concentration in GB1 (0.54±0.2 mg/kg) and lowest in GA3 (0.2±0.1 mg/kg) which was comparatively lower than pre-rain values (Figures 4.14 and 4.15).

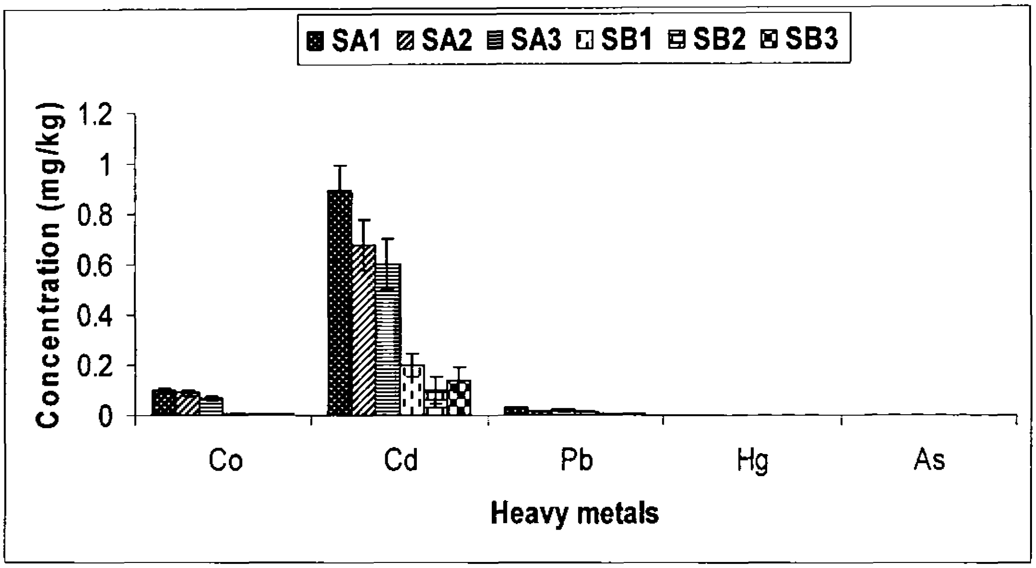

Figure 4.12 Heavy metals from pre-rain soil samples collected from Sialkot

The overall cobalt concentration was higher in Gujranwala due to industrial waste from electrical and electronics industry, batteries and cobalt concentration was significant in each site of both cities during pre-rain and post-rain seasons. Co is considered as an essential element for animals because it is a necessary for the synthesis of vitamin B12 (Chatterjee and Chatterjee, 2003; Tripathi and Srivastava, 2007). It is widely distributed in rocks, soils, water and vegetation (Gal *et al.*, 2008; Lock *et al.*, 2006) and is often observed in association with nickel (Ni). Cobalt is toxic to humans along with terrestrial and aquatic animals and plants in higher concentrations (Gal *et al.*, 2008). Its toxicity to cells resulted from inhibition of cellular respiration and citric acid cycle enzymes (Tripathi and Srivastava, 2007). The proper preliminary data about heavy metals contamination in soil of Gujranwala was not reported however, cobalt concentration in current study was relatively higher than previously reported studies on soil of Sialkot conducted by Malik *et al.* (2010) and Nawaz *et al.* (2006).

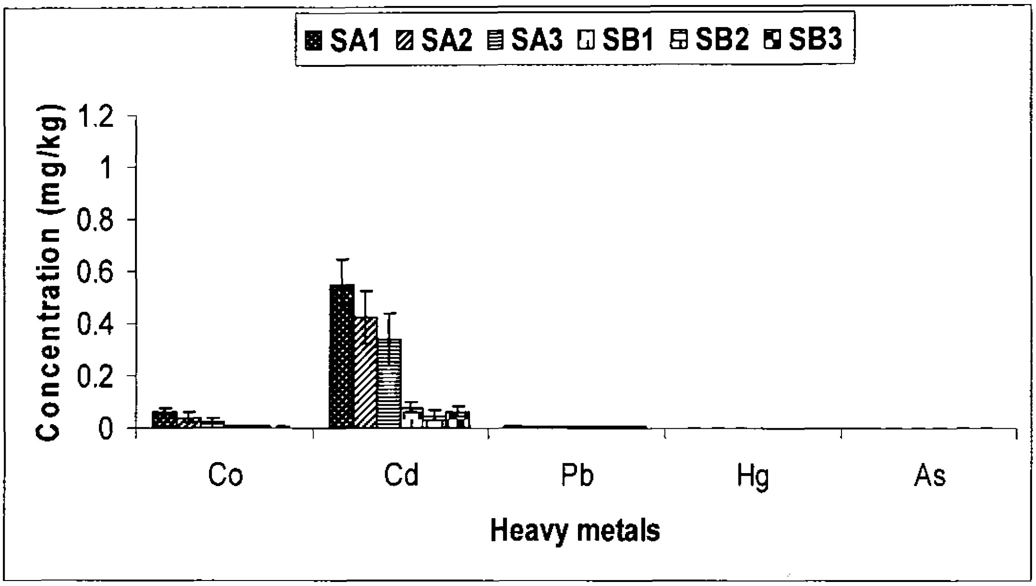

Figure 4.13 Heavy metals from post-rain soil samples collected from Sialkot

4.1.4.7 Cadmium

The highest concentration of cadmium 0.89±0.1 mg/kg and lowest concentration 0.1± 0.05 mg/kg was investigated in SA1 and SB2 respectively in pre-rain soil samples collected from and in vicinity of dumping sites of Sialkot but the post-rain samples had highest concentration in SA1 (0.55±0.1 mg/kg) and lowest in SB2 (0.05±0.02 mg/kg) and this values were lower than pre-rain values due to percolation along with rainwater (Figures 4.12 and 4.13).

The amount of cadmium showed variation between 0.8±0.02 mg/kg and 1.4±0.2 mg/kg in (GA3 and GB1) in pre-rain soil samples collected from and in vicinity of dumping sites of Gujranwala however, AAS results indicated that the post-rain samples had highest Cd content in GA1 (1.01±0.1 mg/kg) and lowest Cd content in GB2 (0.29±0.06) which was comparatively lower than pre-rain values (Figures 4.15 and 4.16).

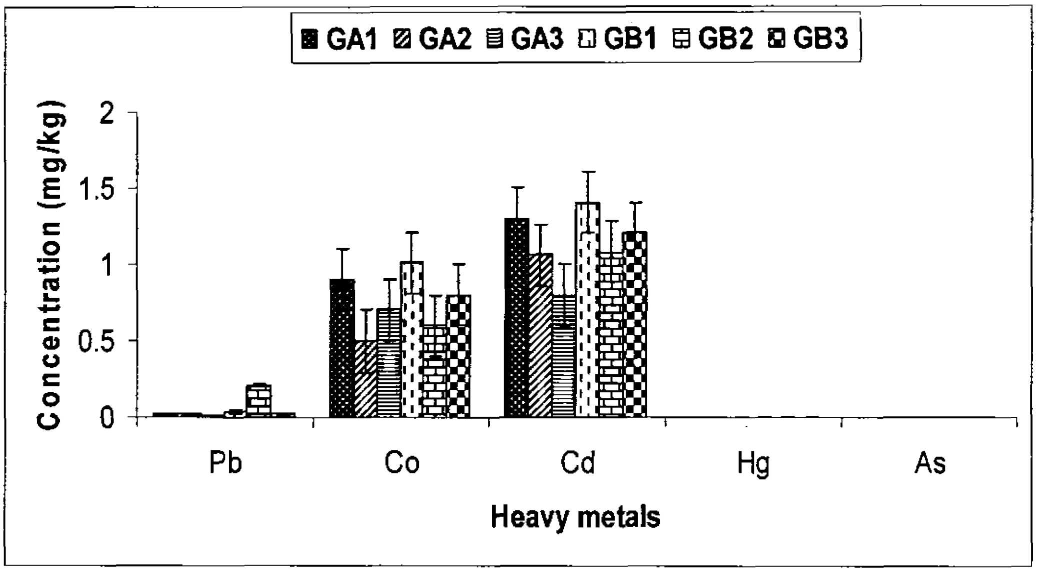

Figure 4.14 Heavy metals from pre-rain soil samples collected from Gujranwala

The overall cadmium concentration was higher in Gujranwala due to industrial waste from electrical and electronics industry, batteries and cadmium concentration was significant in each site of both cities during pre-rain and post-rain seasons.

The major use of Cd is mainly in rechargeable batteries and for the production of special alloys. The industrial workers and for populations living in polluted areas, had serious concern with problems associated to cadmium especially in less developed countries (Sethi and Khandelwal, 2006). Cd dispersed in the environment can persist in soils and sediments for decades like other heavy metals. It was noticed that Cd had highest ability and susceptible to be released from the dumpsite through simple ion exchanged mechanism. It is also observed that the chloride content in the leachate can bind with Cd and enhance its mobility in the solid waste (Kjeldsen et *al.*, 2002). Cd concentrates along the food in addition to its extraordinary cumulative properties, is highly toxic metal that can disrupt a number of biological systems, pulmonary function suggestive of mild obstructive syndrome, bone effects and can cause cancer (Nordberg et al., 2007; Bernard, 2004; Walkes, 2003). The proper preliminary data about heavy metals contamination in soil of Gujranwala was not reported but cadmium concentration in current study was relatively higher than previously reported studies on soil of Sialkot conducted by Malik *et al.* (2010) and Nawaz *et al.* (2006).

4.1.4.8 Other heavy metals

Arsenic and mercury was not detected in any of soil samples collected from all dumping sites of both cites (Figures 4.12 - 4.15). The results had revealed that the lead concentration was less than 0.1 mg/kg in all sites of both cites except soil sample GB2 collected during pre-rain season as shown in figures 4.12, 4.13, 4.14 and 4.15 which were curiously less than previously reported studies by Malik *et al.* (2010) and Nawaz *et al.* (2006) due to shifting of most vehicles from diesel and petrol to CNG and tremendous reduction in use of lead in pipe

Heavy metals absorbed by plants can be harmful to the animals that consume them, both domestic and wild animals. Sanchez-Chardi and Nadal (2007) quantified the bioaccumulation of metals (Pb, Hg, Cd, Fe, Mg, Zn, Cu, Mn, Mo, and Cr) from the landfill. The heavy metal concentration present in soil was in order of:

Zn>Fe>Cu>Cr>Ni>Cd>Co>Pb>As>Hg. It was also observed that the dumping site B of Gujranwala was most contaminated site due to highest age (20 years) and highest area.

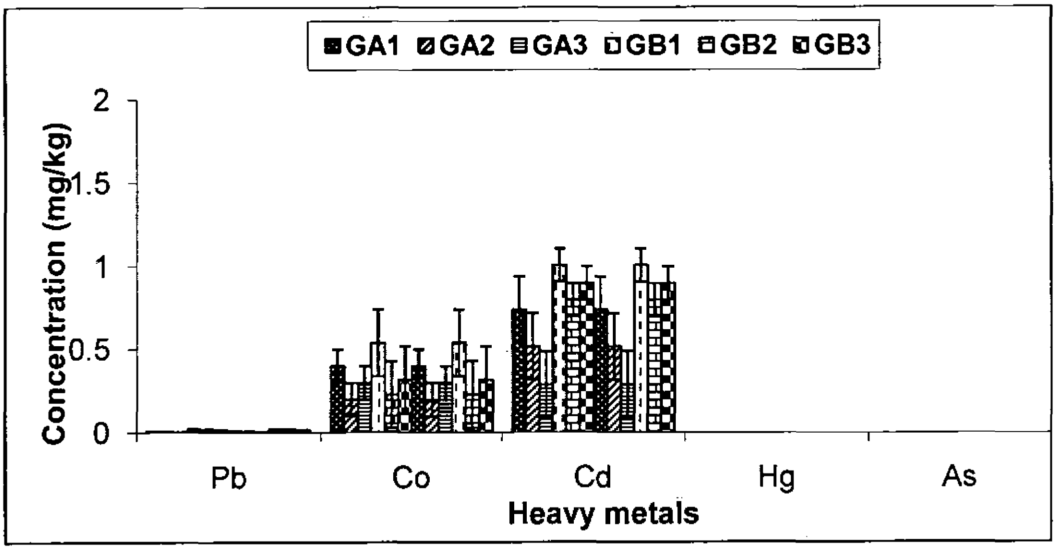

Figure 4.15 Heavy metals from post-rain soil samples collected from Gujranwala

4.1.5 Organic compounds in soil samples

According to chromatographic analysis, dioxins and furans in soil samples were detected however their peaks were non-significant. In addition, other hydrocarbons and organic compounds i.e. PAHs and PCBs were also found in trace amount but required further investigation in order to confirm their presence.

4.2. Physico-chemical Analysis of Ground Water

Quality of ground water is affected by soil leachates. The operations of solid waste disposal sites resulted in leaching and mobility of contaminants into water resources which is categorized as one of major environmental problem (Castaneda *et al.,* 2012). It was therefore analyzed for any unwanted physical or chemical characteristics.

4.2.1 Physical parameters

The colour, odor, taste and turbidity was non objectionable and within the WHO/NEQS values (WHO, 2004; Pak EPA, 2008).

4.2.1.1 pH of ground water

The maximum pH value 8.61±0.38 was recorded in the water sample SA3 collected from dumping site A of Sialkot while the minimum value 7.61±0.38 was recorded in SB1 during pre-rain season but a decrease in pH value was observed during post-rain season and its maximum value was 8±0.27 in SA1 and minimum value 7.3±0.27 was found in SB1 (Figure 4.16).

The highest pH value in GB1 (8.71±0.38) but lowest value in GB2 (8.36±0.38) was found in the water sample collected from dumping site B of Gujranwala during pre-rain season but a decrease in pH value was observed during post-rain season and its highest value (8.43±0.27) and minimum value (7.8±0.27) was found in GA3 and GB3 respectively (Figure 4.17).

