ASSESSMENT OF SELECTED TOXIC HEAVY METALS IN INDUSTRIAL EFFLUENTS AND DRINKING WATER AND THEIR EFFECTS ON THE VEGETATION AND NUTRITIONAL STATUS OF PESHAWAR

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INSTITUTE OF CHEMICAL SCIENCES
UNIVERSITY OF PESHAWAR

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By

FAZAL AKBAR JAN

A Thesis Submitted to the University of Peshawar in Partial Fulfillment of the Requirements for the Degree of

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It is recommended that the Thesis prepared by Fazal Akbar Jan entitled "ASSESSMENT OF SELECTED TOXIC HEAVY METALS IN INDUSTRIAL EFFLUENTS AND DRINKING WATER AND THEIR EFFECTS ON THE VEGETATION AND NUTRITIONAL STATUS OF PESHAWAR" ***be accepted as fulfilling this part of the requirements for the Degree of "DOCTOR OF PHILOSOPHY IN CHEMISTRY"***

Approved By

Supervisor	:	________________________
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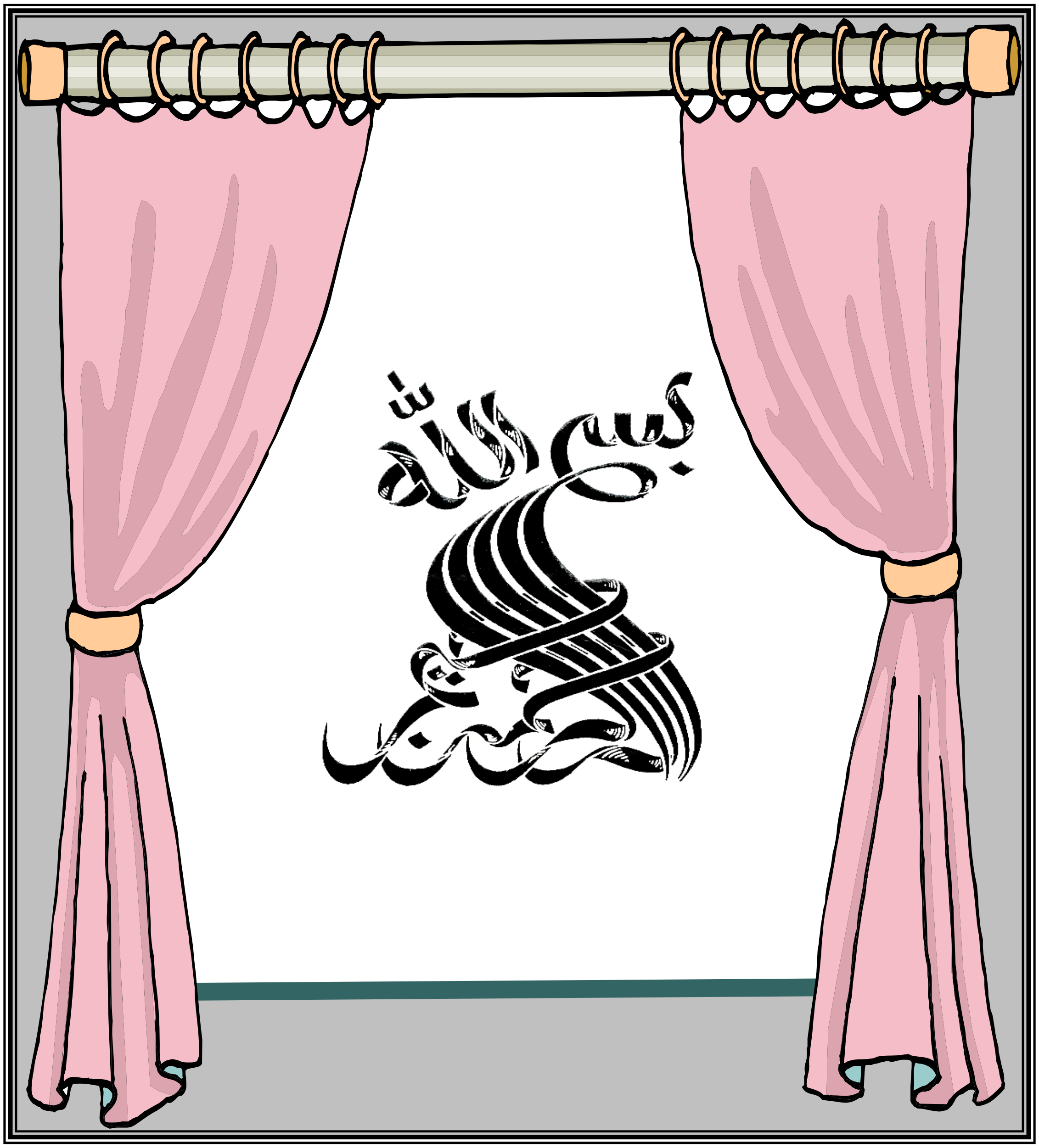

IN THE NAME OF ALMIGHTY ALLAH,
THE MOST BENEFICENT,
THE MOST MERCIFUL

Dedicated to my parents, brothers and to those whom prayers enabled me to do this job

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

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SUMMARY

The purpose of the present study was to find out the points sources of mercury and arsenic pollution of drinking and irrigation water, their downstream dilution in the industrialized area, Peshawar the capital of Khyber Pukhtunkhwa, Pakistan. Samples of effluents, soil and water were collected from the study area, background area and from the relatively less polluted area the district Dir lower considered as control area. Along with other physicochemical parameters determination of these samples, Hg was determined by cold vapor generation techniques while arsenic was determined by electro thermal atomic absorption technique. The data was compared with the water quality data of background area, control area, national, WHO and some international drinking water quality standards. The results showed that some parameters i.e.TDS, DO, pH and hardness were out of the permissible levels while some are within the range. Arsenic and mercury was determined in nearly all the samples, with higher concentration in the effluents. Textile industries and glass factory were found to be the majors contributing sources of Hg and As pollution. Downstream dilution of these contaminants was also observed.

Multivariate and univariate statistical techniques i.e., cluster analysis PCA, regression and correlation analysis, one way ANOVA were applied to the metal data of effluents soil and ground water to point out the contribution of different industries towards the metals pollution, their source identification and distribution. The samples were collected from different industries and different downstream points of the main effluents and from the relatively less polluted area considered as control area. The samples were analyzed for metal concentration levels by flame atomic absorption spectrophotometer. The, metal concentration data in the three media of the polluted area was compared with background data and control data as well as with the WHO safe limits. The results showed that soil has high metals concentration compared to effluents and water. The data also showed elevated levels of Mn and Pb in water that are 8.268 and 2.971mg/L respectively. Principal component analysis along with regression analysis showed that the elevated levels of metals in the effluents contaminate adjacent soil and ultimately the ground water. The other elements Co, Cd, Ni and Cu were also found to have correlation in the three media.

Food crops irrigated with wastewater are mostly contaminated with heavy metals and considered as a main pathway for human exposure. In this study, soil and food crops samples were collected from wastewater irrigated soils, background and relatively less polluted areas. Results of the sequential extraction and total metals concentrations in soils indicated that wastewater irrigation has significantly increased ($p \geq 0.001$) the bioavailable and total metal contents in wastewater irrigated soil as compared to background and control soils. Heavy metal concentrations in the food crops grown on wastewater irrigated soil were higher than those grown on background and control soils but were found within WHO/FAO permissible limits except for Zn. Health risk index values were less than 1 for both control and wastewater irrigated soils (except Mn). Finally, the food crops grown on wastewater irrigated area can cause human health risks in the study area.

This study was conducted to investigate the bioaccumulation of heavy metals in human's blood from different sources. Blood samples were collected from different age group subjects such as children (1-12 years), adolescent (12-18 years), adults (18-45 years) and old age (above 45 and 55 years for males and females, respectively) from polluted and control areas. Forage grasses, meat and milk samples were also collected from the study area. The results revealed that the contaminated forage grasses have led to increase the concentrations of metals in meat and milk. The subsequent uses of meat, milk and food crops were significantly increased the concentrations of trace metals in the human's blood. This was further supported by correlation and regression analyses of the data. Moreover, Cu, Zn and Mn concentrations were significantly higher ($p < 0.05$) in the blood samples collected from the polluted site as compared to control. Similar trends were also observed between the different age groups within the same area. Old people accumulated high concentrations of metals in their bodies as compared to the younger ones. Similarly, males accumulated higher concentrations of metals as compared to females.

The anthropometric data provides valuable information regarding the nutritional status of the people. In order to asses and compare the nutritional status of the people from Peshawar and Dir data was taken for the measurement of Body Mass index (BMI).The BMI values indicated that mostly males and females from both the areas were normal, only a few percent of the people were underweight, very less were overweight and negligible were obese. Comparing the nutritional status based on the BMI of the people the males individual from Dir were found healthier than the people from Peshawar. This healthier nature can be attributed to the strong muscular activities, including, farming, labor, etc in the area. Underweight females were also very less in percentage in Dir as compared to Peshawar which may be due to socio-economic conditions of the people. Only 2 % females in Dir were found obese which can be explained in terms of luxurious life due to large families, where work is done by the younger ones allowing the elders just for praying and supervision of the household. The data indicated that the people were of different age, height and weight. Only few dwarf cases were noticed in the individuals from both the areas.

Chapter 1

INTRODUCTION

1.1 Water pollution by industrial wastes

Water pollution is caused mainly by domestic and industrial wastes. Due to the wet nature of most of the large industries which requires water for processing and waste disposal, produces a large quantities of wastewater. Water pollution caused due to industrial wastes is far greater than domestic one. For example if we consider a tannery, for the production of one tone of hides per day that requires almost 50 m^3 of water. This amount of water is the daily water consumption of about 250 urban people at the rate of 200 liter per day. In other words 1m^3 of tannery effluent can pollute the same amount of water as by 10 m^3 of domestic waste water (1). Tanneries are considered to be the most tremendous polluting source of the water bodies. Though industrialization is inevitable yet it has caused devastating ecological, environmental and human disasters to significant magnitudes. The toxic substances present in industrial effluents not only destroy the fish life but also reduces dissolved oxygen (DO) to a level that it cannot be used for agricultural purposes, recreational activities, like swimming etc. Industrial wastes contain several toxic substances like, heavy metals (Hg, As, Pb, Cr, Mn, Ni, Co, Cu, Cd and Zn etc), toxic organic chemicals (pesticides, Polychlorinated Biphenyls (PCBs), Polyaromatic Hydrocarbons (PAHs), petrochemicals and phenolic compounds. The outbreak of "Minamata" and "Ita Itai" diseases in Japan were due to the consumption of fish and rice contaminated with mercury and Cadmium respectively (2).The pollution of the environment by toxic heavy metals has now become a global issue due to their sources, widespread distribution and effects on the ecosystems. Wastewater deteriorates the ground water quality to an extent that renders it unfit for drinking. Effluent water from industries also contain pathogens that causes communicable diseases in human including typhoid, cholera, salmonella type diseases, and non communicable diseases from occupational injuries of the workers, and those which may be caused due to the consumption of effluent irrigated food crops (3-4).

1.2 Multivariate statistical techniques for the assessment of environmental pollution

A large data set is required in order to study the geochemistry of ground water contamination by wastewater which includes the concentrations of various ions and other physicochemical parameters. The classification, modeling and interpretation of the complex data are the important steps in order to study the ground water quality. For this purpose some multivariate statistical techniques such as one way ANOVA, MNOVA, Factor Analysis like Principal Component Analysis (PCA), Cluster analysis (CA), Correlation, and linear regression analysis has been used by many researchers. One way analysis of the variance (ANOVA) is univariate techniques while multivariate analysis of the variance (MNOVA) is a multivariate technique. Techniques i.e. ANOVA and MNOVA can be used in order to compare two data sets which have more than two variables i.e metals concentrations. It finds out significant difference between two data sets. Factor analysis has been applied by most of the authors for the explanation of the hydro chemical problems pertaining to groundwater quality. Factor analysis comprised of three important stages:

i. Determination of correlation matrix which contain information about geochemical variables
ii. Extraction of eign values and eign vectors of the correlation matrix and discarding the least important ones

iii. Retaining variable in the factors and summing the elements in each variable. Generally lower eign values are discarded and high are retained for the interpretation of the results.

Cluster analysis (CA) is also a multivariate technique used to delineate the stations for bringing relationships among those factors that are responsible for the total overload of the ground water contamination. Cluster analysis classifies various points based on the variables into clusters and finds relationships between different points. The simple output for the classification of variables given by cluster analysis is in the form of dendogram. In simple words in order to know the effect of wastewater on the surrounding soil and ground water, first correlation study between metals pairs is undertaken which is further supported by Principal Components Analysis. Principal component analysis (PCA), Cluster analysis (CA), correlation and linear regression analysis evaluate the relationship between the levels of pollution in these receiving soil and aquatic media and then identify their mutual concentration dependence to their source. PCA provides a base for interpreting different cluster of metals based on their co-variation while cluster analysis provides a source identification for a given metal distribution pattern in the effluents or any other medium (5-8).