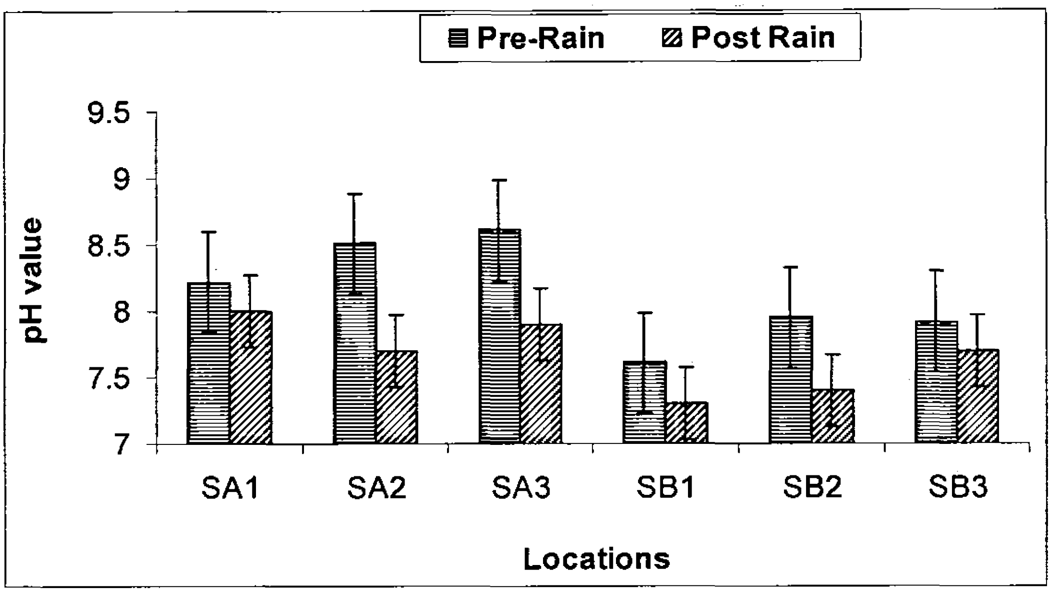

Figure 4.16 pH of ground water samples collected from Sialkot

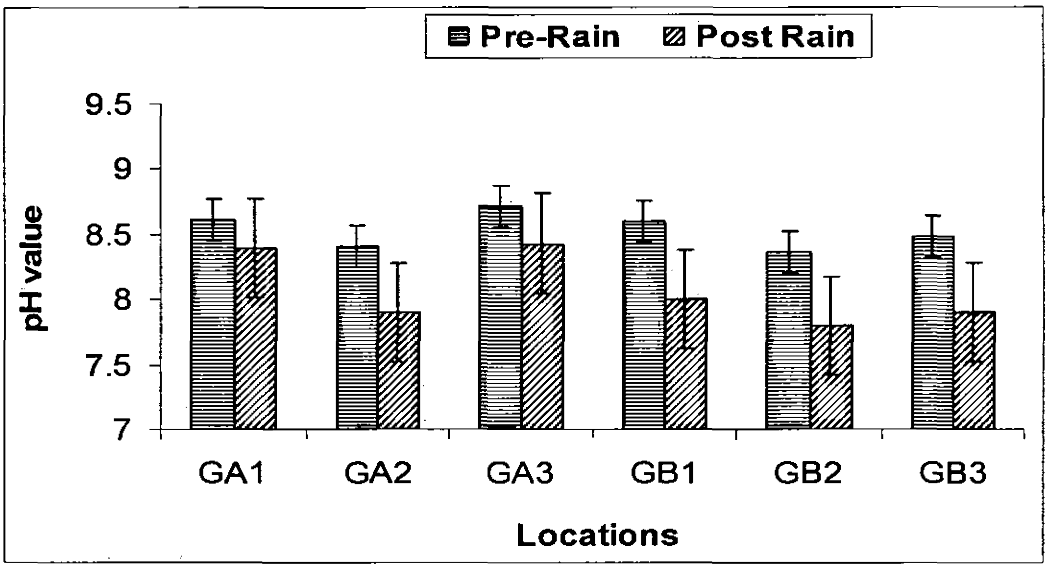

Figure 4.17 pH of ground water samples collected from Gujranwala

It was also observed that the most of pre-rain samples had pH value near to or higher than WHO/NEQS standard (WHO, 2004; Pak EPA, 2008) for pH of drinking water in both cities but the pH value of post-rain samples was less the stipulated value prescribed by WHO.

4.2.1.2 Total dissolved solids (TDS), electrical conductivity (EC) and hardness of ground water

The TDS in pre-rain water samples of Sialkot was found in range (115±5-385±13 mg/l) and in the SA3 and SB1 respectively but a significant increase in TDS value was examined in water samples collected after the rain and the maximum TDS value 576±15 mg/l and minimum value 142±8 mg/l was observed in SB1 and SA1 respectively (Figure 4.18). The similar trend was observed in case electrical conductivity in which rain had increased its maximum value 770±26 mg/l to 1152±30 mg/l found both in SBl and minimum value 230±10 mg/l in SA3 to 284±16 mg/l in SA1 respectively. The maximum hardness of pre-rain water samples was 104±4 mg/l in SB1 and minimum hardness 58±6 mg/l was determined in SA3 while the post-rain samples had maximum hardness 118±6 mg/l and minimum hardness 75±6 mg/l in SB1 and SA1 respectively (Figure 4.18).

The TDS in pre-rain water samples of Gujranwala was found between GB2 (501±15 mg/l) and GA3 (345±11 mg/l) but variations in TDS was examined within GB2 (376±7 mg/l) and GA3 (562±30 mg/l) in water samples collected after the rain from Gujranwala (Figure 4.19). However, in case of electrical conductivity, rain had increased its maximum value (1002±30 mg/l) to (1152±60) mg/l found in GA3 and minimum value (690±22) mg/l to (752±14) mg/l in GB2 respectively.

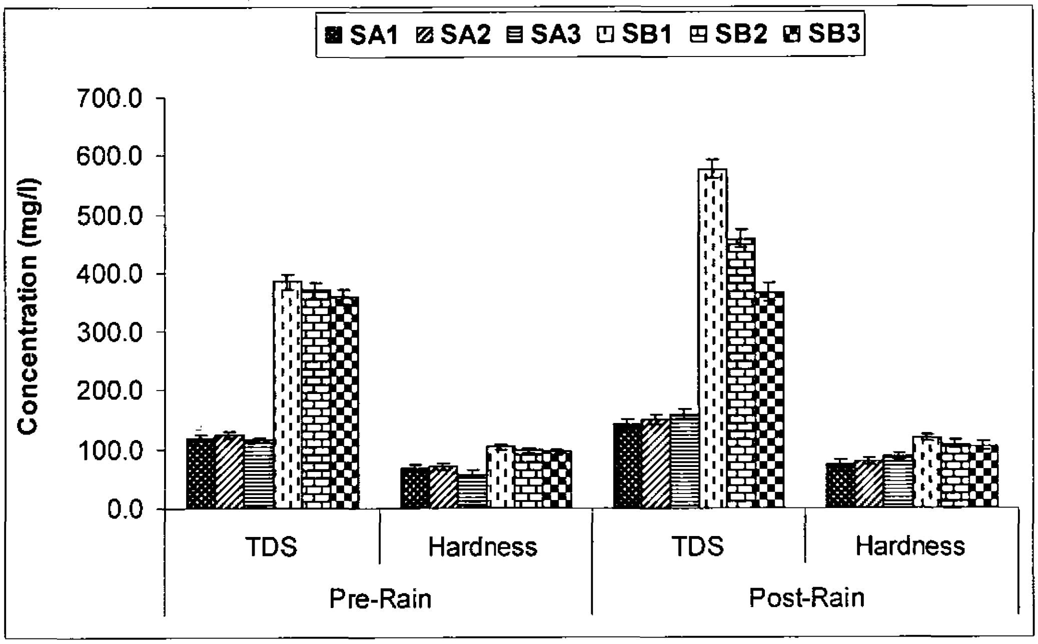

Figure 4.18 TDS and hardness of ground water samples collected from Sialkot

The maximum hardness of pre-rain water samples was (96±8 mg/l) in GA3 and minimum hardness (79±8 mg/l) was assessed in GA2 while the post-rain samples had maximum hardness (124±7 mg/l) and minimum hardness (101±8 mg/l) in GB2 and GA2 respectively ground water samples collected from Gujranwala (Figure 4.19).

Total dissolved solids, electrical conductivity and hardness values were comparatively higher in post-rain samples than pre-rain due to the percolation of water soluble salts from soil to ground water. Their values were found significantly different in each site and overall ground water samples collected from Gujranwala had higher TDS, EC and hardness than samples collected from Sialkot. TDS, EC and hardness values were found to be within WHO/NEQS standards (WHO, 2004; Pak EPA, 2008).

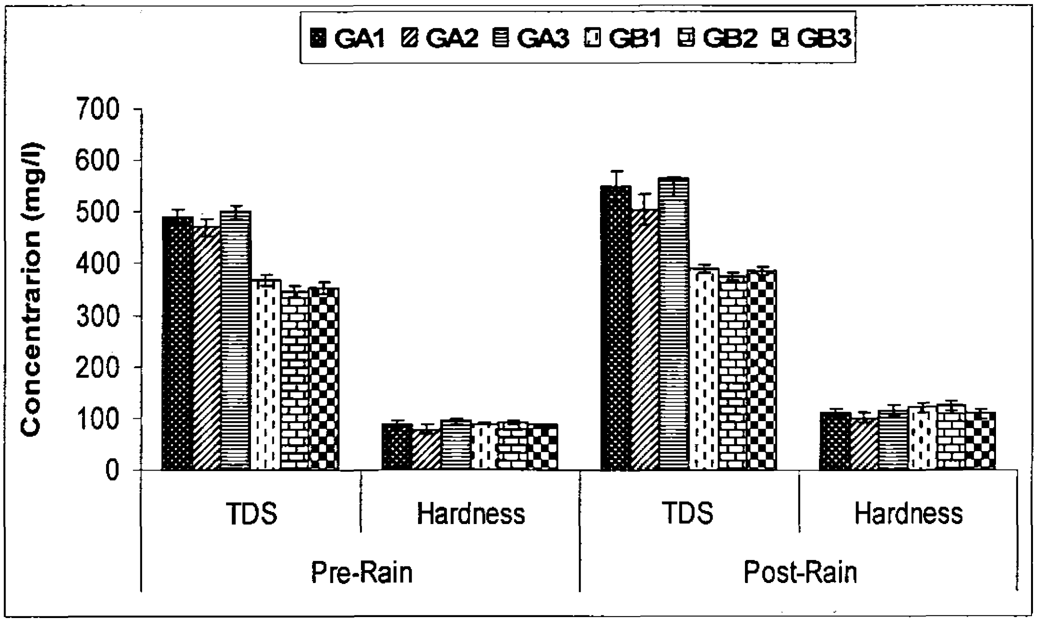

Figure 4.19 TDS and Hardness in ground water samples collected from Gujranwala

4.2.2 Anions in ground water samples

4.2.2.1 Nitrates in ground water samples

The ground water samples collected from Sialkot before rain had highest nitrate concentration in SB2 (4.9±2 mg/l) and lowest concentration in SA3 (0.9±0.5 mg/l) in while the maximum nitrate concentration 27±2 mg/l and minimum nitrate concentration 18±2 mg/l was found in SB2 and SA1 respectively in ground water samples collected after rain (Figures 4.20 and 4.21). The pre-rain ground water samples collected from Gujranwala had maximum nitrates in GA3 (5.1±2 mg/l) and minimum in GA2 (1±2 mg/l) while the nitrates in post-rain samples were fluctuated from 28±2mg/l to 36±2 mg/l in GB1 and GA2 respectively (Figures 4.22 and 4.23).

A significant variation in nitrate value was observed after rain due to the percolation of water soluble salts from soil to ground water.

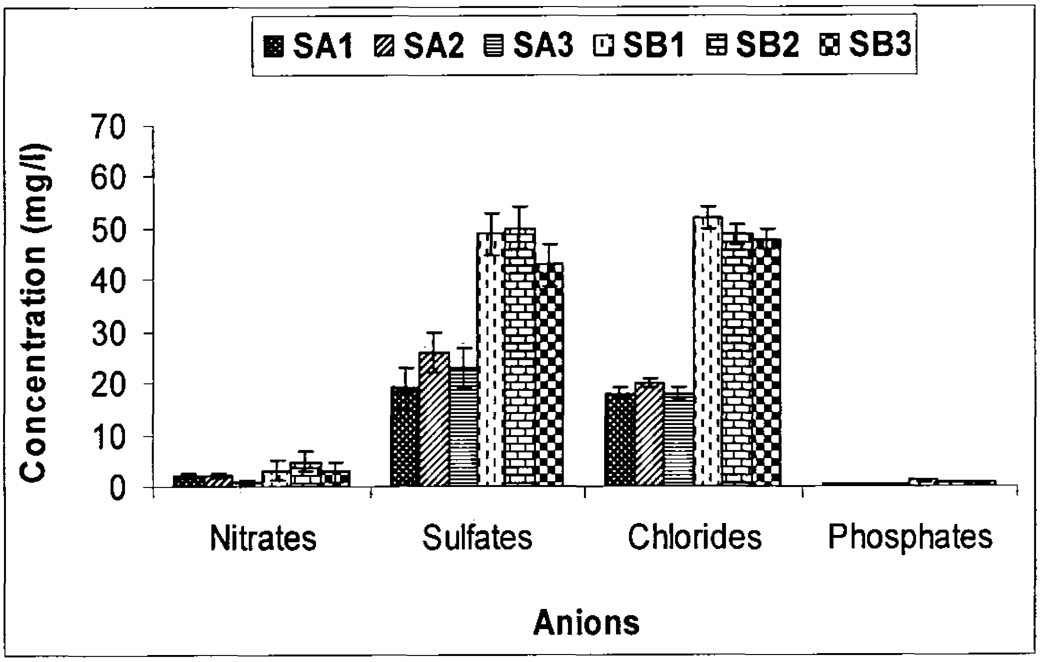

Figure 4.20 Anions in pre-rain ground water samples collected from Sialkot

4.2.2.2 Sulfates in ground water samples

However, the sulfate concentration in pre-rainwater samples was assessed between SA1 (19±4 mg/l) and SB2 (50±4 mg/l) but rain had increased maximum sulfate concentration to 57±3 and minimum concentration to 37±10 in SB1 and SA3 respectively (Figures 4.20 and 4.21). The experimental results depicted that the sulfate concentration varied between GA2 (27±6) and GB1 (54±2 mg/l)in pre-rainwater collected from Gujranwala but rain had increased maximum sulfate concentration to 88±8 mg/l and minimum concentration to 76±8 mg/l in GA1 and GA2 respectively (Figures 4.22 and 4.23).