1.3 Effect of irrigation with wastewater on soil quality

Growing population, increase of irrigated areas and water over consumption has resulted in the reduction of surface and ground water and shortage of fresh water supply for agriculture use in most parts of the world. Long-term application of wastewater results in substantial build-up of heavy metals in the receiving soils. When the retention capacity of soil for heavy metals decreases due to repeated application of wastewater then, heavy metals leach into the groundwater and soil solution available for plant uptake. Anthropogenic contamination of food crops with heavy metals poses a threat to its quality and safety. Concentrations of heavy metals in soil, atmospheric deposition, climatic conditions, nature of soil and the degree of maturity of plants at the time of harvest are the major factors that affect the uptake and bioaccumulation of heavy metals in vegetables The use of wastewater and those from treatment plants have been gained a considerable attention in the recent years to be used as a source of irrigation. Due to the potential benefit it offers over its costly treatment process, nutrient rich nature for plant growth, wastewater is used as a source of irrigation worldwide. The plentitude of nutrients in the wastewater reduces the requirements of inorganic fertilizers and also increases crop production (9). Soil acts as vital source for sustaining basic human needs and providing a quality food supply and a livable environment and also serves as a sink and recycling factory for liquid and solid substances (10). Soil irrigated with wastewater accumulate substantial amount of organic pollutants and heavy metals. The anthropogenic activities i.e. the use of fertilizers, manure, pesticides, fungicides, herbicides, that are used to improve crop production, organic chemicals ,radioactive substances and acids facilitates the accumulation of undesirable substances in plants and effect the quality of soil adversely. Excessive use of fertilizers for increasing the crop yield is dangerous because it not only contain major essential elements necessary for plant nutrients but also contain small amount of trace elements such as Cd, As, Pb, Hg, Ni and Cr and is therefore considered as a possible source of soil contamination with heavy metals (11). Several studies revealed that the presence of toxic heavy metals reduces soil fertility and results in the reduction of crop yield. Heavy metals are non biodegradable and can accumulate in the environment to a considerable extent.

1.4 Effect of waste water irrigation on food crops

Vegetables contain proteins, vitamins and essential metals and forming an important part of the diet as well as act as buffering agents for acidic products formed during the digestion process. However the plants contain a range of concentrations of both essential and toxic elements (12). Wastewater is mostly used for the irrigation of crops in the urban environment due to freshwater shortage generally, wastewater irrigation is responsible for soil contamination with heavy metals which further lead to contaminate the food crops. It is a fact that heavy metals have adverse impact on soil ecosystem and lead to numerous human health risks because of the absence of proper excretion from the body and their toxicity. The heavy metals uptake in high concentrations by food crops can cause serious health problems for consumers. Human health exposure to metals occurs as a result of the consumption of contaminated food crops and inhalation of contaminated dust particles. Typically, heavy metals excessively concentrate in the leafy vegetables as compared to other food crops. A number of factors such as climate, atmospheric deposition, the concentrations of heavy metals in soil, the nature of soil on which vegetables are grown and the degree of maturity of plant affect concentration of heavy metals in vegetables (13, 14).

1.5 Speciation of bioavailable metals in the soil

The determination of the total metal contents in any medium is not sufficient to evaluate environmental impacts because their mobilization capacity and their behavior in a given medium are equally important which depends upon their chemical form (15). Chemical speciation is the identification and quantification of different forms and phases in which a particular specie is present in the medium. Speciation includes sequential extraction which determines the different form of a species present in any medium. Different schemes have been developed for the sequential extraction in the recent decades. But some of them were reported with the difficulty due to the lack of phase , selectivity, redistribution of analytes between phases, and variability between operators etc but the scheme developed by Tassier et al(16) is the most widely applicable and in use in majority of the metals study in the soil. This scheme generally comprises of four steps.

Step-1: Exchangeable fraction and those associated with carbonate phases: In this fraction the metals are absorbed into the clays, iron-manganese hydroxides and humic acids. Usually this fraction represent the high bioavailability of the metal since the metals adsorption depends upon changes in ionic composition of water which in turn affect the adsorption-desorption and mobility of metals on the ground.

Step-2: Reducible fraction or those associated with the Fe and Mn oxides: In this fraction the Fe and Mn oxides acts cement and are present as a nodules between the particles or cover the particles. This is the second fraction which increases the mobility of metals on the ground because the under anoxic condition the metal could remain available.

Step-3: Oxidizable fraction or bound to organic matter: In this fraction the metals are bound to natural organic matter by complexation or pepetization. The metals bound to this fraction can be released when the organic matter is attacked in oxidizing conditions.

Step-4: Residual fraction: The metals associated with this fraction do not show any high environmental risks because the primary and secondary solids in this fraction occlude the metals in their crystalline structure (17, 18).

1.6 Transfer of metals from soil to plants

The accumulation and migration of the metals in the cultivable soil is a complex process which involve run off sorption, leaching, and capillary rise, root uptake and resuspension into the atmosphere. For the assessment of such process plant /soil concentration ratio usually called Metal Transfer Factor (MTF) is used to estimate the transport of element through food chain. This ratio denotes the amount of element that is expected to enter to plant from soil. There are also some factors such as soil characteristics, type of plant, climatic conditions, part of the plant concerned, chemical form, the metal and the effect of competitive species that affect MTF values. The MTF can be calculated using the formula such as $MTF = \frac{C_{plants}}{C_{soil}}$ -----------(1) (19-21).

Plant/soil ratios (0.1) for any particular element indicate that the plant is excluding the element from its tissues. Only a portion of source metal uptake by the root and then translocate to the leaves, giving a leaf/soil concentration ratio of about 0.2 though the concentration of the particular metals in the soil may be high. Transfer factors >0.2 indicate that the contamination of plants caused by anthropogenic activities. However, soil pH, soil organic matter, cation exchange capacity (CEC), and plant genotype can markedly affect metal uptake.

1.6.1 Classification of plants based on their metals accumulation

Plants absorb numerous elements from the soil. Some elements are required for the plant's life cycle are called essential elements. While some elements i.e Fe, Mn, Mo, Zn, Cu, and Ni are required by the plants in minute quantity and are called micronutrients. Other non-essential elements such as Au, Ag, Co and Al have been investigated to have a stimulatory effect on the plants growth. It is also found that the plants absorb non-essential elements which have no biological function and are toxic even at low concentration from the soil. Among these As, Pb, Hg and Cd are well known (22,23).Micronutrients also becomes toxic when accumulated by plants beyond threshold values. Plants take up both essential and non essential elements from the soil in response to the concentration gradient induced by the selective uptake of ions by the roots, or by diffusion of elements in the soil (24). Based on the differences in the accumulation of elements by the plants species, plants can be classified into three categories:

1. Excluders: These are those species that grow on contaminated soil and prevent the metals from entering their aerial parts over broad range of metals concentration in the soil. However they still contain high levels of metals in their roots.
2. Metals Indicators: These plants accumulate metals in their aerial tissues and the metals level in their tissues generally reflects the metals level in the soil.
3. Accumulators: These plants species can concentrates metals in their aerial tissues to the level far exceeding those present in the soil or the non accumulating species nearby. It has been reported that plants containing more that 0.1% of Ni, Co, Cr and Pb or 1% Zn in their leaves on dry weight basis are called hyper accumulators irrespective of metals concentration in the soil (25).

1.6.2 Distribution and assimilation of metals by the plants

Plants distribute metals internally in different ways. They may localize the selected metals in roots and stem or they may accumulate and store other metals in non toxic form for later distribution and use. A mechanism of accumulation of metals in some plants involve binding of potentially toxic metals at the cell walls of the cells and leaves away from the sensitive sites within the cells or storing them in the vascular compartment. It is of great interest that plant species which have no exclusion mechanism in the roots absorb and translocate large quantities of metals in their growing parts specially the leaves without showing any toxic symptoms via a sort of internal resistance or accumulation mechanism. The assimilation of trace elements by the plants varies greatly as a function of soil conditions. High metal concentrations in the soil do not indicate correspondingly high level of metals in plants. This depends upon several factors such as pH, cation exchange capacity (CEC), organic matter, humidity and others. Toxic metal ions penetrate cells using the same adsorption process of essential micronutrient ions. The quantity absorbed by the plant depends upon the concentration of metal in the soil together with its successive moment from the soil to the root surface and from the root to the aerial parts. The translocation of these metallic ions to the aerial parts depends upon plant specie, the metal involved and environmental conditions (26, 27).

1.7 Risk assessment due to the consumption of contaminated food crops by the human

Risk assessment provides valuable information regarding the exposure of the population by consumption of contaminated food crops. Risk assessment by the following method does not provide quantitative information on the probability of exposed population experiencing a reverse health effects, it is of course provide information about the estimation of the risk level due to pollution exposure. Risk assessment can be done by the following methods

1.7.1 Daily Intake of Metals (DIM)

The average daily intake of food crops both for adults and children can be calculated from the data obtained during questionnaire survey. The respondents may be asked for full detail of their diet per week. The daily intake of metals (DIM) can be determined by the equation such as $DIM = \frac{C_{metals} \times C_{factors} \times D_{food intake}}{B_{average\ weight}}$ ------------(2).

Where C_{metal}, C_{factor}, $D_{food\ intake}$ and $B_{average\ weight}$ represent the heavy metal concentrations in plants (mg kg^{-1}), conversion factor, daily intake of vegetables and average body weight, respectively. Fresh to dry weight conversion factor of (0.085) is used worldwide. Both male and female adults (18-60 years) and children (5-17 years) can be considered for questionnaire survey.

1.7.2 Risk assessment

Health risk indices (HRI) for intake of any metal through consumption of contaminated food crops can be calculated using the following equations. $HRI = \frac{DIM}{RfD}$ ----------(3)

Where HRI is the human risk index through consumption of vegetables, DIM is the daily intake of metal (mg metal/kg body weight/day) and RfD is the reference dose. The RfD values for some metals such as Zn, Cd, Pb, Ni, Cu, Cr and Mn are 0.30, 0.001, 0.004, 0.02, 0.04, 1.5 and 0.033 mg/kg bw /day, respectively (28-30).

1.8 Effect of contaminated fodder crops on the quality of meat, milk and milk products

Meat, milk and the milk products form an important part of the human diet. While as an excretion of the mammary gland milk carry various substances like pesticides, disinfectants, drugs, metals and various environmental contaminants which contribute a technological risk factor for dairy products for the related commercial image and consumer health. Today consumer is demanding more "healthy" milk than in the past which is to be rich in nutrients with high biological value but without health risk. The metal contamination of meat, milk through the consumption of the metal contaminated fodder crops by the cattle has been reported. There is a great concern not only for food safety but also for food quality and human health risks, therefore the determination of the metal residues in the milk could be important direct indicator of the hygienic status of the milk and an indirect indicator of the degree of pollution of the environment where the milk is produced(31,32).

1.9 Bioaccumulation of heavy metals in human's blood through different food chains and their health effects

The dietary intake of heavy metals through consumption of metal contaminated-food-crops can cause serious health effects in animals and human beings. The level of metals in blood depends on the bioaccessiblity rate and considered as an index of biologically active metals in the body reflecting the environmental exposure of a population. Concentration of metal in blood is a significant factor for the public health (33-36). Heavy metals are toxic when accumulated beyond the permissible levels and can cause profound biochemical changes in the body. Children are more sensitive to heavy metals and hence are at more risk than young and older ones. Though some metals i.e Cu, Zn and Fe are essential for human beings, chronic metabolic disturbances may results from excessive or deficiency of these metals. High concentration of Cu, could induce growth proliferation and cancer, particularly, due to its ability to change between Cu(I) and Cu(II), whereby highly reactive oxygen species are generated, which produce hydroxyl radicals that adversely modify proteins, lipids and nucleic acids. Likewise, Ni forms the complexes with certain amino acids, peptides and proteins, which can produce DNA damage or genome alterations, including DNA-protein cross links, DNA strand breaks, and chromosomal aberrations. Breast cancer mortalities in different countries were studied to be directly correlated with the estimated dietary intake of Zn, Cr and Cd and inversely correlated with Se (37). Fe is essential for the normal physiological functions in humans, since it is an integral part of many proteins and enzymes. The excessive accumulation of Fe in humans may be associated with an increased risk of cancer. It causes tissue damage by acting as a catalyst in the conversion of hydrogen peroxide to free-radical ions, which attack cellular membranes, cause DNA strand breaks, inactivate enzymes, depolymerize polysaccharides and initiate lipid per oxidation.

Excessive dietary intake of Pb was linked with the cancers of stomach, small intestine, large intestine, ovary, kidney, lungs, myeloma, all lymphorms and all leukemia (38-41).

1.9.1 Anthrophometry

Anthropometry is the measurments of an individual, which consists of the measurment of the Wt (Weight), Ht (Height), TSF (Tricep Skin Foldthickness), MUAC (Muscal Upper Arm Cicumferences) ,BMI (Body Mass Index), Wrist Circumfernces, Fram Size and Suscapular region, abdominal area etc. It is one of the basic component for the determination of nutritional status of the human. Although we can not rely fully on anthropomatric readings but it give a basic frame of the nutritional status of the human body(42). It is an important part of the clinical examination especially in infants, children, adolescent and pregnant women for evaluation of growth and development. Anthropomatric information is most valuable when obtained over a period of time with regular, accurate and consistent recording of anthropomatric data and development. Physical measurments reflect the total nutritional status over a life time. Some measurments, such as height and head circumference, reflect past nutrition or chronic nutritional status. Others such as mid upper arm cicumferences, weight and TSF reflect present nutritional status and are used to assess the skeletal energy reserves both as fat and as protein.

Weight and height are the most common measurment modes, but because of their significance and importants are not appriciated,that is why they are frequently measured slopely, incorrectly or inconsistantly. Heigtht is a measure of chronic nutriton or under nutrition and should be measured as accuretly as possible. Weight reflects more recent nutritional of the child or adults than does length or height. In adults regular weights measurments are particularly important when there is chronic illness.

Weight should be measured in all participants, except pregnant women, wheelchair bound individuals, or persons who have difficulty in standing steady (43).

Height should be measured in all participants, except wheelchair bound individuals, persons who have difficulty of standing steady or straight, and participants with hairstyle (e.g. Afro or Mowhawk) or head dress (e.g. turban) that prevents proper use of the height measuring equipment. By anthropometric measurements we can determine the total calocaries per day requirements of the individuals.