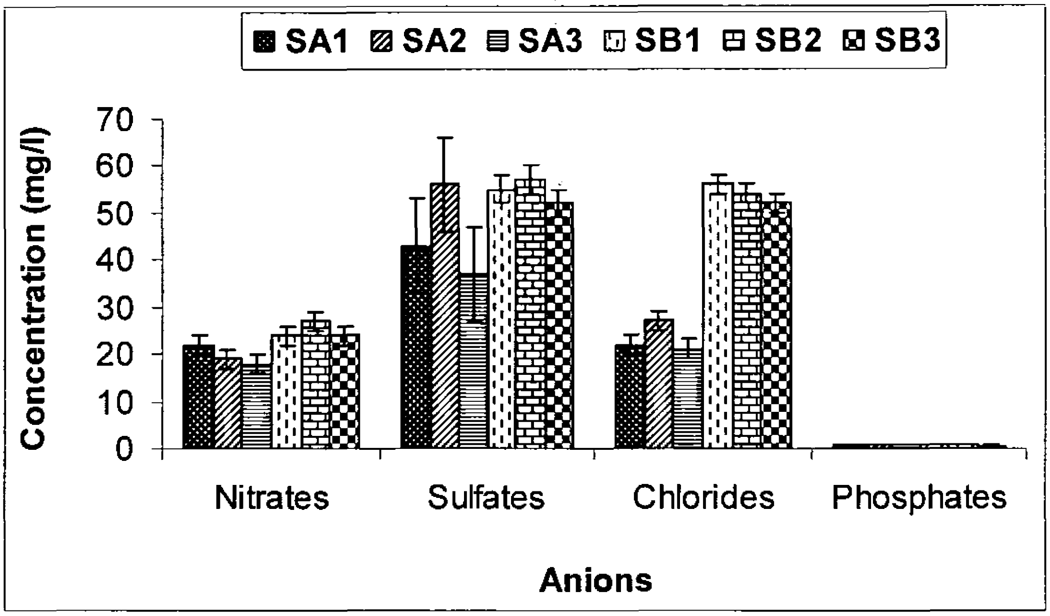

Figure 4.21 Anions in post-rain ground water samples collected from Sialkot

4.2.2.3 Chlorides in ground water samples

The ground water samples collected before rain had highest chloride concentration 52±2 mg/l and lowest concentration 18±1mg/l in SB1 and SA3 respectively while the highest concentration 56±2 mg/l and lowest concentration 21±2 mg/l was found in SB1 and SA3 respectively in samples collected after rain from Sialkot which was relatively higher than pre-rain samples (Figures 4.20 and 4.21). The amount of chlorides present in ground water samples collected before rain concentration was observed at its maximum level in GA1 (70±4 mg/l) and lowest level in GB1 (30±7 mg/l) while the in post-rain samples from Gujranwala indicated fluctuations in chloride concentration in range of GB1 (43±2 mg/l) and GA1 (82±2 mg/l) which was relatively higher than pre-rain samples (Figures 4.22 and 4.23)

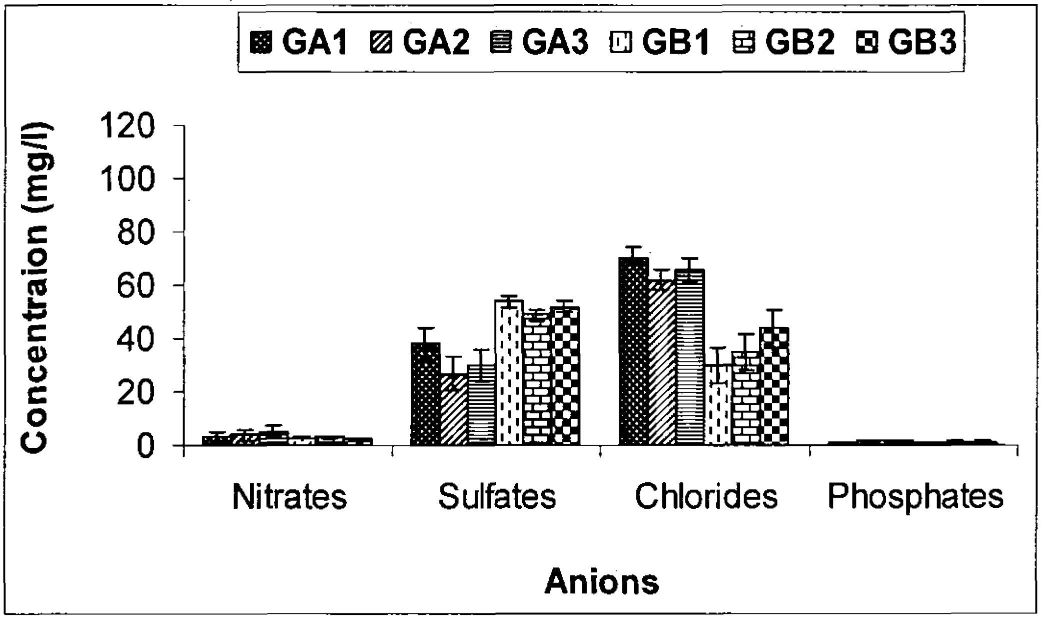

Figure 4.22 Anions in pre-rain ground water samples collected from Gujranwala

4.2.2.4 Phosphates in ground water samples

The maximum concentration of phosphates was found to be 1.1±0.16 mg/l in SB1 and minimum concentration 0.3±0.2 mg/l in SA1 in pre-rain samples but the maximum concentration of phosphates examined in post-rain samples was 0.88±0.05 mg/l and minimum concentration 0.65±0.08 mg/l in SA1 and SB3 (Figures 4.20 and 4.21). The concentration of phosphates was showed variations within GA3 (1.6±0.14 mg/l) and GB1 (0.6±0.5 mg/l) in pre-rain samples and similarly, concentration of phosphates examined in post-rain samples was in range of GB1 (1.2±0.6 mg/l) and GA3 (2.5±0.14 mg/l) (Figures 4.22 and 4.23).

It was also observed that the nitrate, sulfates, chlorides and phosphates concentrations were comparatively higher in post-rain samples than pre-rain and found to be significantly different in each site and overall ground water samples collected from Gujranwala had higher nitrate, sulfates, chlorides and phosphates concentrations as compared to samples collected from Sialkot. Furthermore, nitrate, sulfates, chlorides and phosphates concentrations were found to be within WHO/NEQS permissible standards (WHO, 2004; Pak EPA, 2008).

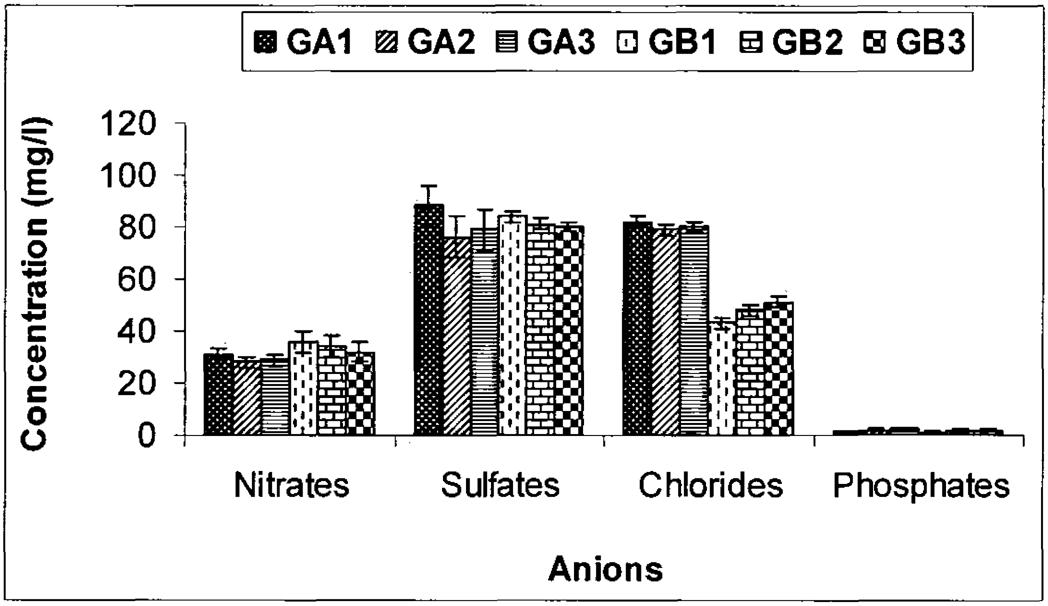

Figure 4.23 Anions in post-rain ground water samples collected from Gujranwala

4.2.3 Heavy Metals in Ground Water Samples

4.2.3.1 Chromium

The maximum concentration of chromium 0.2±0.07 mg/l and minimum concentration 0.07±0.2 mg/l was found in SA2 and SB3 respectively in ground water samples collected before rain from and in vicinity of dumping sites of Sialkot while the post-rain samples had highest concentration 1.1±0.05 mg/l and lowest 0.79±0.1

mg/l of chromium in SA2 and SB2 respectively and its concentration was comparatively higher than pre-rain due values due to the run off and mobility from tannery areas soil to ground water (Figures 4.24 and 4.25).

The highest concentration level of chromium in pre-rain samples collected from Gujranwala was 0.08±0.5 mg/l assessed in GA1 and minimum level in Gujranwala was 0.01±0.01 mg/l in GB3 while highest concentration 0.9±0.2 of post-rain samples and lowest concentration 0.6±0.02 mg/l was found in GB1 andGB3 respectively which was relatively higher than pre-rain samples (Figures 4.26 and 4.27).

It was important to mention that the chromium concentration level in most of the samples from both cities except few pre-rain samples collected from Gujranwala was higher than the permissible limits of WHO/NEQS (WHO, 2004; Pak EPA, 2008). The excessive exposure had potential to cause serious ailing effects through excessive ingestion or environmental exposure (inhalation etc). It may cause perforation of nasal septum, lung cancer, and skin ulceration along with growth depression, damage to kidney and liver and cancer. The international agency for Research on Cancer categorized chromium as carcinogenic to human beings (Frisbie *et al.*, 2002).

The chromium concentration in ground water samples of Sialkot was higher than the Gujranwala and its value were significantly different in each site. The chromium level in current study was found to be higher than examined by Rizwan

Ullah *et al.* (2009) and Kahlown *et al.* (2008) in ground water of Sialkot and Gujranwala.

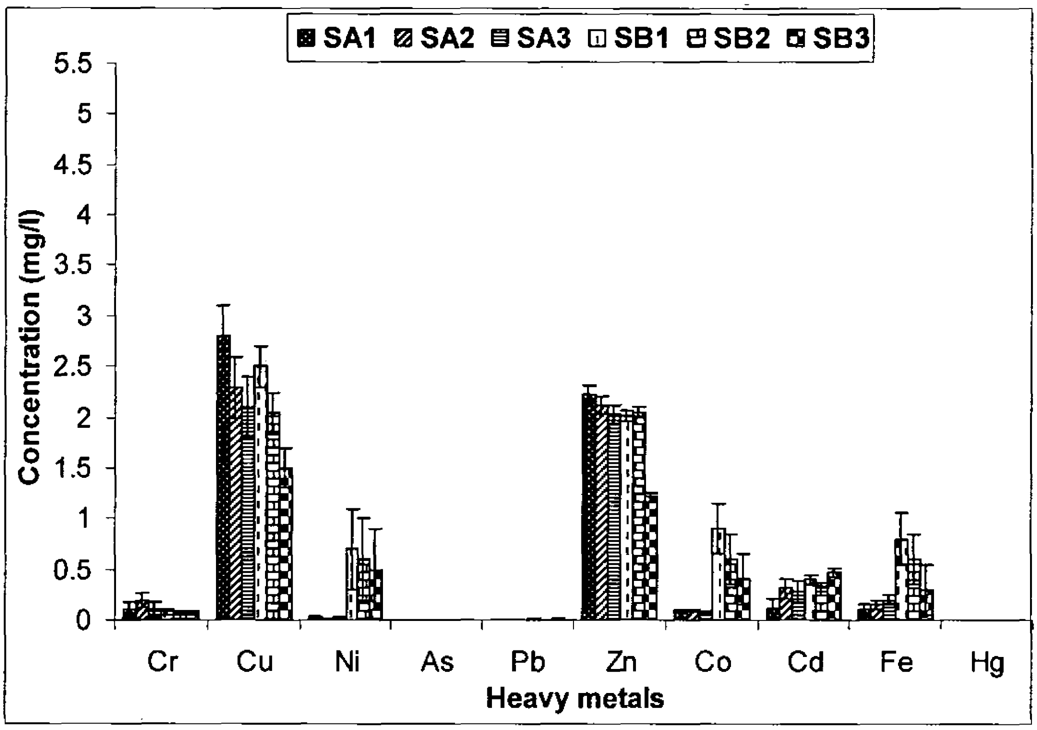

Figure 4.24 Heavy metals in pre-rain ground water samples collected from Sialkot

4.2.3.2 Copper

The copper had highest concentration 2.8±0.3 mg/l and lowest concentration 1.5±0.2 mg/l in SA1 and SB3 respectively in ground water samples collected before rain from locality of dumping sites of Sialkot while highest copper concentration 3.9±0.3 mg/l and lowest 2.7±0.5 mg/l was present in SA1 and SB3 respectively in water samples collected after rain from Sialkot (Figures 4.24 and 4.25).

The maximum concentration level of copper in pre-rain samples collected from Gujranwala was 2.9±0.5 mg/l assessed in GA3 and minimum level in Gujranwala was 2.1±0.01 mg/l in GA1 while highest concentration 4.1±0.3 mg/l of post-rain samples and lowest concentration 3.5±0.3 mg/l was observed in GA3 andGA2 respectively which was relatively higher than pre-rain samples (Figures 4.26 and 4.27).

Copper concentration level in all ground water samples from both cities except SB3 pre-rain sample collected from "B" duping site of Sialkot was higher than the permissible limits of WHO/NEQS (WHO, 2004; Pak EPA, 2008). The over dose of copper can case neurological complications, hypertension, liver and kidney dysfunction (Gowd and Govil, 2008; Rao *et al.*, 2001). The copper concentration in ground water samples of Sialkot was lower than the Gujranwala and its value were significantly different in each site. The copper level in current study was found to be higher than examined by Rizwan Ullah *et al.* (2009) and Kahlown *et al.* (2008) in ground water of Sialkot and Gujranwala.

4.2.3.3 Nickel

The samples collected before rain had nickel had highest concentration 0.7±0.4 mg/l and lowest concentration 0.01±0.007 mg/l in SB1 and SA2 respectively in ground water samples collected from dumping sites of Sialkot while highest nickel concentration 1.6±0.5 mg/l and lowest 0.51±0.03 mg/l was present in SB1 and SA2 respectively in water samples collected after rain from Sialkot (Figures 4.24 and 4.25).

The highest concentration level of nickel in pre-rain samples collected from Gujranwala was 0.58±0.01 mg/l assessed in GB3 and minimum level in Gujranwala was 0.51±0.03 mg/l in GA2 while highest concentration 0.94±0.6 mg/l of post-rain samples and lowest concentration 0.6±0.01 mg/l was observed in GB1 and GA1 respectively which was relatively higher than pre-rain samples (Figures 4.26 and 4.27).

The nickel concentration level in all ground water samples from both cities was higher than the stipulated values of WHO/NEQS (WHO, 2004; Pak EPA, 2008). Nickel is considered as one of the most mobile of the heavy metals when released to water, mainly in polluted waters having organic material will keep nickel soluble (Khan, 2011).

The nickel concentration in ground water samples of Sialkot was higher than the Gujranwala and its value were significantly different in each site. The primary source of nickel in drinking-water is the leaching of metals in water network (WHO, 2005). Nickel and its compounds are associated with classic noxious agents encountered in industry but are also recognized to affect non-occupationally exposed individuals (Boustani *et al.*, 2012).

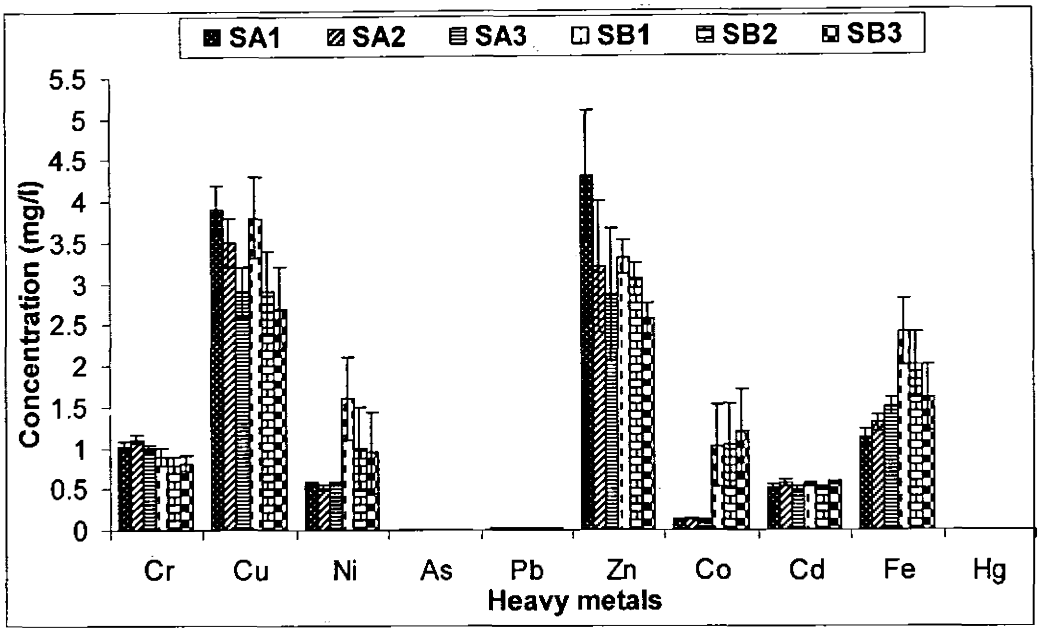

Figure 4.25 Heavy metals in post-rain ground water samples collected from Sialkot

The toxicity and carcinogenicity of some nickel compounds (in the nasal cavity, larynx and lungs) in experimental animals, as well as in the occupationally exposed people, are well documented and reported (Cempel and Nikel, 2006). The nickel level in current study was found to be relatively higher than previously reported by Rizwan Ullah *et al.* (2009) and Kahlown *et al.* (2008) in ground water of Sialkot and Gujranwala.

4.2.3.4 Zinc

The maximum concentration 2.22±0.09 mg/l of zinc and minimum concentration 1.21±0.05 mg/l of zinc was observed in SA1 and SB3 respectively in ground water samples collected in dry season from dumping sites of Sialkot while highest zinc concentration 4.3±0.8 mg/l and lowest 2.57±0.2 mg/l was analyzed in SA1 and SB3 respectively in water samples collected after rain from Sialkot (Figures 4.24 and 4.25).

The pre-rain ground water samples had maximum concentration level 2.23±0.2 mg/l of zinc in GA3 and minimum level in Gujranwala was 1.01±0.5 mg/l in GA2 while highest concentration 3.17±0.3 mg/l of post-rain samples and lowest concentration 2±0.3 mg/l was assessed in GA1 and GB3 respectively which was relatively higher than pre-rain sample (Figures 4.26 and 4.27).

The zinc concentration level in all pre-rain and few post-rain ground water samples from both cities was within the WHO/NEQS limits (WHO, 2004; Pak EPA, 2008) while most of post-rain samples had zinc concentration higher than or near to the stipulated values of WHO/NEQS. Zn had been known to have low toxicity to man but its prolonged consumption of large doses can be resulted in some health complications such as fatigue, dizziness, and neutropenia (Hess & Schmid, 2002). The zinc concentration in ground water samples of Sialkot was higher than the Gujranwala and its value were significantly different in each site. The zinc level in current study was found to be relatively higher than previously reported by Rizwan Ullah *et al.* (2009) and Kahlown *et al.* (2008) in ground water of Sialkot and Gujranwala.

4.2.3.5 Cobalt

The highest cobalt level 0.9±0.5 mg/l and lowest cobalt level 0.07±0.1 mg/l was found in SB1 and SA3 respectively in ground water samples collected in dry season from dumping sites of Sialkot while highest cobalt level 1.2±0.5 mg/l and lowest 0.11±0.007 mg/l was analyzed in SB3 and SA3 respectively in water samples collected after rain from Sialkot (Figures 4.24 and 4.25).

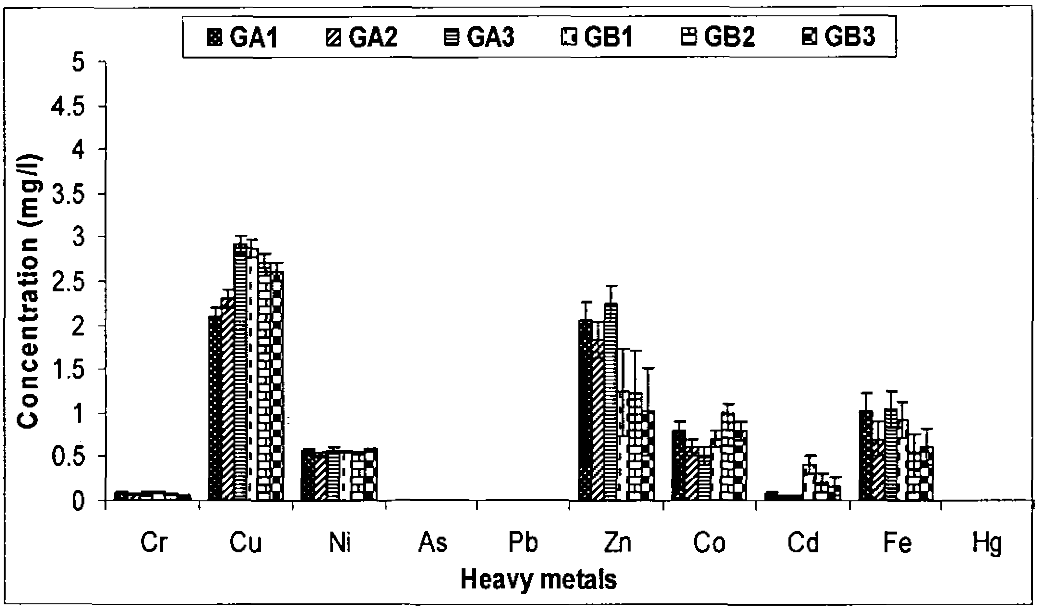

Figure 4.26 Heavy metals in pre-rain ground water samples collected from Gujranwala

The ground water samples had maximum cobalt level 1±0.1 mg/l and minimum level 0.5±0.1 mg/l in pre-rain GB2 and GA3 respectively in Gujranwala but highest concentration 1.13±0.04 mg/l of post-rain samples and lowest concentration 1.03±0.3 mg/l was assessed in GA1 and GB3 respectively which was relatively higher than pre-rain samples (Figures 4.26 and 4.27). WHO/NEQS limits for cobalt are not available. Furthermore, cobalt concentration in ground water samples of Sialkot was comparatively lower than the Gujranwala and its value were significantly different in each site. The cobalt level in current study was found to be relatively higher than previously reported by Rizwan Ullah *et al.* (2009) and Kahlown *et al.* (2008) in ground water of Sialkot and Gujranwala.

4.2.3.6 Cadmium

The maximum concentration of cadmium 0.47±0.04 mg/l and minimum concentration 0.28±0.2 mg/l was found in SB3 and SA3 respectively in ground water samples collected before rain from and in vicinity of dumping sites of Sialkot while the post-rain samples had highest concentration 0.57±0.05 mg/l and lowest 0.49±0.04 mg/l of cadmium in SA2 and SA3 respectively and its concentration was comparatively higher than pre-rain due values due to the run off and mobility from dumping sites to ground water (Figures 4.24 and 4.25).

The highest concentration level of cadmium in pre-rain samples collected from Gujranwala was 0.4±0.02 mg/l assessed in GB1 and minimum level in Gujranwala was 0.02±0.02 mg/l in GA2 while highest concentration 0.5±0.05 mg/l of post-rain samples and lowest concentration 0.3±0.03 mg/l was found in GA1 and GB3 respectively which was relatively higher than pre-rain samples (Figures 4.26 and 4.27).

The cadmium concentration in all ground water samples from both cities was higher than or the stipulated values of WHO/NEQS (WHO, 2004; Pak EPA, 2008).

The major target organs for cadmium are the kidney and liver where it accumulates in high concentrations which lead to chronic kidney dysfunction (Taiwo 2010). It had been reported that chronic exposure to Cd in animals and humans resulted in kidney dysfunction, hypertension, anemia, liver damage, gastrointestinal effects such as nausea, vomiting, salivation, and diarrhea as well as reduction in male fertility and cancer (Shelton, 2002). The cadmium concentration in ground water samples of Sialkot was higher than the Gujranwala and its value were significantly different in each site. The cadmium level in current study was found to be relatively higher than previously reported by Rizwan Ullah *et al.* (2009) and Kahlown *et al.* (2008) in ground water of Sialkot and Gujranwala.

4.2.3.7 Iron

The highest concentration 0.8±0.0.4 mg/l and lowest concentration 0.1±0.05 mg/l of iron was examined in SB1 and SA1 respectively in ground water samples collected before rain from locality of dumping sites of Sialkot while highest iron concentration 2.4±0.4 mg/l and lowest 1.12±0.1 mg/l was found to be in SB1 and SA1 respectively in water samples collected after rain from Sialkot (Figures 4.24 and 4.25).

The maximum concentration level of iron in pre-rain samples collected from Gujranwala was 1.03±0.5 mg/l assessed in GA3 and minimum level in Gujranwala was 0.11±0.4 mg/l in GB3 while highest concentration 2.29±0.6 mg/l of post-rain samples and lowest concentration 1.11±0.6 mg/l was observed in GA3 and GA2 respectively which was relatively higher than pre-rain samples (Figures 4.26 and 4.27).

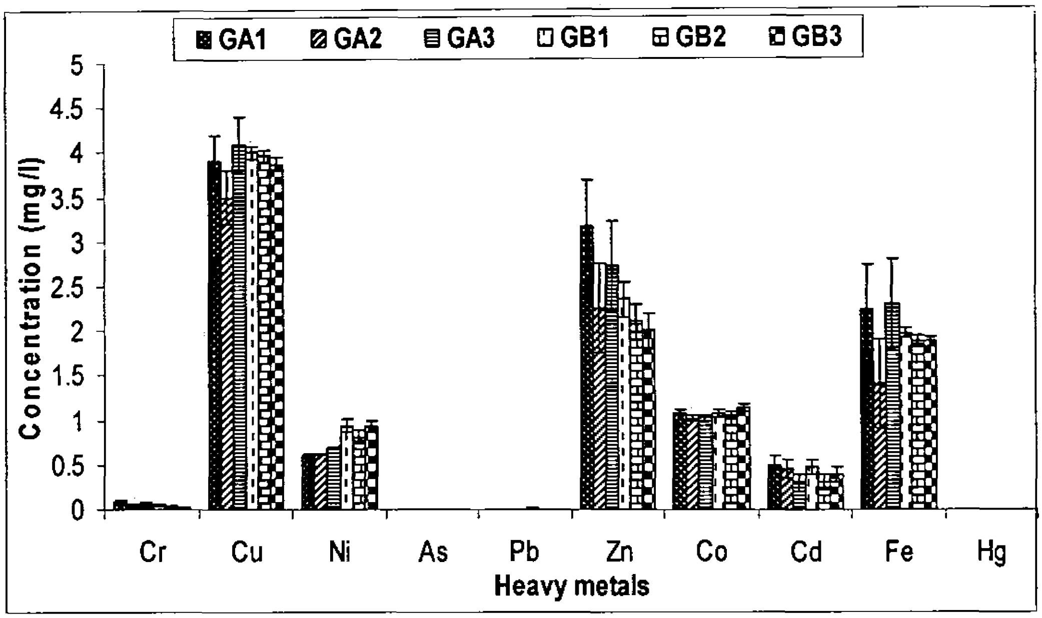

Figure 4.27 Heavy metals in post-rain ground water samples collected from Gujranwala

The iron concentration level in most of the ground water samples collected from both cities was found to be higher than permissible limits of WHO/NEQS (WHO, 2004; Pak EPA, 2008) except few pre-rain ground water samples from "A" duping site of Sialkot was within the WHO/NEQS limits (WHO, 2004; Pak EPA, 2008) and its value were significantly different in each site. The level of iron may enhance the level of iron in blood which can damage the cells of the gastrointestinal tract, preventing them from regulating iron absorption (El-Harbawi *et al.*, 2010). The iron levels play a major role in producing atherosclerosis through interaction of iron and cholesterol in promoting oxidative damage, causing both atherosclerosis and neuro degeneration and disorders (Sullivan, 2007; Perez *et al.*, 2010). Ong and Halliwell, (2004) reported the involvement of iron in Alzheimer's disease. The iron level in current study was found to be high as compared to previously reported by Rizwan Ullah *et al.* (2009) and Kahlown *et al.* (2008) in ground water of Sialkot and Gujranwala.