Determining frame size is an attempt at attributing weight to specific body compartments. Frame size identifies an individual relative to the bone size, but does not differentiate muscle mass from body fat. Because it is the muscle mass that is metabolically active and the body fat that is associated with disease states, Body Mass Index (BMI) is used to estimate the body-fat mass. BMI is derived from an equation using weight and height.

To estimate body fat, skin fold measurements can be made using skin-fold calipers. Most frequently, triceps and sub scapular (shoulder blade) skin-folds are used. Measurements can then be compared to reference data and to previous measurements of the individual, if available. Accurate measuring takes practice, and comparison measurements are most reliable if done by the same technician each time (44).To estimate desirable body weight for amputees, and for paraplegics and quadriplegics, equations have been developed from cadaver studies, estimating desirable body weight, as well as calorie and protein needs. Calorie needs are determined by the height, weight, and age of an individual, which determine an estimate of daily needs. Anthropometrics was first used in the 19th and early 20th century in criminalities, to identifying criminals by facial characteristics. Francis Galton was a key contributor as well, and it was in showing the redundancy of Bertillon's measurements that he developed the statistical concept of correlation. Bertillon's system originally measured variables he thought were independent—such as forearm length and leg length but Galton had realized were both the result of a single causal variable (45).

Though a number of studies (46,47,48) have been undertaken from time to time on metals pollution of different industries and in the study area, as well as on the industries located in the city of Peshawar away from industrial zone but they have only analyzed the effluents of those particular industries i.e textile industry and tannery and leather industry and studied their effect on the surrounding soil and ground water only in the vicinity of the installation . No study is available for the information of the public to show the contamination of the soil and ground water where the stream passes. The present study is the first of its nature in the area designed with the aim to know about the contribution of different industries towards the metal contents of the main effluents stream and then to point out the combined effects of these effluents on the contamination of the surrounding soil and ground water of the stream catchment's localities. The effects of wastewater irrigation on the soil heavy metal concentrations, uptake by food crops and health risk through consumption of contaminated food were studied. Thus the present study was carried out with the aim to investigate the effect of contaminated food chain including crops meat and milk consumption on the blood metals composition of the people from Peshawar and lower Dir. The metal concentrations in blood of different age groups (children, adolescent, adults and old age) including males and females in the polluted area and to compare the status of the blood metal composition with the relatively less polluted area (lower Dir) were investigated. The study was undertaken with the following objectives.

1. To asses and determine the toxic heavy metal-based pollutants in the effluents of the Hayatabad Industrial State.
2. To use different statistical technique for the source identification of pollutants and ground water quality.
3. To asses the phytoavailable metal fractions in agricultural soil of the study areas.
4. To asses the levels of toxic heavy metals in agricultural foods in various locations in around Peshawar and District Dir (Control) consumed in the regions and to determine the circulatory levels of toxic elements from selected sites in Peshawar.
5. To measure the nutritional status of population using anthropometric body mass index (BMI) procedures and to collect data for various parameters through food frequency questionnaire
6. To develop relationship between toxic metals and nutritional status of population.
7. To unveil the down stream dilution of selected toxic heavy metals from the point source.

8. To help in planning of abatement methods or remedial measures for control of hazardous wastes discharged directly into rivers and other water resources in order to avoid health hazards.
9. This study will provide sufficient data to the city government and to the people to know about the actual hazards of these pollutants.

LITERATURE REVIEW

Arain *et al* (49) studied the arsenic level in the lake water, ground water, sediments, soil, vegetables, grain crops and fish samples collected from southeast parts of Sindh Pakistan and analyzed using electrothermal atomic absorption spectrophotometer. They also evaluated the potential health risks caused due to higher level of arsenic intake by the people of the study area. They found that the level of arsenic in lake and ground water were higher than permissible limits set by WHO. They also observed that leafy vegetable accumulated higher concentration of arsenic compared to ground vegetables and grain crops. Mutengu *et al* (50) characterized effluents water for different parameters and studied the effect of wastewater irrigation on crops, vegetables and also investigated the potential health risk to the inhabitants of the area through consumption of these vegetables. They found that the respondents of the survey had no symptoms of diseases that are caused due to the consumption of contaminated food crops. They reported that mean value of pH, average temperature, electrical conductivity, were within the WHO permissible limits while faecal coliform, Cd level were higher in the effluents. They detected no Cd and Pb concentration in vegetables and calculated no obvious risks to the consumers. Itai *et al* (51) investigated the geochemical and hydrological constrains on the groundwater in Sonargaon (Bangladesh) to ascertain mechanism of arsenic release into groundwater from sediments. They collected 230 water samples from tube wells in rainy and dry seasons in the study areas. They found high level of arsenic in Holocene unconfined aquifer compared to Pleistocene aquifer. They attributed the high level of arsenic in Holocene aquifer to the weathering of minerals as well as the application of the fertilizers use for crops production. They also found that change in the Fe concentration in aquifer with the change of the season but no change was noticed in arsenic concentration. They concluded that the reduction in the Fe concentration and weathering of biotite or other basic minerals were the primary causes of As mobilization in the Holocene aquifer. Susanne *et al* (52) studied the pollution, environmental impacts and possible risk associated with mercury near the chlor-alkali plants in Kazakhstan. They collected water, soil, plants meat, and various species of the fishes to find out the bioaccumulation of Hg in the food chain. They found that levels of the mercury in fishes were higher than the permissible limits. They also observed the contamination of the soil, plants, with Hg in the surrounding areas of the factory and subsequent bioaccumulation in the meat of the grazing cattle. They concluded that, fishes consumption was the main exposure route of the public to Hg. Karunsagar *et al* (53) analyzed water, sediments and fish samples form different lakes near and away from the thermometer factory for the possible Hg contamination in India where they compared the water quality of the different lakes and found that Hg especially in the form of methyl mercury was higher in lakes near the factory while low in the other lakes away from the factory. Dan Azumil *et al* (54) investigated the effect of industrial wastewater on the water quality of River Chalawa in Nigeria which is located at the downstream of the industrial discharge. They determined the concentration of Cr, Cu, Pb, Zn, Fe and Mn in the river water after the discharge of the effluents into it. They also determined other physicochemical parameters such as suspended solids, total dissolved solids, pH and conductivity of the effluent water. They noticed that except Fe and Mn the level of other pollutants has been increased beyond the permissible limits. They also observed the effects of the industrial wastewater pollution on the drinking water quality. Sial *et al* (55) studied the impacts of sewage water irrigation on ground water quality in Pakistan. They also compared the effects of irrigation with pure canal water, and wastewater. They found that the use of waste water for irrigation not only produces salinity but also increasing sodicity of the groundwater to affect its quality. They reported that wastewater irrigation destroy the characteristics of the soil as compared to irrigation with canal water and excess of Fe concentration in the wastewater increased its concentration in the soil but the concentrations of other heavy metals such as Mn, Cr, Ni, Pb, Zn were within permissible limits. J.C Akan (56) determined pollutants in wastewater and vegetables samples in Kano Metropolis Nigeria. He measured pH, Biological Oxygen Demand (BOD) Chemical Oxygen Demand (COD) temperature, turbidity, conductivity , total dissolved solids, total suspended solids, sulphates nitrates, phosphates and heavy metals such as Mn, Ni, Cd, Pb, Na, Co, Cu, Fe, K and Ca in the wastewater. He found that all the pollutants in the wastewater were higher than the maximum permissible limits set by WHO and maximum contaminant level (MCL). He found that vegetables irrigated with wastewater accumulated high levels of metals and thus were unfit for consumption. Olobaniyie *et al* (57) characterized groundwater by factor analysis in the deltaic plains aquifer in Nigeria. They analyzed ground water for various physicochemical parameters such as p H, total dissolved solids, K, Na, Mg, Cl, bicarbonates and sulphates. They obtained three factors for the data.Factor1 was showing the saline water incursion from seepage into aquifer, factor 2 showed the input from the rainwater recharge and factors-3 showed the inclusion of sulphates and other from the weathering of rocks, vehicular activities and petroleum refining process. They also found that with the increasing the distance from the river the water quality of the aquifer was improving thereby indicated that the effect on water contamination decreased with the distance. Li *et al* (58) measured the ground water quality and identified pollutants of concerns in of the plateau lakes in Yunan, China. They applied multivariate statistical techniques i.e. Cluster Analysis (CA) and Factor Analysis (FA) for the source identification and groundwater quality. They employed box plots to visually interpret the spatiotemporal variation of water pollutants. Krishna *et al* (59) studied the environmental heavy metal pollution using multivariate statistical techniques in industrial area in India. They examined thirteen water quality parameters including heavy metals (Mn, Cr, Cu, Fe, Co, Ni, Zn, As, Sr, Pb and Ba).They applied Factor Analysis and Principal components Analysis (PCA) for the interpretation of complex data structure. They obtained two factors the first one indicated the contribution of geogenic and anthropogenic processes towards the metals pollution of the ground water while the second factor indicated the heavy metals loading in ground water specially from anthropogenic sources. Manzoor *et al* (60) applied multivariate statistical techniques to find the distribution and source identification of heavy metals pollution in effluents, soil and groundwater in Hattar Industrial Estate Pakistan. The PCA showed that the effluents were contaminating the receiving soil and ground water especially with Cr and Pb while the other toxic metals i.e. Zn, Ni, Mn, Co, Cd and Fe were found to have the same origin in the industrial effluents. Tariq *et al* (61) applied multivariate statistical techniques to asses the effect of tannery effluents on the soil in Kasur Sindh, Pakistan. They determined Cr, Pb, Co, Ni, Ca, Na, K, Zn and Fe in the two media .They found that the tannery effluents had high level of Cr which was correlated with Cr in the soil. Using PCA they obtained two factor the first one indicated the loading of the soil with heavy metals from tannery effluents while factor second indicated the inclusion of Na, K Mg and Co to the soil during hide/skin treatment process. Lone *et al* (62) conducted field study in order to know the effect of wastewater irrigation on the accumulation of heavy metals in some vegetables. They also gave the vegetable the a particular dose of N and P. They found that the heavy metals were higher in wastewater irrigated vegetables compared to canal water and a mixture of wastewater and canal water irrigated vegetables. Andaleeb *et al* (63) studied the effect of the Cr on the growth of sunflower They gave different doses of Cr to the three varieties of the sunflower and recorded their morphological, chemical yield parameters of the crop. They found that the length of root shoot and germination were decreased with the increase in Cr concentration. They also noticed significant absorption of Cr by the roots, slow uptake by the other parts of the plants, the decrease in morphological features and yield of the crops with increase in Cr concentration. Khan *et al* (64) determined the health risk associated with the consumption of heavy metals contaminated food crops in Beijing, China. They found that wastewater significantly increases the level of heavy metals in the soil, and food crops compared to the reference samples. They also found that children and adults ingest higher amount of metals through consumption of contaminated food crops in those areas where wastewater is used for irrigation. But their health risk indices values indicated no obvious risk to the people. Carlos *et al* (65) studied different metal fractions in the soil irrigated with the waste water using multivariate statistical techniques in Mixico. They sequentially extracted soil using Tessier *et al* scheme. They found that other heavy metals were accumulated in the agricultural soil within permissible limits set by the European Union but the contents of Pb in most mobile fractions were significantly higher. Applying multivariate statistical techniques they showed that there is a correlation between Boron contents and other variables of the soil that caused the soil salinity. They also reported that with increase in the irrigation time the contents of Cd, Cr, B and organic matter significantly increased in the soil. Sanchez-Martin *et al* (66) sequentially extracted the different metal fractions in the sludge amended soil as a function of incubation time. They noticed increase in organic matter content and modification in composition of the soil with the addition of the sludge. They applied multivariate statistical techniques and found that most of the metals concentrated in the residual fraction with higher percentage with increase in incubation time. They reported that pollution of the soil resulted from the addition of the sludge was low but the organic matter contents could be of major importance. Huang *et al* (67) studied different baiovailable metal fractions in the soil samples collected from

Yanzhomg China using sequential extraction method. They found high accumulation of Hg, Cd, Cu, Pb, Zn, As, Ni, Cr and organic matter in topsoil as compared to subsoil. They also reported increase in these metals concentration in the soil with time due to atmospheric deposition and urban anthropogenic activities. They also reported that sub alkaline nature of the soil affects mobility of metals and hence limits concentration of metals in vegetables and cereals. Bedel *et al* (68) studied the effect of water drainage from sediments on vegetation. The drainage contaminated water of different pollutants levels was given to the soil on which maize and rye grass were grown. Biomass parameters and heavy metals were then measured in roots and shoots of the test plants. They found that the biomass parameters and metals accumulation capacity of plants were affected by the drainage water treatment. Hang *et al* (69) studied the pollution of soil and rice caused by the waste water irrigation in Changshu China. They found that the wastewater irrigation has increased the level of toxic metals in soil and vegetable beyond the permissible limits. They also calculated the target hazard quotient (THQ) and noticed that the values were lower than 1 for each metal to cause any potential risk to the inhabitants of the study area.