4.2.3.8 Other Heavy metals

The lead concentration in all samples in both cities was within WHO/NEQS standards (WHO, 2004; Pak EPA, 2008), moreover, arsenic and mercury was not detected in any samples.

Previously it has been reported that wastes resulted from iron and steel industries, refuse incineration, domestic sewage and urban water runoffs are responsible for the wide distribution of Cd, Zn, Pb, and other trace metals in our water bodies (Fatoki *et al.*, 2002).

It is also important to discuss that the highly contaminated, "A" dumping site of Sialkot was situated at the bank of Upper Chenab Canal and this site was continues source of contamination of surface water. Furthermore, the ground water samples collected from the vicinity of that site was least contaminated as compared to other three sites due to continuous dilution by the canal. The presence of high concentration of heavy metals like Cd, Zn, Fe, Cr, Cu, Ni was the indication of deleterious effects on ground water quality by dumping sites. The previous studies have also confirmed that the concentration of heavy metal contents, such as Cr, Cd, Zn, Fe, Cu, Ni and Mn were higher in the groundwater due to leachate (Prechthai *et al.*, 2008; Ogundiran and Afolabi, 2008; Biswas *et al.*, 2010; Long *et al.*, 2011).

4.3 Organic compounds in water samples

Based on chromatographic analysis of water samples, hydrocarbons and organic compounds i.e. PAHs and PCBs were suspected and also found in trace amount but requires further investigation in order to confirm their presence. It could be due to lipophilic nature of compounds that requires individual evaluation.

V. CONCLUSIONS AND RECOMMENDATIONS

The uncontrolled, non-engineered and aged open-dumping sites located in or around residential areas and at the banks of canals pose a potential risk to human health and environment through leaching of toxic chemicals. It has been revealed from current study that the dumping of a mixed industrial and household waste magnifies the health risk and could result in increased concentrations of salts, ions and trace elements. Such spiking can produce harmful effects for the both biotic and abiotic components of the surrounding ecosystems. The physico-chemical characterization of soil samples collected from open dumping sites of both Sialkot and Gujranwala city indicated that soil was slightly alkaline and was found rich in nitrogen content and total organic carbon due to the biological degradation of huge amount of organic waste. The sodium and potassium levels were relatively lower than normal levels. Among heavy metals, chromium concentration was higher in dumping sites of Sialkot due to dumping of tanneries waste when compared to Gujranwala dumping sites data. Whereas, copper, nickel, zinc, iron, cobalt and cadmium concentrations were comparatively high in soil samples collected from Gujranwala as compared to Sialkot dumping sites due to industrial waste from electrical and electronics industry and batteries manufacturing plants. Moreover, arsenic and mercury was not detected in any of soil samples collected from all dumping sites irrespective of Sialkot or Gujranwala. The results revealed that the lead concentration was less than 0.1 mg/kg in all sites of both cities except soil sample (GB2) collected during pre-rain season. The heavy metal concentration present in soil was in order of: Zn > Fe > Cu > Cr > Ni > Cd > Co > Pb > As and Hg; whereas site wise contamination order was: GB > GA > SA > SB. The results illustrated that the rain had played a significant role on physico-chemical parameters and it was observed that the total organic carbon, nitrogen content in both cities, while chromium concentration was high only in post-rain samples collected from Sialkot. Furthermore, the rain had significantly decreased the values of pH, TDS, K, Na, Zn, Fe, Cu, Cr, Ni, Cd, Co, and Pb.

The damaging environmental prospects associated with leaching of toxic chemicals from dumping sites were: the contamination of adjacent water bodies and ground water in addition to soil contamination. It was also found that pre-rain samples had pH value near to or higher than WHO/NEQS standard for drinking water in both cities. However, the pH value of all post-rain samples was less than stipulated value prescribed by WHO. On the other hand, TDS, EC, hardness, nitrate, sulfates, chlorides and phosphates concentrations were found to be within the WHO/NEQS permissible standards.

It was important to mention that the chromium concentration level in most of the samples from both cities except few pre-rain samples collected from Gujranwala, was higher than the permissible limits of WHO/NEQS while copper concentration level in all ground water samples from both cities except SB3 pre-rain sample collected from "B" dumping site of Sialkot, was higher than the permissible limits of WHO/NEQS. The nickel and cadmium concentration level in all ground water samples from both cities was higher than the stipulated values of WHO/NEQS, but

WHO/NEQS limits for cobalt are not available. Among other heavy metals, lead concentration in all samples in both cities was found to be within WHO/NEQS standards, moreover, arsenic and mercury was not detected in any samples. The zinc concentration level in all pre-rain and few post-rain ground water samples from both cities was within the WHO/NEQS limits while most of post-rain samples had zinc concentration higher than or near to the stipulated values of WHO/NEQS. The iron concentration level in most of the ground water samples collected from both cities was found to be higher than permissible limits of WHO/NEQS except few pre-rain ground water samples from "A" duping site of Sialkot was within the WHO/NEQS limits.

As a whole, the water samples collected from both cities were not fit for drinking due to high contamination level of heavy metals. The rain had significantly increased the concentration of most of the parameter tested for water quality. The presence of high concentration of heavy metals like Cd, Zn, Fe, Cr, Cu, Ni was the indication of deleterious effects on ground water quality by dumping sites. Therefore, results of study deduced that continuous disposal of all categories of solid waste in open dump sites could result in degradation of quality of the soil and ground water. Such a higher level of contamination could have damaging effects on human and other organisms. The people living in that area are at risk of toxic effects of heavy metals on their organ system due to accumulation of metals. Furthermore, soils in receipt of released leachates could also become potential source of entry into the human food web.

Consequently, it is absolutely necessary to reduce the toxic level as depicted by this study and the health effects of leachates flowing from dumping sites of Sialkot and Gujranwala could have on health and environment. Therefore, the following recommendations are proposed for handling this problem:

- The waste should be segregated at source before disposal to the dumping/landfill sites.
- The toxic waste from industry and hospitals should be disposed of through an appropriate method for hazardous waste disposal.
- The illegal open dump sites should be banned and the illegal activities of using dumping waste in construction sites for site-filling should be prohibited.
- The dumping sites close to water distribution network, i.e., at the bank of Upper Chenab, should be immediately removed.
- The local authorities responsible for disposal of waste should construct properly engineered landfill sites in accordance with international standards away from urban and residential areas.
- Littering of solid waste with in the cities, towns and urban areas should be strongly prohibited.
- Municipal authorities should maintain the storage, transportation and disposal facilities to avoid unhygienic and unsanitary conditions.
- The Environmental Protection Agency (EPA), Punjab EPD should streamline the monitoring system for waste disposal and take immediate strict action to stop illegal dumping

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Appendix 1 Physico-Chemical Analysis of Soil Samples Collected from Gujranwala & Sialkot

Appendix 1.1 Physico-chemical analysis of pre-rain soil samples collected from Sialkot (Site A)

Parameters	Locations											
	SA1				SA2				SA3			
	Mean	St. Dev.	Variance	P-value	Mean	St. Dev.	Variance	P-value	Mean	St. Dev.	Variance	P-value
pH	7.8	±0.1	0.004	0.03	8.01	±0.1	0.004	0.03	7.9	±0.1	0.004	0.03
TDS (mg/kg)	2566	±354	525	0.05	2184	±354	525	0.05	1857	±354	525	0.05
TOC (% age)	3	±0.4	0.2	0.03	2.8	±0.4	0.2	0.03	2.1	±0.4	0.2	0.03
Sodium (mg/kg)	34	±4	16	0.05	26	±4	16	0.05	30	±4	16	0.05
Potassium (mg/kg)	19	±3	6	0.04	17	±3	6	0.04	14	±3	6	0.04
Nitrogen (mg/kg)	30	±2	4	0.03	28	±2	4	0.03	26	±2	4	0.03
Cr (mg/kg)	3.7	±0.3	0.09	0.04	3.1	±0.3	0.09	0.04	3.5	±0.3	0.09	0.04
Cu (mg/kg)	1.9	±0.3	0.07	0.04	1.4	±0.3	0.07	0.04	1.8	±0.3	0.07	0.04
Ni (mg/kg)	1.17	±0.03	0.1	0.03	1.14	±0.03	0.1	0.03	1.1	±0.03	0.1	0.03
As (mg/kg)	N.D	-	-	-	N.D	-	-	-	N.D	-	-	-
Pb (mg/kg)	0.03	±0.001	0.0004	0.03	0.017	±0.001	0.0004	0.03	0.02	±0.001	0.0004	0.03
Zn (mg/kg)	6	±0.6	0.4	0.01	4.8	±0.6	0.4	0.01	5.2	±0.6	0.4	0.01
Co (mg/kg)	0.1	±0.01	0.0003	0.03	0.09	±0.01	0.0003	0.03	0.07	±0.01	0.0003	0.03
Cd (mg/kg)	0.89	±0.1	0.02	0.05	0.68	±0.1	0.02	0.05	0.6	±0.1	0.02	0.05
Fe (mg/kg)	4.8	±1	0.9	0.05	3.5	±1	0.9	0.05	2.9	±1	0.9	0.05
Hg (mg/kg)	N.D	-	-	-	N.D	-	-	-	N.D	-	-	-

Appendix 1.1 Physico-chemical analysis of pre-rain soil samples collected from Sialkot (Site B)

Parameters	Locations											
	SB1				SB2				SB3			
	Mean	St. Dev.	Variance	P-value	Mean	St. Dev.	Variance	P-value	Mean	St. Dev.	Variance	P-value
pH	7.93	±0.06	0.004	0.02	7.8	±0.06	0.004	0.02	7.86	±0.06	0.004	0.02
TDS (mg/kg)	2215	±276	356	0.05	1921	±276	356	0.05	1663	±276	356	0.05
TOC(% age)	1.9	±0.3	0.06	0.04	2.2	±0.3	0.06	0.04	1.6	±0.3	0.06	0.04
Sodium (mg/kg)	26	±4	17	0.05	18	±4	17	0.05	24	±4	17	0.05
Potassium (mg/kg)	20	±2	2	0.04	16	±2	2	0.04	9	±2	2	0.04
Nitrogen (mg/kg)	24	±2	4	0.03	21	±2	4	0.03	20	±2	4	0.03
Cr (mg/kg)	2.3	±0.6	0.4	0.05	1.3	±0.6	0.4	0.05	1.1	±0.6	0.4	0.05
Cu (mg/kg)	1.26	±0.09	0.008	0.008	1.08	±0.09	0.008	0.008	1.2	±0.09	0.008	0.008
Ni (mg/kg)	1.24	±0.03	0.003	0.03	1.3	±0.03	0.003	0.03	1.35	±0.03	0.003	0.03
As (mg/kg)	N.D	-	-	-	N.D	-	-	-	N.D	-	-	-
Pb (mg/kg)	0.013	±0.001	0.0001	0.04	0.008	±0.001	0.0001	0.04	0.0067	±0.001	0.0001	0.04
Zn (mg/kg)	4.6	±0.8	0.6	0.04	3.1	±0.8	0.6	0.04	4.3	±0.8	0.6	0.04
Co (mg/kg)	0.01	±0.001	0.00002	0.03	0.009	±0.001	0.00002	0.03	0.008	±0.001	0.00002	0.03
Cd (mg/kg)	0.2	±0.05	0.003	0.05	0.1	±0.05	0.003	0.05	0.14	±0.05	0.003	0.05
Fe (mg/kg)	2.7	±0.3	0.09	0.03	2.1	±0.3	0.09	0.03	2.3	±0.3	0.09	0.03
Hg (mg/kg)	N.D	-	-	-	N.D	-	-	-	N.D	-	-	-

Appendix 1.2 Physico-chemical analysis of post-rain soil samples collected from Sialkot (Site A)

Parameters	Locations											
	SA1				SA2				SA3			
	Mean	St. Dev.	Variance	P-value	Mean	St. Dev.	Variance	P-value	Mean	St. Dev.	Variance	P-value
pH	7.73	±0.6	0.01	0.03	7.6	±0.6	0.01	0.03	7.7	±0.6	0.01	0.03
TDS (mg/kg)	2087	±291	350	0.05	1850	±291	350	0.05	1507	±291	350	0.05
TOC(% age)	4.01	±0.4	0.2	0.03	3.9	±0.4	0.2	0.03	3.3	±0.4	0.2	0.03
Sodium (mg/kg)	27	±3	7	0.04	21	±3	7	0.04	22	±3	7	0.04
Potassium (mg/kg)	13	±2	2	0.04	12	±2	2	0.04	10	±2	2	0.04
Nitrogen (mg/kg)	35	±2	4	0.03	32	±2	4	0.03	30	±2	4	0.03
Cr (mg/kg)	4.5	±0.3	0.09	0.04	3.9	±0.3	0.09	0.04	4.1	±0.3	0.09	0.04
Cu (mg/kg)	1.3	±0.3	0.07	0.04	0.8	±0.3	0.07	0.04	1.1	±0.3	0.07	0.04
Ni (mg/kg)	1.03	±0.07	0.005	0.03	1.08	±0.07	0.005	0.03	0.9	±0.07	0.005	0.03
As (mg/kg)	N.D	-	-	-	N.D	-	-	-	N.D	-	-	-
Pb (mg/kg)	0.01	±0.01	0.0001	0.03	0.008	±0.01	0.0001	0.03	0.009	±0.01	0.0001	0.03
Zn (mg/kg)	4	±0.4	0.2	0.01	3.1	±0.4	0.2	0.01	3.9	±0.4	0.2	0.01
Co (mg/kg)	0.06	±0.02	0.0004	0.03	0.04	±0.02	0.0004	0.03	0.02	±0.02	0.0004	0.03
Cd (mg/kg)	0.55	±0.1	0.01	0.05	0.42	±0.1	0.01	0.05	0.34	±0.1	0.01	0.05
Fe (mg/kg)	2.6	±0.5	0.3	0.05	2.01	±0.5	0.3	0.05	1.5	±0.5	0.3	0.05
Hg (mg/kg)	N.D	-	-	-	N.D	-	-	-	N.D	-	-	-