Bhattacharyya *et al* (70) evaluated the effects of heavy metals contaminated wastewater on the soil microbial properties such as microbial biomass carbon, (MBC) and biochemical parameters i.e. flourescen diacetate hydrolyzing activities, b-glycosidase, unease, phosphates, and aryl suphatase activities, in Bengal, India. They sequentially extracted soil for different metal fractions. They reported that metals associated with the soluble and exchangeable fraction exerted a strong inhibitory effect on the soil microbial and biochemical parameters. Zhuang *et al* (71) studied the contamination of soil and food crops with heavy metals from the mining and smelting and their potential health risk for human beings in Dabaoshan mine China. They found higher concentrations of the metals in paddy, garden soil and vegetables as compared to permissible limits. They also reported that leafy vegetables and rice (grain) accumulated higher concentration of Cd and Pb and other metals than non leafy vegetables. They also calculated the daily intake of metals (DIM) and target hazard quotient (THQ) for each metal which were found to be higher than the FAO WHO limits. Sharma *et al* (72) studied the atmospheric deposition of heavy metals in vegetables in Varanasai India. They reported maximum deposition rate for Zn followed by Cu, Cd and Pb. *Brassica oleracae, Abelmoschus* and *Beta Vulgaris* were found to accumulate high concentration of Zn, Cu, Cd and Pb. They also calculated pollution Index (PI) values for these vegetables and found that these values were higher for *Brassica Olerace* followed by *Abelmoschus* and *Beta vulgaris*. They reported that atmospheric deposition increases the contamination of vegetable with metals and thus increases their health risk. Zheng *et al* (73) studied the health risk of heavy metals through consumption of vegetable around the Huludao zinc plant in China. They calculated the metal transfer factor (MTF) values for different metals and found that these values were higher for leaves than other tissues. They also calculated target hazard quotients and found that children were at higher risk as compared to adults. They found that those who were living in the vicinity of plant experienced high health risk as compared to the remote people. Alam *et al* (74) investigated the contamination of vegetables with As and other heavy metals in Samta, Bangladesh. They found that snake guard, ghotkol, taroyl, green papaya, elephant foot and bottle guard accumulated high concentration of the As. They also found that the potential of these vegetables to accumulate Pb was higher than for Cd. They also calculated average daily intake of these metals and found that As concentration was within permissible limits. Charry *et al* (75) studied the human health risks due to the consumption of the metal contaminated vegetables by sewage irrigation and their food chain transfer in India. They analyzed soil, forage grass, milk, leafy and non leafy vegetables for heavy metal contents. They found that high levels of Zn, Cr and Cu were associated with the labile fraction which makes them more mobile and available for plant uptake. They also assessed the bioavailability of metals in human's blood and urine. They reported that leafy vegetables accumulate high concentration of metals as compared to non leafy vegetables. The THQ values were found higher for Zn followed by Cr and Pb. Grytsyuk *et al* (76) studied the effect of metal contaminated soil on the vegetation and productivity of forage grass. They reported that the accumulation of metals in plants depend upon the type of soil, the specie of plant, physicochemical properties of metal, and their contents in the soil. Aurora *et al* (77) studied the accumulation of heavy metals in vegetables irrigated with wastewater from different sources. They found, substantial build up of heavy metals in vegetable as result of wastewater irrigation. They also calculated the daily dietary intake of each metal for children and adults. Wanga *et al* (78) evaluated the health risks to the general public as results of consumption of contaminated vegetables and fish in Taijin, China. They calculated THQ values for metals to determine the risk associated with the consumption of contaminated vegetable but reported that although there is higher daily intake of these metals by the people but yet there was no any risk for the people of study area. Jambhulkar *et al* (79) studied the bioaccumulation of heavy metals in plants grown on fly ash dump near thermal power plant in Nagpur, India. They reported that fly ash contained low level of N, P, organic carbon and trace metals. After plantation of the plant species using bioremediation technique they found that Fe was accumulated to greatest extent in the plant followed by, Mn, Zn, Cu, Cr and Pb. *Cassia siamea* was found to accumulate higher concentration of the selected metals compared to other plants species. They reported that *C.siamea* could be used as a hyper accumulator plant for bioremediation of fly ash. Yang *et al* (80) evaluated the accumulation of Cd in the edible parts of six vegetable that were grown on Cd contaminated soil under different conditions. They found that plant Cd concentration increased linearly as a result of increase in soil Cd concentration. They reported that plants species vary differently in Cd accumulation. Sharma *et al* (81) in their other study reported the heavy metals contents of vegetables collected from production and market sites in India. They found that some vegetables accumulated higher concentration of metals than the permissible limits for example cauliflower accumulated high concentration of Zn and Palak high concentration of Zn and Cd . They found that heavy metals accumulation in the market sites were higher than the production sites. They concluded that the transportation and marketing system exert a pronounce effect on elevating the metals concentration in vegetables thereby threaten its quality and risk for the consumers. Rattan *et al* (82) studied the effect of wastewater irrigation on the metal contents of the agricultural soil, crops and ground water. They grown various cereals, millets, vegetables and fodder crops on sewage irrigated land in Delhi India. They found that sewage effluent contained higher amount of P, N, Zn, Ni ,Cu, Fe, Mn compared to ground water they found increase in organic carbon contents in sewage effluents compared with tube well water. They found that sewage irrigation resulted in build up of substantial amount of phytoavailable metal fraction in the soil. They also found the plant transfer ratio and assessed the risk due to consumption of these food crops. Tripatrhi *et al* (83) studied the dietary intake of essential Zn, Cu and potentially toxic elements Pb and Cd by infants through consumption of milk and milk products. They found that the Pb contents in the cows milk were lowest than the breast milk. Baby food products were found to have higher concentration of metals as compared to different types milk owing to high fat contents. They reported that daily intake of metals through consumption of milk of milk and milk products were below recommended levels. Liacata *et al* (84) evaluated the concentration of heavy metals in cow's milk from various dairy farms in Clebria Italy. High concentrations of As and essential elements i.e. Zn, Se, and Cr were determined in the cow's milk which was attributed to the consumption of contaminated fodder. They found. Patraa *et al* (85) studied the levels of trace metals in cow's milk exposed to different industrial polluted environments. They also studied the effect of Pb and Cd in blood on the Cu, Co, Zn and Fe level in the milk. They compared the data with the reference samples from non polluted areas. Their results indicated high contents of Pb, Cd, Cu, Co, Zn and Fe in milk of cows near steel manufacturing and lead-zinc smelters. They concluded that the exposure of cows to high level of the toxic trace metals significantly increases their level in the blood and milk thereby decreasing its quality and nutritional values. Kazi *et al* (86) evaluated the levels of toxic metals in different processed and unprocessed milk samples. They reported that the environmental conditions and manufacturing process plays an important role in the increasing the level of metals in the raw and possessed milk. Motallebi *et al* (87) determined the lead residue in the milk collected from the different regions in Iran. They found high level of lead in the milk samples in some area due to the consumption of contaminated feed by the cattle which significantly increased the metals levels in the milk. Demirezen *et al* (88) studied Se, Cu, Ni ,Zn Cd, Mn, Fe and Pb in meat and meat products consumed in Turkey. They found high concentration of Zn, Ni and Pb than the recommended permissible limit in some meat, fish and meat products due to environmental contamination. Alma *et al* (89) reported the metals contamination of the cattle horse, goat and sheep's meat due to contamination from the metal processing zone in Kazakhstan. They found high level of Cd, Zn and Pb in meat and feed samples. Horses were found to have accumulated high concentration of metals as compared to cattle and sheep. They concluded that environmental factors significantly increase metals in the meat. Tripathi *et al* (90) in their another research work studied the effect of blood-Pb on the concentration of Cd, Cu, Zn, Fe and hemoglobin level of the children from Mumbai India. They found that the Mumbai children had high level of blood-Pb concentration as compared to Hyderabad children's which can be attributed to environmental pollution. Friedman *et al* (91) studied the blood-Pb level in Ukrainian children and also evaluated the health effects associated with high blood-Pb concentration. They also statistically evaluated the relationship between blood-Pb level in the children with paternal occupation where their fathers worked manual labor jobs in industries associated with Pb exposures and their mothers smoking indoor. They observed no adverse health effects due to Pb exposure in children. Tripathi *et al* (92) in his another research study reported the relation between atmospheric Pb level and blood-Pb level in the children in India. They found that blood-Pb level is a direct indictor of vehicular pollution in the study area. They also reported low level Pb in the atmosphere of those areas which were away from industries and high level in those in the vicinity of industries, they also observed a significant increase in blood-Pb level with increase in concentration of Pb in atmosphere. Schroijen *et al* (93) measured the pollutants in the adolescent's blood as a function of lifestyle and personal characteristics in Belgium. They measured PCBs, DDE and hexachlorobenzenes HCB and heavy metals in their blood and found significant differences in these pollutants as a function of residence. They reported that those adolescent that were living in areas with intensive fruits cultivation and in areas around household waste incinerators had no internal exposure to these pollutants while those living near industrial areas had high contaminants levels in their blood. Reise *et al* (94) studied the heavy metals, especially lead exposure of people near waste incinerators in Portugal. They also took the data regarding the concentrations of the lead in the people before that plant had started work and after its operation. A significant increase in the umbilical and cord blood of the participants of the stud was found due to emissions from the incinerators plants. Pasha *et al* (95) investigated the heavy metals in scalp hair and blood of cancer patients in Pakistan. They reported high concentration of Cd and Cr in the plasma of patients as compared to control samples. They reported that the concentrations of Fe and Zn were higher in control while in scalp hair Zn , Fe, Pb Cu and Cd were found higher in patients than control. They concluded that the carcinogenesis affects the concentration and mutual variation of metals in the cancerous patients as compared to control. Meyer *et al* (96) studied the effect of lead in tap water on the blood-Pb level in children in Germany near the smelters. They applied statistical techniques to find out the correlation between lead in tap water and blood-Pb. They found that the lead in tap water was significantly correlated with the blood-Pb. They also reported that gender, area of residence, lead in house dust regular contact with dogs, dirtiness of the children playing indoor affected the Pb concentration in their blood. Adak *et al* (97) evaluated the nutritional status of adults population in Maharashtra India using body mass index procedures. They reported significant variation in BMI among the population due to chronic energy deficiency (CED) due to their low social and economical status. Hien *et al* (98) studied the nutritional status of the three years old children in Veithnam. They got data through questionnaire and BMI measurements and found that most of the children were underweight, stunted and wasted. They also reported that area of residence, ethnic, mother occupation, initiation of breast feeding, house hold size, mother BMI, number of children in a family, weight at birth were found to be significantly related to malenutrition. Prasong *et al* (99) worked on the procedures for the BMI of boys and girls in Thailand. They reported that there is no any significant difference in the weight height and BMI of the bys and girls from different villages. Boys were found to have more body fats than girls. They also studied the children and found that majority of the children were suffered from various diseases due to micronutrient deficiency i.e. fatty acid vitamin B2, C and D.

Chapter 2

EXPERIMENTAL

2.1 Description of the study areas

2.1.1 Peshawar

Peshawar is the capital of Khyber Pakhtunkhwa that occupies an area of 77 km^2 with a population of more than one million. It is a water rich valley through which flows River Kabul. The surrounding area of Peshawar consists of irrigated plains as a part of the huge basin drained and irrigated by River Kabul. Industrial zone in Peshawar is Hayatabad Industrial State where all the major industries i.e. pharmaceutical, glass rubber, plastic, textile, ghee, woolen mills and marbles mills, etc are housed. The effluents from these industries is directly discharged into two streams which join together shortly after passing through the industrial zone that flow all along the way passing through different localities of Peshawar from southwest to northeast. It joins Shalam River a part of canal from the River Kabul and again flow into River Kabul in the East. River Kabul is the main irrigation source in district Peshawar and surrounding areas (100). Kankola is a major food crops producing area situated in the northeast of Peshawar (Fig-1). Food crops from Kankola are transported to Peshawar. Though the main irrigation source is a canal originated from Shalam River but on the other side a wastewater stream (originated from industrial zone located in Hayatabad) is also used for irrigation purposes.

2.1.2 Dir

Topographically Dir has been dominated by mountains and hills which are parts of ranges /branches of Hindukush and Hindu Raj. The mountain ranges run from north to south and from northeast to southwest along the northern borders with Chitral district. The important river is Panjkora which enters the district from northeast and flows south west along boundary with the Bajour Agency up to its co-fluence with Swat River. Panjkora River is made up of several streams in the lower Dir and a main stream form Upper Dir called Dir River. Though individual streams in the catchment areas are used as a source of irrigation, River Panjkora is the main irrigation source in the downstream plain areas of Lower Dir. The sources of drinking water in district Dir are pipelines, hand pumps, wells and springs. Dir is a hilly area and the mineral contents of water may be enhanced when it passes through the hills (101). Though individual streams in the catchments areas are used as a source of irrigation. River Panjkora is the main irrigation source in the downstream plain areas of Lower Dir .

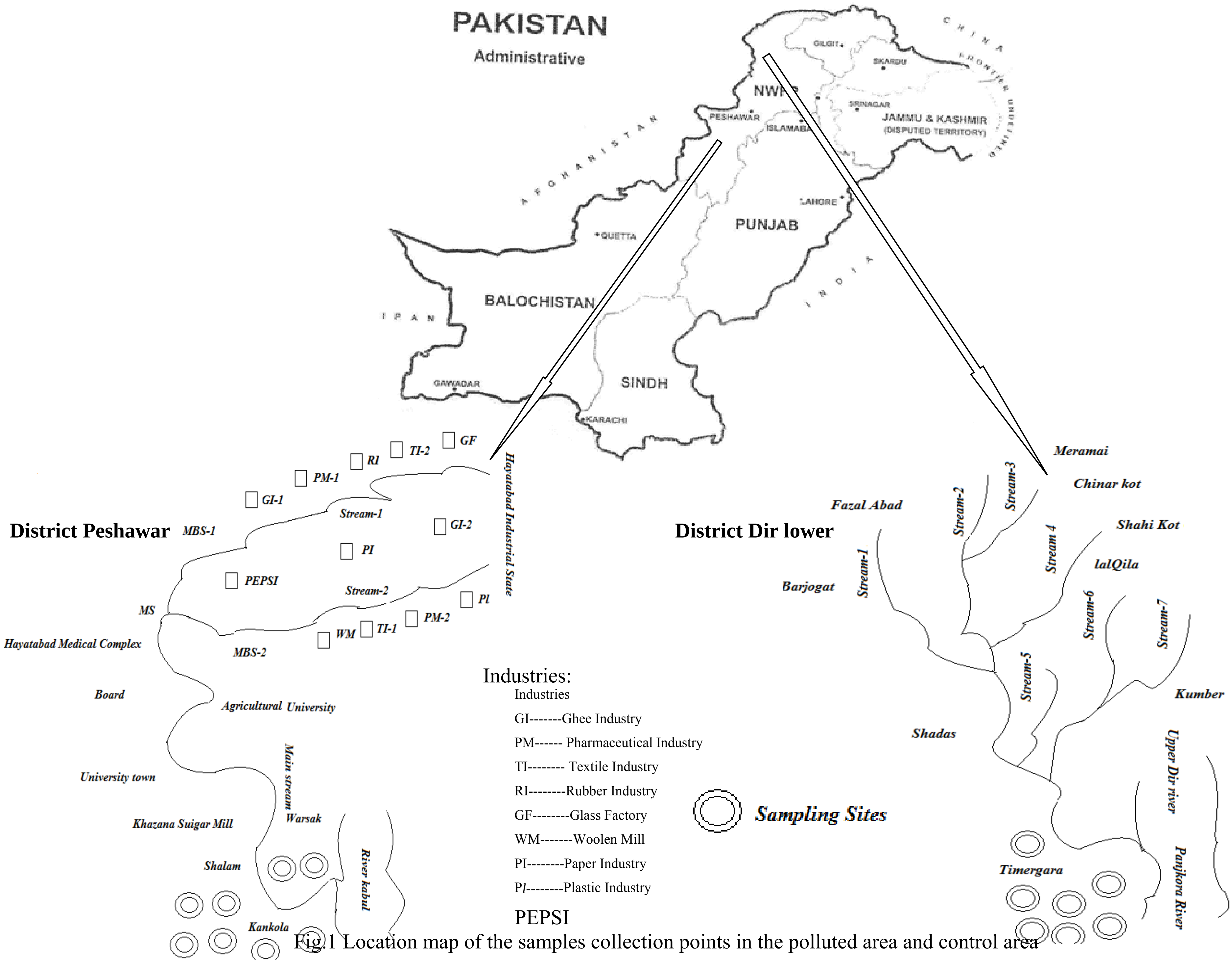

Fig.1 Location map of the samples collection points in the polluted area and control area

2.1.3 Sampling plan

In sampling plan for the metal characterization in effluents, soil, drinking water, food crops, meat, milk and blood samples, factors which are of significant importance in the chemistry of these samples were included to ensure accuracy and precision. Replicate samples of effluents, soil, ground water, food crops, meat and milk were drawn from each sampling point. The samples were collected both from industrial area and relatively less polluted area, the district lower Dir.

2.2.1 Collection and pretreatment of effluents, soil and ground water samples

Samples from effluents of different industries were collected from their drainage outlets. Effluent and soil samples were also collected from and in the surrounding of the two main stream that join together shortly after their exit from the industrial zone. Other effluents, soil and water samples were collected at a distances of about 2 Km from the main effluents stream till it joins the River Kabul. Samples of water and soil were also collected from and in surroundings of River Kabul where canals have been drained to be used as a source of irrigation. Ground water samples were collected from the outlets of tube wells or machine driven hand pumps. A similar plan for sample collection from background area and control area that is district Dir was adopted, where water and soil samples were collected from and in surrounding individual streams up to River Panjkora. A sample of soil and water was also collected from and in surroundings of River Panjkora.Ground water samples were collected from the springs, pipelines, hand pumps and wells in different areas where these streams pass through both the polluted area and the control area. Collection of water and soil samples was conducted during Oct 2008 to Dec 2009 when the industries were running at their peak capacity. Water samples were kept in 2L polyethylene plastic bottles cleaned with metal free soap, rinsed many times with distilled water, soaked in 10% HNO_3 for 24 hours and finally rinsed with de-ionized water. All samples were stored in the insulated cooler containing ice and delivered on the same day to the laboratory and all the samples were kept a 4^{o}C until processing and analysis (102). Soil samples were dried at 110^{o}C and ground to pass through 200 mesh sieve and transferred to polyethylene bottles until analysis.

2.2.2 Collection and pretreatment of agricultural soil and food crops samples

About 20 different food crops (*Spinacia oleracae L*, *Corriandum sativum*, *Daucus carota, Malva neglecta*, *Solanum tuberosum, Brasssica compestress*, *Allium sativum*, *Lactuca sativum*, *B. rapa*, *Lycopersicum esculantum, Triticum aesativum* L, *Allium*, *Mentha viridis, B. oleracae botrytis, B.oleracae capitita,* *Zea mays* L , *Oryza sativa* L, *Pisum sativum*, *Hebiscus esculantum* and *Portulaca oleracae*) and soil samples (0–20 cm) were collected from agricultural fields present in the study area (Fig-1). The fresh vegetable samples were put in clean plastic bags and transported to the laboratory for analyses. These samples were cleaned with de-ionized water and separated into leaf, stalk, fruit and root. All air-dried sub-samples of vegetables were grounded to fine powder and stored in polythene bags.

2.2.3 Collection and pretreatment of blood Samples

The population in each of the study area was divided into different age groups i.e children (1-12 years), adolescents (12-18 years), adults (18-45 years incase of females and 18-55 years incase of males) and old age (above 45 and 55 years for male and female, respectively). Blood samples were collected in April, 2009 from the subjects present in different locations. Blood samples (2 ml) were collected from vein puncturing using clean disposable syringes and needles into a haparinized pretreated clean polypropylene tubes and then transported to lab under ice-cold conditions.

2.2.4 Collection and pretreatment of forage grass, milk and meat samplings

A major part of agriculture land in the study areas is also used for fodder cultivation. Buffalo's milk is locally preferred, and has relatively low cholesterol and high fat contents than cow's milk, thus most of the fodder is consumed by buffaloes. The forage grass is chopped into small pieces and fed to the cattle. Milk samples were collected soon after calving during early hours of the day before milking. After discarding the first 5-6 drops, samples of milk (300 ml each) were collected from buffaloes and cows fed on this forage grass. Meat samples were purchased from the local markets which were of the buffalos fed on forage grasses, packed and stored at -18^0 C till analysis.

2.2.5 Anthropometry

2.2.5.1 Collection of data

The data was collected carefully. To get accurate reading we insist all the volunteers to remove their extra clothing's (sweater, caps),shoes, cell phones, watches, violets etc.The name, age height, weight , frame size, BMI, were determined and recorded on the paper.

2.2.5.2 Determination of height

The height of the individuals was taken with ordinary measuring tape. The individual was asked to remove his shoes and cap and stand against the wall. Backing to the wall and looking straight in front. Then a ruler was kept on his, her head, touching his head on one side and the wall on the other side. A sign on the wall was made with a pencil. The individual was asked to move from his place. The height was measured from the marked point to the bottom of the wall with ordinary measuring tape. The height was taken in centimeters.

2.2.5.3 Determination of weight

The weight of individual was determined with ordinary health scale. The individual was asked to remove his shoes and extra clothes and to step up on the scale. The weight was taken in the Kg.

2.2.5.4 Determination of the Mid Upper Arm Circumference (MUAC) and Triceps Skin Fold (TSF)

First the person should be stand. Hold the hand of the person at 90 degree across the chest. With the non stretchable measuring tap, measure the distances from acromion and olecronion bones. Locate the mid point. And measure the arm circumference in cm while let the arm hang loosely. With the fore finger and thumb grip the fold of skin and subcutaneous tissue vertically above one cm of the marked mid point. Pull the fold away from the underlying muscle tissue. Place caliper on the marke and take reading in cm for TSF. Put the values in formula for finding muscles circumferences Formula.

AMC = MUAC- (0.314 x TSF)

2.2.5.5 Determination of the Body Mass Index (BMI)

The body mass index actually means for to determine that whether the weight of an individual match with his/her height with respect to his/her age or not or in other words we can say that BMI has been proposed for determining ideal body weight for height . This index W/H^2 (W=weight in kg , H=height in meters\) has been found to have the least correlation with body height and the highest correlation with independent measurement of body fatness. A BMI greater than 27 for either sex is indicative of obesity. A BMI between 24(female) or 25(males) and 27 is defined as overweight, not obesity.

Thus, one may compare the body weights of individuals by using standard weight tables or a body mass index such as w /H^2.As stated earlier individual have been arbitrarily classified as obese

If they are 20% above “ideal” weight or have a BMI greater than 30.

2.2.5.6 Determination of frame size

First wrist circumference is measured just distal to the styloid process at the wrist crease on the right arm using a tape measure. For the determination of frame size the following relationship is used.

Fram size =Height (cm)/ Wrist circumference (cm)

The calculated frame size of each individual can be compared with the following values reported in the literature.

Males	**Females**
r > 10.4 small	r>11.4 small
r=9.6-10.4 medium	r=10.1-11.0 medium
r<9.6 large	r<10.1 large

2.2.5.7 Energy requirement for the individual

Estimating Energy out put for Basal Metabolism Rate (BMR) we used the factor 1.0 Cal per kg of body wt per hour for the men, and 0.9 Cal for women.

For man energy for BMR = Body wt x 1.0 Cal per kg per hour

For woman = Body wt x 0.9 Cal per kg per hour

For 24 hours the factor was multiplied with 24.

Energy Estimation for Voluntary Muscles Activity.

Add 50% of the BMR for Sedentry Activity Like a typers.

Add 60% for light Activity like a teacher.

Add 70% for Modrate Activity like a nurse.

Add 100% for heavey work like a hard worker, player.

Estimating Eenergy Out Put For the standard daily allowance (SDA) of Food.

Add 10% of the BMR both for men and women.

Estimating Total Energy out put of the Person.

Total Energy = BMR+ Physical Activity+SDA

These information were collected through a questionnaire filled on the spot from individuals.

Table.1 Food Frequency Questionnaire

District…………………………….…..   Date………

General information of the respondent

Information about diet:

S.No			*S.No*		
1	Name S/O, D/O		12	Flour using	Flour mill/domestic
2	Village		13	Dairy farm, Fish farm /poultry farm	
3	Age(years)		14	No. of cattles/chikens/fishes	
4	Weight(Kg)		15	Have diabetes	Yes/No
5	Height(cm)		16	No. of Diabetes Patients in family	
6	Waist(cm)		17	No. of family members	
7	Farmer	Yes/No	18	Source of income	
8	Agriculture land	Yes/ No	19	Monthly income	
9	Agriculture land(Area)				
10	Food crops grown				
11	Irrigated land/rainy				

Diet/drinks	*Quantity(per day)*			*Quantity(per day)*		
	Mon/Tue	Wed/Thr	Fri/Sat	Mon/Tue	Wed/Thr	Fri/Sat
	Breakfast				**Brunch**	
Tea	Cups:	Cups:	Cups:	Cups:	Cups:	Cups:
Dairy products	Glass:	Glass:	Glass:	Glass:	Glass:	Glass:
Green tea	Cups:	Cups:	Cups:	Cups:	Cups:	Cups:
Parata	No.:	No.:	No.:	No.:	No.:	No.:
Loaf/Bread	No.:	No.:	No.:	No.:	No.:	No.:
Egg	No.:	No.:	No.:	No.:	No.:	No.:
Butter						
Curry (name)	No.of Plates:	No.of Plates:	No.of Plates:	No.of Plates:	No.of Plates:	No.of Plates:
Fruit(name)	No.:	No.:	No.:	No.:	No.:	No.:
Juice(name)	Glass:	Glass:	Glass:	Glass:	Glass:	Glass:
Biscuits	No.:	No.:	No.:	No.:	No.:	No.:
Samosas	No.:	No.:	No.:	No.:	No.:	No.:
Pakora	No.:	No.:	No.:	No.:	No.:	No.:
Sweets	No.:	No.:	No.:	No.:	No.:	No.:

Other(name)						
Diet/drinks	Quantity(per day)			Quantity(per day)		
	Mon/Tue	Wed/Thr	Fri/Sat	Mon/Tue	Wed/Thr	Fri/Sat
Lunch					**Dinner**	
Loaf/Bread	No.:	No.:	No.:	No.:	No.:	No.:
Maize bread	No.:	No.:	No.:	No.:	No.:	No.:
Rice	No.of plates:	No.of plates:	No.of plates:	No.of plates:	No.of plates:	No.of plates:
Chicken	Pieces:	Pieces:	Pieces:	Pieces:	Pieces:	Pieces:
Beaf	Pieces:	Pieces:	Pieces:	Pieces:	Pieces:	Pieces:
Mutton	Pieces:	Pieces:	Pieces:	Pieces:	Pieces:	Pieces:
Fish	Pieces:	Pieces:	Pieces:	Pieces:	Pieces:	Pieces:
Kabab	No.:	No.:	No.:	No.:	No.:	No.:
Pulses(name)	No.of plates:	No.of plates:	No.of plates:	No.of plates:	No.of plates:	No.of plates:
Vegetables(name)	No.of plates:	No.of plates:	No.of plates:	No.of plates:	No.of plates:	No.of plates:
Fruits(name)	No.:	No.:	No.:	No.:	No.:	No.:
Other						
Diet/drinks	Quantity(per day)			Quantity(per day)		
	Mon/Tue	Wed/Thr	Fri/Sat	Mon/Tue	Wed/Thr	Fri/Sat
Between lunch and dinner					**After dinner**	
Tea	Cups:	Cups:	Cups:	Cups:	Cups:	Cups:
Green tea	Cups:	Cups:	Cups:	Cups:	Cups:	Cups:
Milk/dairy products	Glass:	Glass:	Glass:	Glass:	Glass:	Glass:
Halwa	No.of plates:	No.of plates:	No.of plates:	No.of plates:	No.of plates:	No.of plates:
Juice(name)	Glass:	Glass:	Glass:	Glass:	Glass:	Glass:
Biscuits	No.:	No.:	No.:	No.:	No.:	No.:
Samosas	No.:	No.:	No.:	No.:	No.:	No.:
Pakora	No.:	No.:	No.:	No.:	No.:	No.:
Sweets	No.:	No.:	No.:	No.:	No.:	No.:
Other						
Ice cream	Cups:	Cups:	Cups:	Cups:	Cups:	Cups:
Desert	No. of Plates:	No. of Plates:	No.of Plates:	No.of Plates:	No.of Plates:	No. of Plates:
Custard	No.of Plates:	No.of Plates:	No.of Plates:	No.of Plates:	No.of Plates:	No. of Plates:

2.3 Fractionation of soil

Soil samples were sequentially extracted following a slight modification of Tessier et al., method. The soil was first extracted for easily soluble fraction of elements with doubly distilled water (2 g of soil shacked for 4h in double-distilled water with conductance of about <0.02AμScm^{-1}, followed by centrifugation).Exchangeable fraction of elements was extracted using 1N $MgCl_2$ at pH 7. The residue from the subsequent step was extracted with CH_3COOH/CH_3COONa at pH 5 for fractions of metal bound to carbonates. Then the residue from the previous step was extracted with 0.04 M $NH_2OH.HCl$ in 25% CH_3COOH for the metal fraction bound to Fe and Mn oxides. The residue from the previous step was then extracted with 8 .8M H_2O_2 in 0.02M HNO_3 ,for 5h at 85^0C followed by addition of a solution of 3.2M CH_3COONH_4 in HNO_3 for the metal fraction bound to organic matter and sulphides. The total metals contents or the residual fraction was extracted with the addition of 10mL of HNO_3 to 0.5 g of soil followed by digestion on hot plate (103,104).