Appendix 1.2 Physico-chemical analysis of post-rain soil samples collected from Sialkot (Site B)

Parameters	Locations											
	SB1				SB2				SB3			
	Mean	St. Dev.	Variance	P-value	Mean	St. Dev.	Variance	P-value	Mean	St. Dev.	Variance	P-value
pH	7.67	±0.1	0.01	0.02	7.4	±0.1	0.01	0.02	7.5	±0.1	0.01	0.02
TDS (mg/kg)	1722	±264	345	0.05	1449	±264	345	0.05	1194	±264	345	0.05
TOC(% age)	2.3	±0.2	0.04	0.04	2.7	±0.2	0.04	0.04	2.4	±0.2	0.04	0.04
Sodium (mg/kg)	17	±2	6	0.05	12	±2	6	0.05	15	±2	6	0.05
Potassium (mg/kg)	14	±3	2	0.04	11	±3	2	0.04	7	±3	2	0.04
Nitrogen (mg/kg)	29	±2	5	0.05	27	±2	5	0.05	24	±2	5	0.05
Cr (mg/kg)	3.1	±0.2	0.2	0.05	2.8	±0.2	0.2	0.05	2.3	±0.2	0.2	0.05
Cu (mg/kg)	0.92	±0.05	0.02	0.008	0.82	±0.05	0.02	0.008	0.9	±0.05	0.02	0.008
Ni (mg/kg)	1.07	±0.07	0.004	0.03	1.15	±0.07	0.004	0.03	1.09	±0.07	0.004	0.03
As (mg/kg)	N.D	-	-	-	N.D	-	-	-	N.D	-	-	-
Pb (mg/kg)	0.006	±0.001	0.0001	0.04	0.0053	±0.001	0.0001	0.04	0.0047	±0.001	0.0001	0.04
Zn (mg/kg)	2.8	±0.7	0.5	0.04	2.4	±0.7	0.5	0.04	2.5	±0.7	0.5	0.04
Co (mg/kg)	0.007	±0.02	0.00001	0.03	0.005	±0.02	0.00001	0.03	0.0037	±0.02	0.00001	0.03
Cd (mg/kg)	0.08	±0.02	0.0002	0.05	0.05	±0.02	0.0002	0.05	0.063	±0.02	0.0002	0.05
Fe (mg/kg)	1.9	±0.3	0.09	0.03	1.3	±0.3	0.09	0.03	1.5	±0.3	0.09	0.03
Hg (mg/kg)	N.D	-	-	-	N.D	-	-	-	N.D	-	-	-

Appendix 1.3 Physico-chemical analysis of pre-rain soil samples collected from Gujranwala

Parameters	Locations											
	GA1				GA2				GA3			
	Mean	St. Dev.	Variance	P-value	Mean	St. Dev.	Variance	P-value	Mean	St. Dev.	Variance	P-value
pH	8	±0.06	0.003	0.02	8.1	±0.06	0.003	0.02	8	±0.06	0.003	0.02
TDS (mg/kg)	2498	±243	792	0.05	2177	±243	792	0.05	1937	±243	792	0.05
TOC(% age)	2.9	±0.3	0.1	0.01	2.3	±0.3	0.1	0.01	2.1	±0.3	0.1	0.01
Sodium (mg/kg)	36	±4	9	0.05	29	±4	9	0.05	34	±4	9	0.05
Potassium (mg/kg)	26	±4	13	0.05	24	±4	13	0.05	19	±4	13	0.05
Nitrogen (mg/kg)	34	±2	4	0.02	32	±2	4	0.02	30	±2	4	0.02
Cr (mg/kg)	1.9	±0.2	0.02	0.02	1.6	±0.2	0.02	0.02	1.7	±0.2	0.02	0.02
Cu (mg/kg)	2.8	±0.3	0.06	0.04	2.3	±0.3	0.06	0.04	2.5	±0.3	0.06	0.04
Ni (mg/kg)	1.4	±0.1	0.01	0.02	1.28	±0.1	0.01	0.02	1.31	±0.1	0.01	0.02
As (mg/kg)	N.D	-	-	-	N.D	-	-	-	N.D	-	-	-
Pb (mg/kg)	0.024	±0.007	0.0006	0.05	0.021	±0.007	0.0006	0.05	0.0099	±0.007	0.0006	0.05
Zn (mg/kg)	6.4	±0.5	0.3	0.02	5.3	±0.5	0.3	0.02	5.9	±0.5	0.3	0.02
Co (mg/kg)	0.9	±0.2	0.04	0.04	0.5	±0.2	0.04	0.04	0.7	±0.2	0.04	0.04
Cd (mg/kg)	1.3	±0.02	0.06	0.05	1.06	±0.02	0.06	0.05	0.8	±0.02	0.06	0.05
Fe (mg/kg)	5.06	±0.7	0.5	0.05	4.2	±0.7	0.5	0.05	3.7	±0.7	0.5	0.05
Hg (mg/kg)	N.D	-	-	-	N.D	-	-	-	N.D	-	-	-

Appendix 1.3 Physico-chemical analysis of pre-rain soil samples collected from Gujranwala

Parameters	Locations											
	GB1				GB2				GB3			
	Mean	St. Dev.	Variance	P-value	Mean	St. Dev.	Variance	P-value	Mean	St. Dev.	Variance	P-value
pH	8.2	±0.3	0.09	0.04	8.4	±0.3	0.09	0.04	8.78	±0.3	0.09	0.04
TDS (mg/kg)	2721	±275	598	0.05	2237	±275	598	0.05	2429	±275	598	0.05
TOC(% age)	2.4	±0.4	0.2	0.05	1.9	±0.4	0.2	0.05	1.8	±0.4	0.2	0.05
Sodium (mg/kg)	39	±4	9	0.03	33	±4	9	0.03	27	±4	9	0.03
Potassium (mg/kg)	29	±2	4	0.01	25	±2	4	0.01	26	±2	4	0
Nitrogen (mg/kg)	29	±1	2	0.02	27	±1	2	0.02	26	±1	2	0.02
Cr (mg/kg)	2.1	±0.3	0.09	0.03	1.5	±0.3	0.09	0.03	1.8	±0.3	0.09	0.03
Cu (mg/kg)	3.4	±0.4	0.2	0.05	2.6	±0.4	0.2	0.05	2.94	±0.4	0.2	0.05
Ni (mg/kg)	1.6	±0.1	0.01	0.03	1.1	±0.1	0.01	0.03	1.33	±0.1	0.01	0.03
As (mg/kg)	N.D	-	-	-	N.D	-	-	-	N.D	-	-	-
Pb (mg/kg)	0.04	±0.008	0.0006	0.05	0.21	±0.008	0.0006	0.05	0.023	±0.008	0.0006	0.05
Zn (mg/kg)	6.8	±0.7	0.5	0.01	5.3	±0.7	0.5	0.01	5.9	±0.7	0.5	0.01
Co (mg/kg)	1.01	±0.2	0.04	0.04	0.6	±0.2	0.04	0.04	0.8	±0.2	0.04	0.04
Cd (mg/kg)	1.4	±0.2	0.02	0.04	1.08	±0.2	0.02	0.04	1.2	±0.2	0.02	0.04
Fe (mg/kg)	5.1	±0.6	0.4	0.04	3.87	±0.6	0.4	0.04	4.6	±0.6	0.4	0.04
Hg (mg/kg)	N.D	-	-	-	N.D	-	-	-	N.D	-	-	-

Appendix 1.4 Physico-chemical analysis of post-rain soil samples collected from Gujranwala

Parameters	Locations											
	GA1				GA2				GA3			
	Mean	St. Dev.	Variance	P-value	Mean	St. Dev.	Variance	P-value	Mean	St. Dev.	Variance	P-value
pH	7.7	±0.2	0.02	0.02	7.8	±0.2	0.02	0.02	7.5	±0.2	0.02	0.02
TDS (mg/kg)	2029	±244	713	0.05	1794	±244	713	0.05	1496	±244	713	0.05
TOC((% age)	3.5	±0.2	0.04	0.01	3.2	±0.2	0.04	0.01	3.1	±0.2	0.04	0.01
Sodium (mg/kg)	29	±3	13	0.05	23	±3	13	0.05	25	±3	13	0.05
Potassium (mg/kg)	20	±2	4	0.05	16	±2	4	0.05	15	±2	4	0.05
Nitrogen (mg/kg)	39	±1	2	0.02	37	±1	2	0.02	36	±1	2	0.02
Cr (mg/kg)	1.4	±0.06	0.004	0.04	1.28	±0.06	0.004	0.04	1.31	±0.06	0.004	0.04
Cu (mg/kg)	2.2	±0.2	0.05	0.04	1.78	±0.2	0.05	0.04	1.93	±0.2	0.05	0.04
Ni (mg/kg)	1.24	±0.07	0.006	0.04	1.17	±0.07	0.006	0.04	1.09	±0.07	0.006	0.04
As (mg/kg)	N.D	-	-	-	N.D	-	-	-	N.D	-	-	-
Pb (mg/kg)	0.0091	±0.002	0.0005	0.05	0.0062	±0.002	0.0005	0.05	0.004	±0.002	0.0005	0.05
Zn (mg/kg)	4.8	±0.7	0.4	0.02	3.5	±0.7	0.4	0.02	3.9	±0.7	0.4	0.02
Co (mg/kg)	0.4	±0.1	0.01	0.04	0.2	±0.1	0.01	0.04	0.3	±0.1	0.01	0.04
Cd (mg/kg)	0.74	±0.2	0.05	0.04	0.52	±0.2	0.05	0.04	0.29	±0.2	0.05	0.04
Fe (mg/kg)	4.7	±0.7	0.5	0.05	3.96	±0.7	0.5	0.05	2.99	±0.7	0.5	0.05
Hg (mg/kg)	N.D	-	-	-	N.D	-	-	-	N.D	-	-	-

Appendix 1.4 Physico-chemical analysis of post-rain soil samples collected from Gujranwala

Parameters	Locations											
	GB1				GB2				GB3			
	Mean	St. Dev.	Variance	P-value	Mean	St. Dev.	Variance	P-value	Mean	St. Dev.	Variance	P-value
pH	7.65	±0.2	0.03	0.04	8	±0.2	0.03	0.04	7.9	±0.2	0.03	0.04
TDS (mg/kg)	2210	±248	590	0.05	1726	±248	590	0.05	1907	±248	590	0.05
TOC(% age)	3.3	±0.4	0.2	0.05	2.8	±0.4	0.2	0.05	2.5	±0.4	0.2	0.05
Sodium (mg/kg)	32	±3	7	0.03	27	±3	7	0.03	28	±3	7	0.03
Potassium (mg/kg)	21	±2	4	0.01	17	±2	4	0.01	18	±2	4	0.01
Nitrogen (mg/kg)	35	±2	4	0.02	33	±2	4	0.02	31	±2	4	0.02
Cr (mg/kg)	1.6	±0.1	0.02	0.05	1.5	±0.1	0.02	0.05	1.33	±0.1	0.02	0.05
Cu (mg/kg)	2.5	±0.2	0.05	0.05	2.04	±0.2	0.05	0.05	2.3	±0.2	0.05	0.05
Ni (mg/kg)	1.3	±0.1	0.2	0.05	1.1	±0.1	0.2	0.05	1.02	±0.1	0.2	0.05
As (mg/kg)	N.D	-	-	-	N.D	-	-	-	N.D	-	-	-
Pb (mg/kg)	0.022	±0.003	0.00006	0.05	0.019	±0.003	0.00006	0.05	0.015	±0.003	0.00006	0.05
Zn (mg/kg)	4.5	±0.4	0.2	0.01	3.6	±0.4	0.2	0.01	4.1	±0.4	0.2	0.01
Co (mg/kg)	0.54	±0.2	0.02	0.04	0.23	±0.2	0.02	0.04	0.32	±0.2	0.02	0.04
Cd (mg/kg)	1.01	±0.1	0.01	0.04	0.8	±0.1	0.01	0.04	0.9	±0.1	0.01	0.04
Fe (mg/kg)	3.6	±0.7	0.4	0.04	2.2	±0.7	0.4	0.04	3.05	±0.7	0.4	0.04
Hg (mg/kg)	N.D	-	-	-	N.D	-	-	-	N.D	-	-	-

Appendix 2 Physico-Chemical Analysis of Water Samples Collected from Gujranwala & Sialkot

Appendix 2.1 Physico-chemical analysis of pre-rain water samples collected from Sialkot

Parameters	Locations												WHO Limits
	SA1				SA2				SA3				
	Mean	St. Dev.	Variance	P-value	Mean	St. Dev.	Variance	P-value	Mean	St. Dev.	Variance	P-value	
pH	8.22	±0.38	0.15	0.03	8.51	±0.38	0.15	0.03	8.61	±0.38	0.15	0.03	6.5-8.5
TDS (mg/L)	120	±5	25	0.005	125	±5	25	0.005	115	±5	25	0.005	<1000
EC mS/m^3	240	±10	50	0.005	250	±10	50	0.005	230	±10	50	0.005	N/A
Hardness (mg/L)	68	±6	41	0.04	70	±6	41	0.04	58	±6	41	0.04	< 500
Color (TCU)	2	±1	1	0.01	1	±1	1	0.01	3	±1	1	0.01	<1500
Odor	N.O	-	-	-	N.O	-	-	-	N.O	-	-	-	-
Taste	N.O	-	-	-	N.O	-	-	-	N.O	-	-	-	-
Turbidity (NTU)	1	±1	1	0.01	1	±1	1	0.01	2	±1	1	0.01	<5 NTU
Nitrates (mg/L)	2	±0.5	0.4	0.00001	2.1	±0.5	0.4	0.00001	0.9	±0.5	0.4	0.00001	50
Sulfates (mg/L)	19	±4	12	0.02	26	±4	12	0.02	23	±4	12	0.02	250
Chlorides (mg/L)	19	±1	1	0.04	20	±1	1	0.04	18	±1	1	0.04	250
Phosphates (mg/L)	0.3	±0.02	0.0002	0.0008	0.33	±0.02	0.0002	0.0008	0.32	±0.02	0.0002	0.0008	-
Cr (mg/L)	0.1	±0.07	0.003	0.00004	0.2	±0.07	0.003	0.00004	0.11	±0.07	0.003	0.00004	0.05
Cu (mg/L)	2.8	±0.3	0.13	0.04	2.3	±0.3	0.13	0.04	2.1	±0.3	0.13	0.04	2
Ni (mg/L)	0.02	±0.007	0.0001	0.00001	0.01	±0.007	0.0001	0.00001	0.03	±0.007	0.0001	0.00001	0.02
As (mg/L)	N.D	-	-	-	N.D	-	-	-	N.D	-	-	-	0.01
Pb (mg/L)	0.003	±0.001	0.0001	0.01	0.002	±0.001	0.0001	0.01	0.004	±0.001	0.0001	0.01	0.01
Zn (mg/L)	2.22	±0.09	0.01	0.03	2.12	±0.09	0.01	0.03	2.03	±0.09	0.01	0.03	3
Co (mg/L)	0.1	±0.1	0.0002	0.03	0.09	±0.1	0.0002	0.03	0.07	±0.1	0.0002	0.03	-
Cd (mg/L)	0.12	±0.1	0.01	0.01	0.31	±0.1	0.01	0.01	0.28	±0.1	0.01	0.01	0.003
Fe (mg/L)	0.1	±0.05	0.002	0.0005	0.15	±0.05	0.002	0.0005	0.2	±0.05	0.002	0.0005	0.3
Hg (mg/L)	N.D	-	-	-	N.D	-	-	-	N.D	-	-	-	0.001

Appendix 2.1 Physico-chemical analysis of pre-rain water samples collected from Sialkot

Parameters	Locations												WHO Limits
	SB1				SB2				SB3				
	Mean	St. Dev.	Variance	P-value	Mean	St. Dev.	Variance	P-value	Mean	St. Dev.	Variance	P-value	
pH	7.61	±0.38	0.15	0.03	7.95	±0.38	0.15	0.03	7.92	±0.38	0.15	0.03	6.5-8.5
TDS (mg/L)	385	±13	170	0.04	370	±13	170	0.04	359	±13	170	0.04	<1000
EC mS/m^3	770	±26	340	0.04	740	±26	340	0.04	718	±26	340	0.04	N/A
Hardness (mg/L)	104	±4	17	0.05	98	±4	17	0.05	96	±4	17	0.05	< 500
Color (TCU)	4	±2	3	0.02	1	±2	3	0.02	1	±2	3	0.02	<1500
Odor	N.O	-	-	-	N.O	-	-	-	N.O	-	-	-	-
Taste	N.O	-	-	-	N.O	-	-	-	N.O	-	-	-	-
Turbidity (NTU)	2	±0.6	0.3	0.01	2	±0.6	0.3	0.01	3	±0.6	0.3	0.01	<5 NTU
Nitrates (mg/L)	1	±2	4	0.00001	4.9	±2	4	0.00001	2.8	±2	4	0.00001	50
Sulfates (mg/L)	49	±4	14	0.04	50	±4	14	0.04	43	±4	14	0.04	250
Chlorides (mg/L)	52	±2	4	0.05	49	±2	4	0.05	48	±2	4	0.05	250
Phosphates (mg/L)	1.1	±0.16	0.02	0.05	0.9	±0.16	0.02	0.05	0.8	±0.16	0.02	0.05	-
Cr (mg/L)	0.08	±0.2	0.00003	0.00002	0.075	±0.2	0.00003	0.00002	0.07	±0.2	0.00003	0.00002	0.05
Cu (mg/L)	2.5	±0.2	0.5	0.05	2.04	±0.2	0.5	0.05	1.5	±0.2	0.5	0.05	2
Ni (mg/L)	0.7	±0.4	0.01	0.05	0.6	±0.4	0.01	0.05	0.5	±0.4	0.01	0.05	0.02
As (mg/L)	N.D	-	-	-	N.D	-	-	-	N.D	-	-	-	0.01
Pb (mg/L)	0.007	±0.003	0.0001	0.01	0.005	±0.003	0.0001	0.01	0.006	±0.003	0.0001	0.01	0.01
Zn (mg/L)	2.01	±0.05	0.2	0.02	2.04	±0.05	0.2	0.02	1.21	±0.05	0.2	0.02	3
Co (mg/L)	0.9	±0.5	0.06	0.04	0.6	±0.5	0.06	0.04	0.4	±0.5	0.06	0.04	-
Cd (mg/L)	0.4	±0.04	0.002	0.01	0.33	±0.04	0.002	0.01	0.47	±0.04	0.002	0.01	0.003
Fe (mg/L)	0.8	±0.4	0.06	0.006	0.6	±0.4	0.06	0.006	0.3	±0.4	0.06	0.006	0.3
Hg (mg/L)	N.D	-	-	-	N.D	-	-	-	N.D	-	-	-	0.001

Appendix 2.2 Physico-chemical analysis of post-rain water samples collected from Sialkot

Parameters	Locations												WHO Limits
	SA1				SA2				SA3				
	Mean	St. Dev.	Variance	P-value	Mean	St. Dev.	Variance	P-value	Mean	St. Dev.	Variance	P-value	
pH	8	±0.27	0.07	0.03	7.7	±0.27	0.07	0.03	7.9	±0.27	0.07	0.03	6.5-8.5
TDS (mg/L)	142	±8	64	0.005	150	±8	64	0.005	158	±8	64	0.005	<1000
EC mS/m^3	284	±16	128	0.005	300	±16	128	0.005	316	±16	128	0.005	N/A
Hardness (mg/L)	75	±6	43	0.04	80	±6	43	0.04	88	±6	43	0.04	< 500
Color (TCU)	1	0	0	0.01	1	0	0	0.01	1	0	0	0.01	<1500
Odor	N.O	-	-	-	N.O	-	-	-	N.O	-	-	-	-
Taste	N.O	-	-	-	N.O	-	-	-	N.O	-	-	-	-
Turbidity (NTU)	1	±0.5	0.3	0.01	1	±0.5	0.3	0.01	3	±0.5	0.3	0.01	<5 NTU
Nitrates (mg/L)	22	±2	4	0.00001	19	±2	4	0.00001	18	±2	4	0.00001	50
Sulfates (mg/L)	43	±10	94	0.02	56	±10	94	0.02	37	±10	94	0.02	250
Chlorides (mg/L)	22	±2	4	0.04	27	±2	4	0.04	21	±2	4	0.04	250
Phosphates (mg/L)	0.88	±0.05	0.0002	0.0008	0.81	±0.05	0.0002	0.0008	0.78	±0.0.05	0.0002	0.0008	-
Cr (mg/L)	1.02	±0.05	0.003	0.00004	1.1	±0.05	0.003	0.00004	0.99	±0.05	0.003	0.00004	0.05
Cu (mg/L)	3.9	±0.3	0.2	0.004	3.5	±0.3	0.2	0.004	2.9	±0.3	0.2	0.004	2
Ni (mg/L)	0.56	±0.03	0.001	0.00001	0.51	±0.03	0.001	0.00001	0.57	±0.03	0.001	0.00001	0.02
As (mg/L)	N.D	-	-	-	N.D	-	-	-	N.D	-	-	-	0.01
Pb (mg/L)	0.007	±0.007	0.0001	0.01	0.006	±0.007	0.0001	0.01	0.008	±0.007	0.0001	0.01	0.01
Zn (mg/L)	4.3	±0.8	0.5	0.03	3.2	±0.8	0.5	0.03	2.87	±0.8	0.5	0.03	3
Co (mg/L)	0.12	±0.007	0.00001	0.03	0.13	±0.007	0.00001	0.03	0.11	±0.007	0.00001	0.03	-
Cd (mg/L)	0.51	±0.04	0.002	0.01	0.57	±0.04	0.002	0.01	0.49	±0.04	0.002	0.01	0.003
Fe (mg/L)	1.12	±0.1	0.04	0.0005	1.3	±0.1	0.04	0.0005	1.5	±0.1	0.04	0.0005	0.3
Hg (mg/L)	N.D	-	-	-	N.D	-	-	-	N.D	-	-	-	0.001

Appendix 2.2 Physico-chemical analysis of post-rain water samples collected from Sialkot

Parameters	Locations												WHO Limits
	SB1				SB2				SB3				
	Mean	St. Dev.	Variance	P-value	Mean	St. Dev.	Variance	P-value	Mean	St. Dev.	Variance	P-value	
pH	7.3	±0.27	0.07	0.03	7.4	±0.27	0.07	0.03	7.7	±0.27	0.07	0.03	6.5-8.5
TDS (mg/L)	576	±15	220	0.04	457	±15	220	0.04	367	±15	220	0.04	<1000
EC mS/m^3	1152	±30	440	0.04	914	±30	440	0.04	734	±30	440	0.04	N/A
Hardness (mg/L)	118	±6	39	0.05	109	±6	39	0.05	106	±6	39	0.05	< 500
Color (TCU)	7	±3	12	0.02	1	±3	12	0.02	1	±3	12	0.02	<1500
Odor	N.O	-	-	-	N.O	-	-	-	N.O	-	-	-	-
Taste	N.O	-	-	-	N.O	-	-	-	N.O	-	-	-	-
Turbidity (NTU)	4	±1	1	0.01	2	±1	1	0.01	2	±1	1	0.01	<5 NTU
Nitrates (mg/L)	24	±2	3	0.00001	27	±2	3	0.00001	24	±2	3	0.00001	50
Sulfates (mg/L)	55	±3	6	0.04	57	±3	6	0.04	52	±3	6	0.04	250
Chlorides (mg/L)	56	±2	4	0.05	54	±2	4	0.05	52	±2	4	0.05	250
Phosphates (mg/L)	0.8	±0.08	0.007	0.05	0.7	±0.08	0.007	0.05	0.65	±0.08	0.007	0.05	-
Cr (mg/L)	0.89	±0.1	0.003	0.00002	0.79	±0.1	0.003	0.00002	0.81	±0.1	0.003	0.00002	0.05
Cu (mg/L)	3.8	±0.5	0.3	0.05	2.9	±0.5	0.3	0.05	2.7	±0.5	0.3	0.05	2
Ni (mg/L)	1.6	±0.5	0.13	0.05	0.99	±0.5	0.13	0.05	0.94	±0.5	0.13	0.05	0.02
As (mg/L)	N.D	-	-	-	N.D	-	-	-	N.D	-	-	-	0.01
Pb (mg/L)	0.012	±0.002	0.0002	0.01	0.009	±0.002	0.0002	0.01	0.01	±0.002	0.0002	0.01	0.01
Zn (mg/L)	3.31	±0.2	0.1	0.02	3.05	±0.2	0.1	0.02	2.57	±0.2	0.1	0.02	3
Co (mg/L)	1.02	±0.5	0.01	0.04	1.03	±0.5	0.01	0.04	1.2	±0.5	0.01	0.04	-
Cd (mg/L)	0.54	±0.02	0.001	0.03	0.51	±0.02	0.001	0.03	0.56	±0.02	0.001	0.03	0.003
Fe (mg/L)	2.4	±0.4	0.15	0.006	2	±0.4	0.15	0.006	1.6	±0.4	0.15	0.006	0.3
Hg (mg/L)	N.D	-	-	-	N.D	-	-	-	N.D	-	-	-	0.001

Appendix 2.3 Physico-chemical analysis of pre-rain water samples collected from Gujranwala

Parameters	Locations												WHO Limits
	GA1				GA2				GA3				
	Mean	St. Dev.	Variance	P-value	Mean	St. Dev.	Variance	P-value	Mean	St. Dev.	Variance	P-value	
pH	8.62	±0.16	0.03	0.03	8.41	±0.16	0.03	0.03	8.71	±0.16	0.03	0.03	6.5-8.5
TDS (mg/L)	489	±15	244	0.05	470	±15	244	0.05	501	±15	244	0.05	<1000
EC mS/m^3	978	±30	488	0.05	940	±30	488	0.05	1002	±30	488	0.05	N/A
Hardness (mg/L)	88	±8	64	0.03	79	±8	64	0.03	96	±8	64	0.03	< 500
Color (TCU)	5	±2	2	0.02	3	±2	2	0.02	2	±2	2	0.02	<1500
Odor	N.O	-	-	-	N.O	-	-	-	N.O	-	-	-	-
Taste	N.O	-	-	-	N.O	-	-	-	N.O	-	-	-	-
Turbidity (NTU)	3	±2	4	0.03	2	±2	4	0.03	6	±2	4	0.03	<5 NTU
Nitrates (mg/L)	3.1	±2	4	0.00006	1	±2	4	0.0006	5.1	±2	4	0.00006	50
Sulfates (mg/L)	38	±6	32	0.0005	27	±6	32	0.0005	30	±6	32	0.0005	250
Chlorides (mg/L)	70	±4	16	0.004	62	±4	16	0.004	66	±4	16	0.004	250
Phosphates (mg/L)	1.1	±0.14	0.06	0.03	1.3	±0.14	0.06	0.03	1.6	±0.14	0.06	0.03	-
Cr (mg/L)	0.08	±0.5	0.001	0.00002	0.02	±0.5	0.001	0.00002	0.03	±0.5	0.001	0.00002	0.05
Cu (mg/L)	2.1	±0.1	0.2	0.01	2.3	±0.1	0.2	0.01	2.9	±0.1	0.2	0.01	2
Ni (mg/L)	0.56	±0.03	0.001	0.05	0.51	±0.03	0.001	0.05	0.57	±0.03	0.001	0.05	0.02
As (mg/L)	N.D	-	-	-	N.D	-	-	-	N.D	-	-	-	0.01
Pb (mg/L)	0.004	±0.001	0.0001	0.007	0.003	±0.001	0.0001	0.007	0.005	±0.001	0.0001	0.007	0.01
Zn (mg/L)	2.05	±0.2	0.04	0.03	1.83	±0.2	0.04	0.03	2.23	±0.2	0.04	0.03	3
Co (mg/L)	0.8	±0.1	0.02	0.01	0.6	±0.1	0.02	0.01	0.5	±0.1	0.02	0.01	-
Cd (mg/L)	0.08	±0.02	0.0006	0.004	0.02	±0.02	0.0006	0.004	0.05	±0.02	0.0006	0.004	0.003
Fe (mg/L)	1.01	±0.5	0.2	0.04	0.2	±0.5	0.2	0.04	1.03	±0.5	0.2	0.04	0.3
Hg (mg/L)	N.D	-	-	-	N.D	-	-	-	N.D	-	-	-	0.001