2.3.1 Acid digestion of the soil sample

Dried soil samples of (0.5g) were digested with 15ml of HNO_3 , H_2SO_4 and $HClO_4$ in the ratio of 5:1:1 at 80°C until a transparent solution was obtained. The solution was filtered through Watman No. 42 filter paper and diluted to 50 mL with distilled water.

2.3.2 Acid digestion of food crops samples

Food crop samples (0.5 g) were taken in crucibles (triplicates) and perchloric acid and nitric acid solution (1:4) were used for acid digestion. After cooling, the digested samples were filtered and made the final volume of 25 mL using de-ionized water. Precession and accuracy of analysis were also ensured through repeated analysis of the samples against certified reference materials (CRMs) of all metals. Due to the non availability of CRMs of vegetables in our laboratory for quality assurance, recovery studies were conducted using standard spiking method.

2.3.3 Acid digestion of meat and milk samples

Meat samples were homogenized separately and 5-10 g of fresh homogenate was weighed in quartz dishes and dried in an oven at 100^0C then ashed in the muffle furnace at 450^0C overnight. Ashed samples were cooled to room temperature and 0.5 ml of concentrated nitric acid was added and re-evaporated and heated in muffle furnace. The ash was then dissolved in 0.5 ml concentrated nitric acid and diluted to 20 ml with deionized water. For the digestion of milk samples, a known volume of milk sample (25 ml) was evaporated to near dryness, wet-ashed and taken up in 10 ml of 0.25% HNO_3.

2.3.4 Analytical method for acid digestion of blood samples.

Method for the acid digestion of blood samples was first optimized using acid mixtures in different proportions. The precession and accuracy of the method was checked by analyzing the Standard Reference Materials (SRMs Human blood, Batch 1701-3) till the results agree within 94 ± 7% of the certified values. The validity of the method was further ascertained by cross method checks, spiked recovery and replicate analysis. Aliquot of 1 ml of each blood sample was then wet digested with concentrated nitric acid and percholric acid. The digested samples were diluted to the required volume with 0.25% nitric acid. Extreme care was taken to avoid all contamination of samples with selected metals.

Reagents

Analytical grade chemicals were purchased and used for sample preparation and analysis. Solutions were prepared in double deionized water. For each metal, calibration standards were prepared from the stock solution.

2.4 Analytical procedures

2.4.1 Determination of physicochemical parameters of effluents and ground water samples

The parameters like pH, electrical conductance (EC), total dissolved solids (TDS), dissolved oxygen (DO), dissolved oxygen percent saturation of drinking water and effluents were determined in situ using Hydro lab (Hatch Company). The total hardness of water samples was determined by using 0.01M EDTA as titrant and meuroxide and Erichrome Black T as an indicator. In laboratory, replicate aqueous solutions of about 1000mL of each collected sampling sites were filtered through polycarbonate filter (0.45mm pore size) and were treated with 2ml concentrated HNO_3 for metal analysis (105).

2.4.2 Determination of Pb, Ni, Cr, Cu, Co, Mn, Cd and Zn by Atomic absorption spectrophotometer

All the effluents, soil water samples were analyzed for eight heavy metals, Pb, Ni, Cr, Cu, Co, Mn, Cd and Zn by using flame atomic absorption spectrophotometer, Perkin Elmer AAS 700 at the Centralized Resource Laboratory, University of Peshawar. The instrumental parameters for each element are listed in the given table 1. The instrument was calibrated for the determination of each element by analyzing the standard solution concentration usually in ppm of each element provided by the company. Hollow cathode lamps were used as a source of light for each element.

Table 2 Instrumental analytical conditions for analysis of selected heavy metals

Element	*Acetylene (l/min)*	*Air (l/min)*	*Wavelength (nm)*	*Slit width(nm)*	*Lamp current(Ma)*	*Limit of detection(mg/L)*
Pb	2.0	17.0	283.3	0.7	30	0.015
Ni	2.0	17.0	232.0	0.2	25	0.006
Cr	2.5	17.0	357.9	0.7	25	0.003
Cu	2.0	17.0	324.8	0.7	15	0.0015
Co	2.0	17.0	240.7	0.2	30	0.009
Mn	2.0	17.0	279.5	0.2	20	0.0015
Cd	2.0	17.0	228.8	0.7	4	0.0008
Zn	2.0	17.0	213.9	0.7	15	0.0015

Metals such as Pb, Ni, Cr, Cu, Co, Mn, Cd and Zn were analyzed in food crops and blood samples using electro thermal graphite furnace Atomic (GFA) Absorption Spectrophotometer Shamadzu Model AA 6800 (Tokio Japan) equipped with deuterium background corrector.

2.4.3 Determination of Hg

The measurement of Hg in effluents, soil and ground water was performed with a Shamadzu Model AA 6800 atomic absorption spectrophotometer (Tokio Japan) equipped with deuterium background corrector. Mercury hollow cathode lamp was used as a source of radiation with a spectral slit width of 0.1nm to isolate the 253.7 nm resonance line. The flow injection system consists of minipulse 3 peristaltic pump. Sample injection was achieved using a Rheodyne model 50 injection valve. The hydride unit was PS analytical LTD hydride generator and flow speed of reagents was controlled by a Watson Marlow 303 peristaltic pump. Quartz tube (0.8cm internal diameter, 15cm long) was used for mercury determination. Pump tube Tygon ® type was employed to propel reagents and eluent

2.4.4 Determination of Arsenic

Arsenic was determined in effluents water and soil samplers by double beam atomic absorption spectrophotometer (AAS) Perkin Elmer AAS 7000 equipped with graphite furnace HGA-400, pyrocoated graphite tubes with integrate platform and auto sampler AS 800 single hollow cathode lamp for As, AAS was operated at 7.5 mA with spectral band width of 0.7 nm and the wavelength of 93.7nm.$MgNO_3$ and Pd 5µg $MgNO_3$ +3µG Pd (10mL +!0mL from stock solution in 100mL) were used. Portions of both sample or standard and modifier were transferred into the auto sampler cups and 20µL standard or sample volume 10µl+10_µL modifier in each case were injected . Argon gas 200mL/ min was used as purge gas except during atomization step. The graphite furnace heating programme was set for different steps drying, ashing atomization and cleaning as temperature range C (s)80-120/15,300-600/15,200-2100 and 2100-2400/2 respectively.

2.5 Data Analysis

2.5.1 Metal transfer factor

Soil to plant metal transfer factor (MTF) was computed as the ratio of metal concentrations in plants (on dry weight basis) to metal concentrations in soil. The MTF was calculated using the formula such as $MTF = \frac{C_{plants}}{C_{soil}}$ ----------------(4)

Where C_{plant} and C_{soil} represent the heavy metals concentration in extracts of plants and soil on dry weight basis, respectively.

2.5.2 Daily intake of metals by human body

The average daily intake of food crops both for adults and children were calculated from the data obtained during questionnaire survey. The respondents were asked for full detail of their diet for week. The daily intake of metals (DIM) was determined by the equation such as $DIM = \frac{C_{metals} \times C_{factors} \times D_{foodintake}}{B_{average\ weight}}$ -----------(5)

Where C_{metal}, C_{factor}, $D_{food\ intake}$ and $B_{average\ weight}$ represent the heavy metal concentrations in plants (mg kg^{-1}), conversion factor, daily intake of vegetables and average body weight, respectively. Fresh to dry weight conversion factor (0.085) was used for these food crops. The average daily food crops intakes for adults and children were calculated to be 0.250 and 0.165 kg $person^{-1}$ day^{-1}, respectively based on the data obtained during questionnaire survey. Both male and female adults (18-55 years) and children (5-17 years) were considered for questionnaire survey. The average adult and child body weights were considered to be 73 and 32.7 kg, respectively.

2.5.3 Risk assessment

Health risk indices (HRI) for intake of Zn, Cd, Pb, Ni, Cu, Cr and Mn through consumption of contaminated food crops were calculated using the following equations adopted from Khan et al.,(13) $HRI = \frac{DIM}{RfD}$ -----------(6)

Where HRI is the human risk index through consumption of vegetables, DIM is the daily intake of metal (mg metal/kg body weight/day) and RfD is the reference dose. The RfD values for Zn, Cd, Pb, Ni, Cu, Cr and Mn were 0.30, 0.001, 0.004, 0.02, 0.04, 1.5 and 0.033 mg/kg bw/day, respectively (106-108).

2.6 Statistical analysis of the data

The data was statistically analyzed through Software Package for Social Science Students (SPSS) software for window version-16. Univariate statistician techniques i.e. ANOVA, and multivariate techniques such as MNOVA, Factor Analysis (FA), Principal Component Analysis (PCA), Correlation, Multiple Regression Analysis (MRA) and Cluster Analysis (CA) statistical techniques were applied for statistical evaluation of the data.

Chapter 3

RESULTS AND DISCUSSION

3.1 Physicochemical parameters of industrial effluents and its effect on the surrounding soil and ground water quality.

The results of various physicochemical parameters and heavy metals levels in different industrial effluents, at downstream collection points and drinking water and soil samples taken from the polluted area have been summarized in tables 3-6, while for the streams water, ground water and soil samples taken from the control area have been given in table 7-9. Figures 2-6 represent the graphical form of variation of As and Hg in effluent and drinking water samples.

3.1.1 pH

The data indicates the physicochemical parameters of the effluents shown in table-3 and 4 collected from different industries in the polluted area. From the data, it is evident that the pH of the effluents falls in the range of 6.98-13.18. The pH of 13.18 is shown by the effluent of one of the ghee factory which is highly alkaline due to the presence of bases which are used in the alkaline hydrolysis of the fats for soap manufacturing within the ghee industries. This facility is not yet installed in the other ghee factory so the pH of its effluent is not too high. All other industrial effluents have pH in the permissible recommended limit of World Health Organization(WHO) that is 6.5-9.2.The effluents collected at various distances along the main effluent stream have pH range slightly higher than the individual industrial effluents which can be attributed to the mixing of highly alkaline water of one of the ghee industries having excessively high pH. The pH of the effluents collected at the downstream points is in the range of 6.01-8.82, which is not higher than the permissible limits. The pH of drinking water samples in the polluted area is comparable to the effluent samples and falls in the range of

5.9-8.89, which directly indicate the effect of effluent water on the ground water quality. Soil samples collected at various downstream points have pH in the range of 5.1-8.7 from fairly acidic to neutral. The general trend is pH is going to decrease with the distance from the point sources . Stream and drinking water samples collected from control area have pH in the range of 7.03-8.85 and 5.52-9.18 respectively and was within the permissible range. The low pH of 5.52 was noticed only in one case. Soil samples of the control area have pH in the range of 8.07-8.78. Compared with the soil samples from the polluted area these are slightly alkaline. There is no significant decrease in pH with the increasing distance. Water with low pH less than 6.5 would be soft, acidic, corrosive and would result in the leaching of metals ions such as Fe, Mn, Cu, Pb and Zn from the aquifer plumbing fixtures and piping.Therefore, it may contain elevated level of toxic metals and create aesthetic problems such as metallic or sour taste and stains of laundry among acute and chronic diseases esophagious and stomach irritation with pain and vomiting.

3.1.2 Total dissolved solids

Dissolved solids (DS) are any mineral salts, metal catoins or anions frequently dissolved in water, while total dissolved solids (TDS) refer to inorganic salts i.e. bicarbonates, chlorides , sulphates of Ca, Mg, K and Na and some small amount of organic matter which is soluble in water. Industrial wastes or chemicals used in the treatment process, nature of piping or hardware used to convey water, industrial waste water and urban run-off are the main sources of TDS in water. In case of polluted area, paper and glass industries effluents have high TDS level in the range of 300-1000 mg /L which is higher than the WHO permissible limit of 500 mg/L.This trend prevail in the effluents water up to the mixing of different industrial effluents in the study and then dilution occurs down stream. Incase of drinking water samples only two points away from the point sources showed reasonably high TDS level 700 mg/L and 900 mg/L respectively which may be due to the soil erosion an obvious, factor in increasing the TDS level of ground water. Stream water and drinking water samples collected from control area have TDS level in the WHO permissible range.