Appendix 2.3 Physico-chemical analysis of pre-rain water samples collected from Gujranwala

Parameters	Locations												WHO Limits
	GB1				GB2				GB3				
	Mean	St. Dev.	Variance	P-value	Mean	St. Dev.	Variance	P-value	Mean	St. Dev.	Variance	P-value	
pH	8.6	±0.16	0.03	0.03	8.36	±0.16	0.03	0.03	8.48	±0.16	0.03	0.03	6.5-8.5
TDS (mg/L)	367	±11	126	0.02	345	±11	126	0.02	352	±11	126	0.02	<1000
EC mS/m^3	734	±22	152	0.02	690	±22	152	0.02	704	±22	152	0.02	N/A
Hardness (mg/L)	90	±2	4	0.003	92	±2	4	0.003	88	±2	4	0.003	< 500
Color (TCU)	2	±2	3	0.03	1	±2	3	0.03	4	±2	3	0.03	<1500
Odor	N.O	-	-	-	N.O	-	-	-	N.O	-	-	-	-
Taste	N.O	-	-	-	N.O	-	-	-	N.O	-	-	-	-
Turbidity (NTU)	4	±1	1	0.04	2	±1	1	0.04	3	±1	1	0.04	<5 NTU
Nitrates (mg/L)	2.9	±0.5	4	0.00001	3.1	±0.5	4	0.00001	2.1	±0.5	4	0.00001	50
Sulfates (mg/L)	54	±2	6	0.0001	49	±2	6	0.0001	52	±2	6	0.0001	250
Chlorides (mg/L)	30	±7	4	0.05	35	±7	4	0.05	44	±7	4	0.05	250
Phosphates (mg/L)	0.6	±0.5	0.09	0.05	0.9	±0.5	0.09	0.05	1.2	±0.5	0.09	0.05	-
Cr (mg/L)	0.05	±0.01	0.00004	0.001	0.04	±0.01	0.00004	0.001	0.01	±0.01	0.00004	0.001	0.05
Cu (mg/L)	2.86	±0.1	0.02	0.0001	2.71	±0.1	0.02	0.0001	2.6	±0.1	0.02	0.0001	2
Ni (mg/L)	0.55	±0.01	0.0001	0.00001	0.54	±0.01	0.0001	0.00001	0.58	±0.01	0.0001	0.00001	0.02
As (mg/L)	N.D	-	-	-	N.D	-	-	-	N.D	-	-	-	0.01
Pb (mg/L)	0.006	±0.002	0.0007	0.05	0.002	±0.002	0.0007	0.05	0.001	±0.002	0.0007	0.006	0.01
Zn (mg/L)	1.23	±0.5	0.01	0.001	1.21	±0.5	0.01	0.001	1.01	±0.5	0.01	1.23	3
Co (mg/L)	0.7	±0.1	0.02	0.05	1	±0.1	0.02	0.05	0.8	±0.1	0.02	0.7	-
Cd (mg/L)	0.4	±0.02	0.02	0.05	0.21	±0.02	0.02	0.05	0.1	±0.02	0.02	0.4	0.003
Fe (mg/L)	0.91	±0.4	0.2	0.04	0.15	±0.4	0.2	0.04	0.11	±0.4	0.2	0.04	0.3
Hg (mg/L)	N.D	-	-	-	N.D	-	-	-	N.D	-	-	-	0.001

Appendix 2.4 Physico-chemical analysis of post-rain water samples collected from Gujranwala

Parameters	Locations												WHO Limits
	GA1				GA2				GA3				
	Mean	St. Dev.	Variance	P-value	Mean	St. Dev.	Variance	P-value	Mean	St. Dev.	Variance	P-value	
pH	8.4	±0.38	0.1	0.03	7.9	±0.38	0.1	0.03	8.43	±0.38	0.1	0.03	6.5-8.5
TDS (mg/L)	550	±30	903	0.05	505	±30	903	0.05	562	±30	903	0.05	<1000
EC mS/m^3	1100	±60	1806	0.05	1010	±60	1806	0.05	1152	±60	1806	0.05	N/A
Hardness (mg/L)	110	±8	57	0.03	101	±8	57	0.03	116	±8	57	0.03	< 500
Color (TCU)	3	0	0	0.02	3	0	0	0.02	3	0	0	0.02	<1500
Odor	N.O	-	-	-	N.O	-	-	-	N.O	-	-	-	-
Taste	N.O	-	-	-	N.O	-	-	-	N.O	-	-	-	-
Turbidity (NTU)	8	±1	1	0.03	7	±1	1	0.03	9	±1	1	0.03	<5 NTU
Nitrates (mg/L)	31	±2	2	0.00006	28	±2	2	0.00006	29	±2	2	0.00006	50
Sulfates (mg/L)	88	±8	39	0.0005	76	±8	39	0.0005	79	±8	39	0.0005	250
Chlorides (mg/L)	82	±2	2	0.004	79	±2	2	0.004	80	±2	2	0.004	250
Phosphates (mg/L)	1.8	±0.14	0.13	0.03	2	±0.14	0.13	0.03	2.5	±0.14	0.13	0.03	-
Cr (mg/L)	0.83	±0.2	0.002	0.00002	0.8	±0.2	0.002	0.00002	0.89	±0.2	0.002	0.00002	0.05
Cu (mg/L)	3.9	±0.3	0.1	0.01	3.5	±0.3	0.1	0.01	4.1	±0.3	0.1	0.01	2
Ni (mg/L)	0.6	±0.01	0.002	0.05	0.62	±0.01	0.002	0.05	0.69	±0.01	0.002	0.05	0.02
As (mg/L)	N.D	-	-	-	N.D	-	-	-	N.D	-	-	-	0.01
Pb (mg/L)	0.0085	±0.006	0.0002	0.007	0.007	±0.006	0.0002	0.007	0.008	±0.006	0.0002	0.007	0.01
Zn (mg/L)	3.17	±0.5	0.1	0.03	2.25	±0.5	0.1	0.03	2.73	±0.5	0.1	0.03	3
Co (mg/L)	1.08	±0.04	0.001	0.01	1.02	±0.04	0.001	0.01	1.03	±0.04	0.001	0.01	-
Cd (mg/L)	0.5	±0.05	0.01	0.004	0.45	±0.05	0.01	0.004	0.32	±0.05	0.01	0.004	0.003
Fe (mg/L)	2.23	±0.6	0.2	0.04	1.4	±0.6	0.2	0.04	2.29	±0.6	0.2	0.04	0.3
Hg (mg/L)	N.D	-	-	-	N.D	-	-	-	N.D	-	-	-	0.001

Appendix 2.4 Physico-chemical analysis of post-rain water samples collected from Gujranwala

Parameters	Locations												WHO Limits
	GB1				GB2				GB3				
	Mean	St. Dev.	Variance	P-value	Mean	St. Dev.	Variance	P-value	Mean	St. Dev.	Variance	P-value	
pH	8	±0.38	0.1	0.03	7.8	±0.38	0.1	0.03	7.9	±0.38	0.1	0.03	6.5-8.5
TDS (mg/L)	390	±7	49	0.02	376	±7	49	0.02	387	±7	49	0.02	<1000
EC mS/m^3	780	±14	98	0.02	752	±14	98	0.02	774	±14	98	0.02	N/A
Hardness (mg/L)	120	±8	60	0.003	124	±8	60	0.003	109	±8	60	0.003	< 500
Color (TCU)	2	±2	2	0.03	2	±2	2	0.03	5	±2	2	0.03	<1500
Odor	N.O	-	-	-	N.O	-	-	-	N.O	-	-	-	-
Taste	N.O	-	-	-	N.O	-	-	-	N.O	-	-	-	-
Turbidity (NTU)	7	±2	4	0.04	6	±2	4	0.04	3	±2	4	0.04	<5 NTU
Nitrates (mg/L)	36	±4	2	0.00001	34	±4	2	0.00001	32	±4	2	0.00001	50
Sulfates (mg/L)	84	±2	4	0.0001	81	±2	4	0.0001	80	±2	4	0.0001	250
Chlorides (mg/L)	43	±2	16	0.05	48	±2	16	0.05	51	±2	16	0.05	250
Phosphates (mg/L)	1.2	±0.6	0.12	0.05	1.7	±0.6	0.12	0.05	1.9	±0.6	0.12	0.05	-
Cr (mg/L)	0.9	±0.02	0.02	0.001	0.83	±0.02	0.02	0.001	0.6	±0.02	0.02	0.001	0.05
Cu (mg/L)	4	±0.07	0.004	0.0001	3.96	±0.07	0.004	0.0001	3.87	±0.07	0.004	0.0001	2
Ni (mg/L)	0.94	±0.12	0.005	0.001	0.81	±0.12	0.005	0.001	0.93	±0.12	0.005	0.001	0.02
As (mg/L)	N.D	-	-	-	N.D	-	-	-	N.D	-	-	-	0.01
Pb (mg/L)	0.01	±0.002	0.0001	0.05	0.005	±0.002	0.0001	0.05	0.003	±0.002	0.0001	0.05	0.01
Zn (mg/L)	2.35	±0.3	0.03	0.001	2.1	±0.3	0.03	0.001	2	±0.3	0.03	0.001	3
Co (mg/L)	1.08	±0.04	0.001	0.05	1.05	±0.04	0.001	0.05	1.13	±0.04	0.001	0.05	-
Cd (mg/L)	0.47	±0.03	0.01	0.05	0.31	±0.03	0.01	0.05	0.3	±0.03	0.01	0.05	0.003
Fe (mg/L)	1.97	±0.2	0.003	0.004	1.89	±0.2	0.003	0.004	1.87	±0.2	0.003	0.004	0.3
Hg (mg/L)	N.D	-	-	-	N.D	-	-	-	N.D	-	-	-	0.001

SA = Sialkot Dumping Site A   SB = Sialkot Dumping Site B   GA = Gujranwala Dumping Site A   GB = Gujranwala Dumping Site B
SA1 = First Sampling Location at SA   SA2 = Second Sampling Location at SA   SA3 = Third Sampling Location at SA
SB1 = First Sampling Location at SB   SB2 = Second Sampling Location at SB   SB3 = Third Sampling Location at SB
GA1 = First Sampling Location at GA   GA2 = Second Sampling Location at GA   GA3 = Third Sampling Location at GA
GB1 = First Sampling Location at GB   GB2 = Second Sampling Location at GB   GB3 = Third Sampling Location at GB
N.O. = Non Objectionable   N.D. = Not Detected

Appendix 3 National Environmental Quality Standards of Pakistan for Drinking Water

PROPERTIES/PARAMETERS	STANDARD VALUES FOR PAKISTAN	WHO GUIDELINES	REMARKS
Physical			
Colour	≤15 TCU	≤15 TCU	
Taste	Non objectionable/Acceptable	Non objectionable/Acceptable	
Odour	Non objectionable/Acceptable	Non objectionable/Acceptable	
Turbidity	<5 NTU	<5 NTU	
Total hardness as $CaCO_3$	< 500 mg/l	--	
TDS	< 1000	< 1000	
pH	6.5 – 8.5	6.5 – 8.5	
Chemical			
Essential Inorganic	***mg/Litre***	***mg/Litre***	
Aluminium (Al) mg/l	<0.2	0.2	
Antimony (Sb)	<0.005 (P)	0.02	
Arsenic (As)	< 0.05 (P)	0.01	Standard for Pakistan similar to most Asian developing countries
Barium (Ba)	0.7	0.7	
Boron (B)	0.3	0.3	
Cadmium (Cd)	0.01	0.003	Standard for Pakistan similar to most Asian developing countries
Chloride (Cl)	<250	250	
Chromium (Cr)	<0.05	0.05	
Copper (Cu)	2	2	
Toxic Inorganic	***mg/Litre***	***mg/Litre***	
Cyanide (CN)	<0.05	0.07	Standard for Pakistan similar to most Asian developing countries

Appendix 3 National Environmental Quality Standards of Pakistan for Drinking Water

PROPERTIES/PARAMETERS	STANDARD VALUES FOR PAKISTAN	WHO GUIDELINES	REMARKS
Fluoride (F)*	<1.5	1.5	
Lead (Pb)	<0.05	0.01	Standard for Pakistan similar to most Asian developing countries
Manganese (Mn)	< 0.5	0.5	
Mercury (Hg)	<0.001	0.001	
Nickel (Ni)	<0.02	0.02	
Nitrate (NO_3)*	<50	50	
Nitrite (NO_2)*	<3 (P)	3	
Selenium (Se)	0.01(P)	0.01	
Residual chlorine	0.2-0.5 at consumer end 0.5-1.5 at source		
Zinc (Zn)	5.0	3	Standard for Pakistan similar to most Asian developing countries

* indicates priority health related inorganic constituents which need regular monitoring.

Appendix 4 Description of dumping sites

Sr. No.	Site Location	Site Code	Area	Site Age (years)
1	Tannery area at bank of Upper Chenab Canal, Sambrial	S.A	2 km (length)	7
2	Ganda Nallah near Girls Collage Daska roads Sambrial	S.B	1.5 km (length)	5
3	Shaheen Abad GT road Gujranwala	G.A	2 (Acres)	15
4	People Colony Interpass, Haidry Road Gujranwala	G.B	8 (Acres)	19