3.1.3 Hardness

Total hardness which is the sum of calcium and magnesium concentration both expressed as calcium carbonate in mg /L. The permissible limit of hardness by WHO and APHA (American Public Health Association) are 500 mg/L and 250 mg/L, respectively. The total hardness of effluent water from different industries is in the range of 153.3-506.6 mg/L. These values indicate that the hardness is not too high than the permissible limit. The decreases in hardness of water at the increasing distances from the point sources can be attributed to the dilution of salts. The total hardness of downstream collection samples falls in the range of 245.5- 553.4 mg/L. Drinking water samples collected from the polluted area have total hardness in the rage of 106.6-400 mg/L, which is within the permissible range of WHO permissible limits. Stream and drinking water samples collected from the control area have total hardness in the range of 102.3-178.6 and 89.14-155.4 mg/L, respectively.

3.1.4 Dissolved oxygen

The WHO guidelines for the permissible level of dissolved oxygen in drinking water is ≥3mg/L. Most of the industrial effluents have low DO values in the range of 0.83-2.84 mg/L indicating their pollution. The DO level of the effluents increases with the distance which may be due to the long contact time, large surface area for exposure for the absorption of atmospheric oxygen. The drinking water samples collected from both polluted and non polluted area have reasonable DO level in the rage of 5.30-8.90 mg /L.

3.1.5 Electrical Conductance (EC)

The WHO permissible range for the specific conductance for drinking water is 0.40 mS/cm. The effluents of different industries have conductance in the range of 0.523-2.45 mS/cm shown in table 3 and 4 which is higher than the WHO permissible limit. The high specific conductance is due to the presence of ions of different salts present in effluents samples**.** At increasing distances from the point sources, the specific conductance decreases which may be due to the dilution and adsorption of various ions on the soil as indicated by high specific conductance of the soil samples in the range of 1.91-3.52 mS/cm. The drinking water samples of the polluted area have conductance in the range of 0.511-1.405 mS/cm which is higher than the WHO guidelines for drinking water quality. The stream water collected from control area have specific conductance in the range of 0.211-0.436 mS/cm. The drinking water of the control area has conductance in the range of 0.364-0.640.

Table-3 Physicochemical parameters of effluents from different industries in the polluted area

Site	***Hardness (mg/L)***	***Specific Conductance (mS/cm)***	***Dissolved Oxygen (mg/L)***	***pH***	***Total Dissolved Solids (g/L)***	***Dissolved Oxygen (%Sat)***
GI-1	312.6	0.743	2.36	7.79	0.5	14.7
GI-2	506.6	0.540	2.84	13.18	0.5	105.4
PM-1	153. 3	0.808	0.83	7.82	0.5	9.1
PM-2	340.3	0.523	1.17	8.25	0.3	98.9
TI-1	286.6	0.598	2.70	8.26	0.4	32.7
TI-2	306.6	0.633	1.95	7.63	0.4	24.5
RI	220	0.650	1.66	7.59	0.4	14.2
GF	380.3	0.532	1.85	7.70	0.3	22.5
WM	315.6	1.138	1.27	8.01	0.7	11.4
PI	440	0.551	1.33	6.98	1.0	16.3
P*l*	270.3	2.450	1.17	7.59	0.3	21.0
PEPSI	365.3	0.595	1.38	7.65	0.4	17.4

Table-4 Physicochemical parameters of effluents at different collection points downstream in the polluted area

Site	***Hardness (mg/L)***	***Specific Conductance (mS/cm)***	***Dissolved Oxygen (mg/L)***	***pH***	***Total Dissolved Solids (g/L)***	***Dissolved Oxygen (%Sat)***
MBS-1	373.3	0.675	1.06	7.92	0.4	11.8
MBS-2	326.6	1.183	1.62	7.60	0.8	19.7
MS	350.6	1.319	1.06	7.42	0.8	14.3
DSC-1	450.3	1.157	0.93	7.59	0.7	11.5
DSC-2	553.4	1.411	0.93	6.01	0.9	11.3
DSC-3	245.5	0.472	1.40	7.78	0.30	17.3
DSC-4	385.7	0.423	7.79	8.27	0.3	95.2
DSC-5	298.7	0.421	8.22	8.82	0.3	98.3
DSC-6	255.4	0.431	7.60	8.12	0.3	92.6
DSC-7	286.6	0.395	8.20	8.36	0.3	100.5

Table-5 Physicochemical parameters of drinking water collected from different localities in the polluted area

Site	*Hardness (mg/L)*	*Specific Conductance (mS/cm)*	*Dissolved Oxygen (mg/L)*	*pH*	*Total Dissolved Solids (g/L)*	*Dissolved Oxygen (%Sat)*
GI-1	333. 3	0.529	8.03	8.43	0.3	98.3
PM-1	353.3	0.524	7.42	8.34	0.3	92.5
PM-2	200	0.772	7.89	5.9	0.5	10.8
RI	360.3	0.527	8.03	8.54	0.3	98.1
TI-2	173.3	0.519	7.51	8.45	0.3	91.8
TTC	106.6	0.508	8.15	8.89	0.3	100.1
GF	180.6	0.517	7.53	8.24	0.3	91.9
WM	220	0.514	7.81	8.37	0.3	95.8
MS	245.1	0.630	8.68	8.24	0.4	107.8
DSC-1	315.2	0.637	8.90	8.43	0.4	109.2
DSC-2	400	1.386	6.86	7.78	0.2	84.1
DSC-3	350.7	1.008	8.05	8.16	0.7	98.1
DSC-4	310.7	1.406	7.21	8.35	0.9	98.3

Table-6 Physicochemical parameters of soil samples at different collection points downstream in the polluted area

Sites	***Specific Conductance (mS/cm)***	***pH***
MBS-1	2.68	7.6
MBS-2	1.91	7.3
MS	2.17	8.1
DSC-1	1.98	8.7
DSC-2	2.42	8.6
DSC-3	3.52	8.2
DSC-4	2.72	6.2
DSC-5	3.34	6.0
DSC-6	1.93	5.1
DSC-7	2.79	6.1

- **The values given are the mean of five readings**
- **Caption:**

GI-------Ghee Industry

PM------ Pharmaceutical Industry

TI-------- Textile Industry

RI--------Rubber Industry

GF--------Glass Factory

WM-------Woolen Mill

MBS-1-----Main Bridge stream-1

MBS-2 Main Bridge Stream-2

MS-----Mixing Point of two streams

DSC-1, DSC-2, DSC-3, DSC-4, DSC-5, DSC-6, DSC-7---

Downstream Collection Points

Table-7 Physicochemical parameters of streams water and downstream collection points in the control area.

Site	*Hardness (mg/L)*	*Specific Conductance (mS/cm)*	*Dissolved Oxygen (mg/L)*	*pH*	*Total Dissolved Solids (g/L)*	*Dissolved Oxygen (%Sat)*
CS-1	154.8	0.352	8.17	8.63	0.2	103.5
CS-2	134.5	0.406	7.44	6.92	0.3	99.5
CS-3	178.6	0.400	7.64	8.1	0.3	101.0
CS-4	98.62	0.211	7.32	7.51	0.1	97.8
CS-5	102.3	0.391	7.8	8.28	0.4	103.3
CS-6	116.6	0.365	7.42	7.06	0.2	98.0
CS-7	125.4	0.245	7.62	7.03	0.2	100.1
CS-8	136.3	0.263	7.65	8.45	0.2	100.2
CMS-1	142.3	0.436	7.62	8.85	0.3	101.4
CMS-2	156.3	0.297	7.50	8.17	0.2	103.0

Table-8 Physicochemical parameters of drinking water collected from different localities in the control area

Site	*Hardness (mg/L)*	*Specific Conductance (mS/cm)*	*Dissolved Oxygen (mg/L)*	*pH*	*Total Dissolved Solids (g/L)*	*Dissolved Oxygen (%Sat)*
CS-1	98.23	0.453	5.30	6.55	0.3	71.3
CS-2	102.3	0.364	7.92	8.66	0.2	105.0
CS-3	89.14	0.461	7.08	7.74	0.3	94.7
CS-4	125.4	0.522	7.8	7.97	0.3	96.5
CS-5	168.2	0.632	6.32	7.48	0.4	84.1
CS-6	145.5	0.640	7.91	8.18	0.4	98.2
CS-7	155.4	0.374	7.31	5.52	0.1	94.8
CS-8	134.6	0.400	7.8	9.18	0.3	101.2

Table-9 Physicochemical parameters of soil samples at different streams and at collection points downstream in the control area

Sites	***Specific Conductance (mS/cm)***	***pH***
CS-1	0.295	8.77
CS-2	0.334	8.66
CS-3	0.107	8.07
CS-4	0.284	8.44
CS-5	0.246	8.81
CS-6	0.305	8.55
CS-7	0.185	8.78
CMS-1	0.305	8.58
CMS-2	0.366	8.55

mS/cm. Only two samples showed high values which may be due to the fact that the water collected from these points was spring water and as the water of a spring comes out of a hill so it can dissolve various salts in it. The conductance of the soil samples is comparable with the stream water samples.

3.1.6 Mercury and Arsenic

Arsenic and mercury concentration was detected in all effluents, drinking water and soil samples both from the polluted and control area. The data has been presented in the Table 10-16 and also has been presented in the graphic form (Fig.2-6). The mercury concentration in different industrial effluents ranged from 0.011-0.331µg/L. The high Hg concentration was found in the pharmaceutical industrial effluents that was 0.331µg/L, 0.234 µg/L ,rubber factory effluents that was 0.310 µg/L, woolen mill that was 0.209µg/L and one of the ghee industry where it was 0.184 µg/L, followed by textile industry and glass factory where its concentration was 0.117 µg/L and 0.105 µg/L respectively.

Among the downstream points, Hg concentration was found higher in one of the effluents stream before it joins the main stream where its concentration was 0.519 µg/L because the pharmaceutical industries and rubber factories effluents are directly discharged into this stream. At the mixing point of the two separate streams, obviously high Hg concentration was found that was 0.635 µg/L.Then downstream, further dilution occurs and the concentration decreases from 0.635 µg/L to 0.011 µg/L. Incase of drinking water samples collected from various industries and localities in the polluted areas high Hg concentration was found in case of drinking water of pharmaceutical, rubber industries and woolen mill where it was 0.831µg/L, 0.592 µg/L ,0.592 µg/L and 0.511 µg/L respectively. In these drinking water samples the Hg concentration was found higher compared to their effluents which clearly indicate the effect of effluents percolation into soil affecting the quality of drinking water .The drinking water samples collected from various localities at the downstream also showed high Hg concentration that ranged from 0.013 to 0.344 µg/L. Soil samples collected from various downstream points have Hg concentration in the range of 0.012-0.258 µg/L. High Hg contents were found in the soil sample collected from the mixing point of the two separate streams followed by the first distant point from the point sources where Hg concentration was 0.258 µg/L each at the two collection points. Downstream dilution occurs in the Hg contents of the soil samples. The water samples collected from various streams in the control area have Hg concentration in the range of 0.001-0.095µg/L which is quite low compared with the effluents streams in the polluted area. High Hg concentration was in case of mixing points of streams where it was 0.087µg/L and 0.095 µg/L respectively. Drinking water samples collected from the various localities in the control area have Hg concentration in the range of 0.019-0.078 µg/L Compared to the drinking water from the polluted area this concentration is quite low. Soil samples collected from various downstream points in the control area have reasonably high Hg concentration compared to their stream waters which is due to the settling and adsorption of various inorganic and organic mercurial salts in the water. Hg contents in the soil samples ranged from 0.077 to 0.834µg/L. The dilution along the distance is also quite evident.

Arsenic concentration found in case of effluents from different industries falls in the range of 10.811-66.411µg/L . Higher As contents was found in case of effluents of woolen mill and textile industry effluents where it was 66.411µg/L and 63.242 µg/L respectively. PEPSI rubber and paper industrial effluents have the As contents of 37.452 µg/l,37.026 µg/L and 35.875 µg/L respectively. High As concentration of 35.015µg/L was found in case of effluents from one of the ghee industries which may be due to the contaminated oil as a result of seed contamination due to pesticide use . Similarly like the distribution of Hg high As contents was found in the two streams before mixing that is 60.963µg/L and at the mixing point As was higher that is 71.103 µg/L.Then gradual dilution occurs from 42.675 µg/L to 16.251µg/L. Drinking water samples have As in the range of 4.195-58.921µg/L. Pharmaceutical industry drinking water have high As contents that is 58.921µg/L. Glass factory has 49.126 µg/L, and rubber factory has 42.521µg/L, the other localities where the effluents stream passes have a reasonable As concentration in the drinking water. The effect of effluents water on the drinking water quality is evident from the data. In case of soil samples As is in the range of 17.698-71.532 µg/L at various collection points the dilution effect is also evident.

The streams water from the control area have As concentration in the range of 9.551-38.321µg/L. This is relatively low compared to the effluent water of the polluted area as well as the irrigation water clearly indicating the effect of industrial effluents on the water quality. The drinking water samples from various localities in the control area have As in the range of 5.410-31.023 µg/L. Comparing with the drinking water from the polluted area this is comparatively low. Soil samples collected from various downstream points have As in the range of 1.971-31.206 µg/L. The dilution effect with increasing distance from the point sources is also clear from the results.

Mercury Hg concentration in all effluents, drinking water and soil samples was less than As concentration. Threshold concentrations for concern are somewhat ambiguous because of the complexity of Hg toxicity. USEPA maximum contaminant level (MCL)for Hg is 2µg/L ,Pakistan guidelines is 1µg/L ,Canada maximum acceptable concentration is 1µg/L, European Economic community maximum admissible concentration and Japan limit is 0.5 µg/L, World Health Organization guidelines for Hg is 1µg/L. Effluents, stream water and drinking water samples collected both from polluted area and control area have low level of mercury than the above mentioned permissible concentrations . There were only four sites in the polluted area where drinking water were found to have either equal or slightly higher Hg concentration than the Japan maximum admissible limit. Among them two samples were from the pharmaceutical industries where Hg is used for many applications such as for the production of antiseptic drugs, drinking water from the rubber factory where Hg compounds are used as catalyst and for the improvement of the qualities of the rubber and in the drinking water of the area where two individual streams from the industrial zone mixes to form a main stream showed high Hg concentration.

In case of the control area one of the stream water showed a slightly high Hg concentration than the Japanese standards which may be due to the disposal of hospital wastes. USEPA maximum contaminant level(MCL) for As is 50 µg/L, Pakistan guidelines is 5µg/L, Canada maximum acceptable concentration is 25µg/L, European Economic Community maximum admissible concentration is 50 µg/L, Japan maximum admissible concentration is 10µg/L and WHO guidelines are 10µg/L. As concentration in nearly all the effluents and drinking water samples is higher than the Canada ,Japan and WHO limits, Pakistan but in some samples it is within USEPA and European Economic Community permissible limits. Higher concentration of As was found in case of effluents from textile industry and woolen mill where As compounds are used for dyeng purposes and in glass factory effluents where As compounds are used for the improvement of glass quality. There also occurs dilution of both As and Hg with downstream as clear from the results. Highest concentration of As was found in case of mixing point of two effluent streams.

Drinking water samples collected form various industries and localities also have higher As concentration than the Japan, Pakistan, Canada and WHO limits. This clearly indicates the effect of effluents on the drinking water quality. The accumulation and settling of As and Hg compound on the soil is also evident from the As and Hg concentration which is going to decrease down stream. Stream water and drinking water collected from the control area have comparatively low As and Hg concentration compared to the polluted water samples.

Table-10 Mercury and Arsenic concentration (µg/L) of the effluents from different industries in the polluted area

Site	*Hg(µg/L)*	*As(µg/L)*
GI-1	0.184±0.0024	35.015±4.3281
GI-2	0.038±0.0052	18.783±3.0587
PM-1	0.331±0.0123	10.811±1.8721
PM-2	0.234±0.0018	33.569±5.6792
TI-1	0.117±0.0032	63.242±7.2321
TI-2	0.011±0.0023	28.962±4.3228
RI	0.310±0.0112	37.026±5.6621
GF	0.105±0.0083	57.768±8.2532
WM	0.209±0.0115	66.411±9.3218
PI	0.012±0.0035	35.875±8.3431
P*l*	0.086±0.0123	32.240±6.3241
PEPSI	0.061±0.0087	37.452±7.3218

Table-11 Mercury and Arsenic concentration (µg/L) of the effluents at different collection points downstream in the polluted area

Site	***Hg(µg/L)***	***As(µg/L)***
MBS-1	0.519±0.0324	60.963±4.3167
MBS-2	0.012±0.0032	25.334±6.3173
MS	0.635±0.0524	71.103±10.324
DSC-1	0.259±0.0322	42.363±3.2210
DSC-2	0.541±0.0331	24.675±2.3244
DSC-3	0.138±0.0221	22.421±4.3326
DSC-4	0.135±0.0524	20.103±10.324
DSC-5	0.071±0.0052	20.712±7.3522
DSC-6	0.108±0.0113	18.123±10.2331
DSC-7	0.011±0.0022	16.251±2.2415

Table-12 Mercury and Arsenic concentration (µg/L) of drinking water collected from different localities in the polluted area

Site	*Hg(µg/L)*	*As(µg/L)*
GI-1	0.021±0.0012	7.235±1.2351
PM-1	0.831±0.0331	4.195±5.3321
PM-2	0.592±0.0524	58.921±7.5571
RI	0.753±0.0675	42.521±4.6721
TI-2	0.171±0.3216	37.026±8.2413
TTC	0.039±0.0067	27.808±5.3217
GF	0.105±0.0234	49.126±7.3285
WM	0.511±0.0321	24.063±4.4321
MS	0.219±0.0189	24.473±5.2432
DSC-1	0.219±0.0331	35.315±6.5241
DSC-2	0.344±0.0354	38.811±7.3236
DSC-3	0.065±0.0032	28.512±4.3245
DSC-4	0.013±0.0033	37.294±6.3211

Table-13 Mercury and Arsenic concentration (µg/L) of the soil samples at different collection points downstream in the polluted area

Sites	***Hg(µg/L)***	***As(µg/L)***
MBS-1	0.117±0.0351	71.532±9.3251
MBS-2	0.181±0.0523	58.223±8.4252
MS	0.258±0.0135	55.630±4.3241
DSC-1	0.258±0.0332	46.832±6.2413
DSC-2	0.191±0.0225	42.523±3.1194
DSC-3	0.155±0.0231	38.698±4.3252
DSC-4	0.131±0.0325	35.192±7.5544
DSC-5	0.012±0.0021	27.201±8.2351
DSC-6	0.074±0.0032	20.108±7.3553
DSC-7	0.043±0.0054	17.698±8.2253

Table-14 Mercury and Arsenic concentration (µg/L) of streams water and downstream collection points in the control area.

Site	***Hg(µg/L)***	***As(µg/L)***
CS-1	0.011±0.0324	16.482±3.2421
CS-2	0.021±0.0232	9.551±0.6789
CS-3	0.001±0.0543	12.844±2.3821
CS-4	0.031±0.0523	14.361±1.9321
CS-5	0.089±0.0783	22.467±2.1195
CS-6	0.039±0.0583	16.112±0.0853
CS-7	0.083±0.0324	28.446±3.8652
CS-8	0.081±0.0245	38.321±6.3622
CMS-1	0.095±0.0441	30.586±5.8621
CMS-2	0.087±0.0024	25.304±4.2314

Table-15 Mercury and Arsenic concentration (µg/L) of drinking water collected from different localities in the control area

Site	*Hg(µg/L)*	*As(µg/L)*
CS-1	0.021±0.0011	31.023±4.3182
CS-2	0.019±0.0018	5.410±0.72812
CS-3	0.035±0.0076	16.708±3.4212
CS-4	0.045±0.0534	28.530±3.1242
CS-5	0.078±0.0771	24.621±5.2325
CS-6	0.033±0.0087	28.446±5.3324
CS-7	0.065±0.0213	17.523±3.6532
CS-8	0.015±0.0011	14.251±2.1041

Table-16 Mercury and Arsenic concentration (µg/L) in soil samples at different streams and collection points downstream in the control area

Sites	***Hg(µg/L)***	***As(µg/L)***
CS-1	0.834±0.0567	31.206±0.3216
CS-2	0.473±0.0785	28.751±4.2513
CS-3	0.418±0.0543	27.981±0.7215
CS-4	0.338±0.0753	17.914±0.0835
CS-5	0249±0.0721	10.835±2.3245
CS-6	0.219±0.0083	7.325±1.1124
CS-7	0.084±0.0054	1.971±0.3224
CMS-1	0.093±0.0035	05.017±3.9215
CMS-2	0.077±0.0025	05.288±6.3078

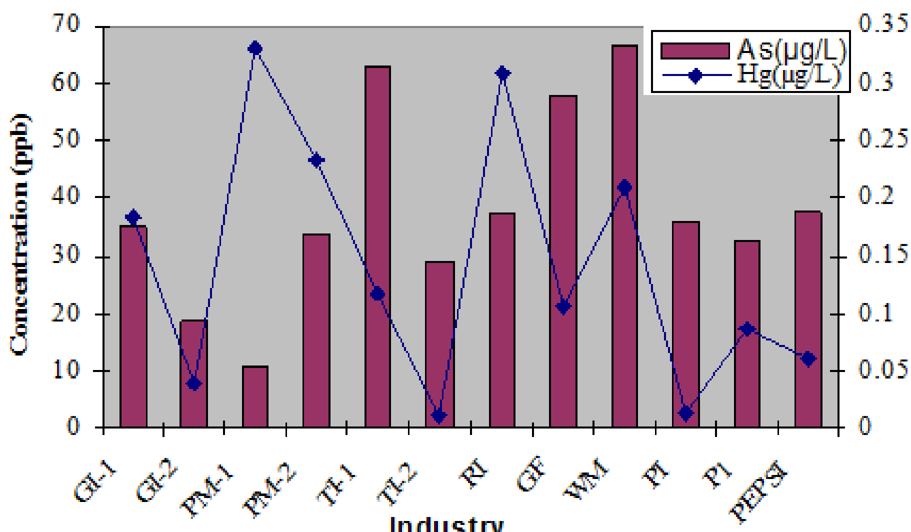

Fig.2. Arsenic and mercury concentration (ppb) in different industrial effluents

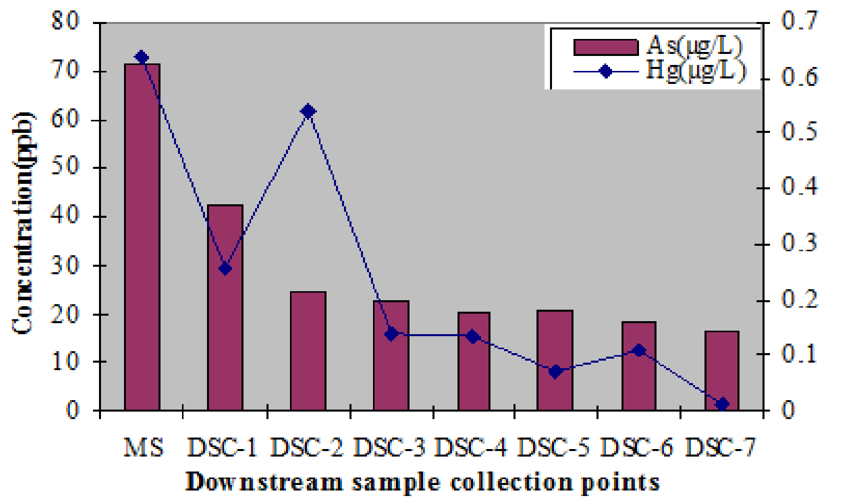

Fig.3. Variation of Arsenic and mercury concentration(ppb) in effluent stream with increasing distance from the point sources

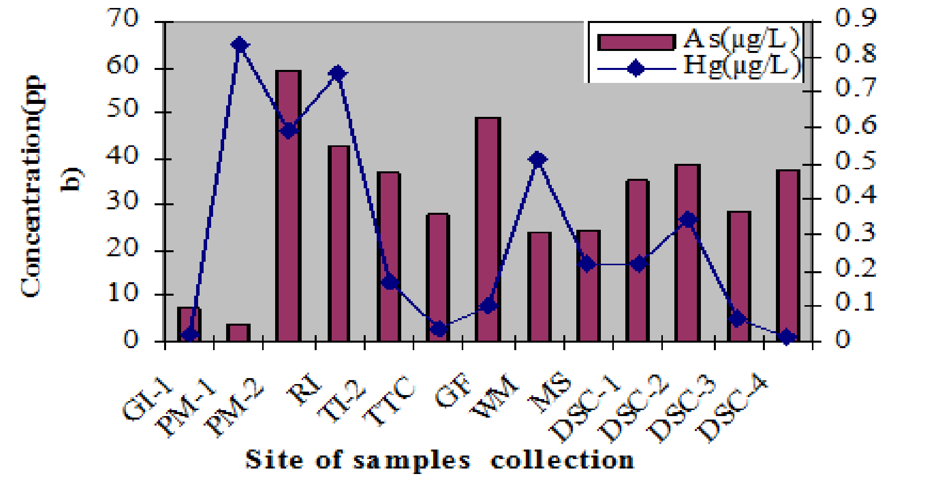

Fig.4. Arsenic and mercury concentration (ppb) in drinking water collected from different industries and localities in the polluted area

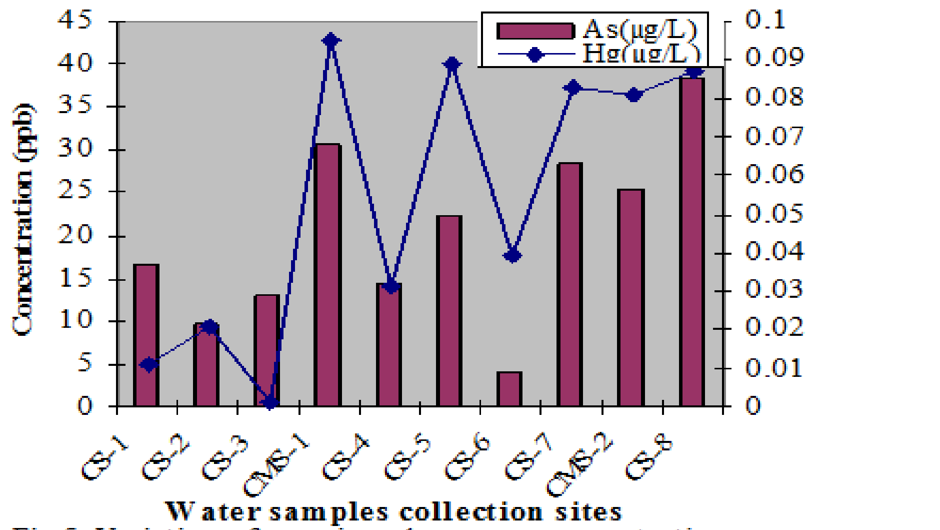

Fig.5. Variation of arsenic and mercury concentration (ppb) in different stream and their mixing sites in the controle area

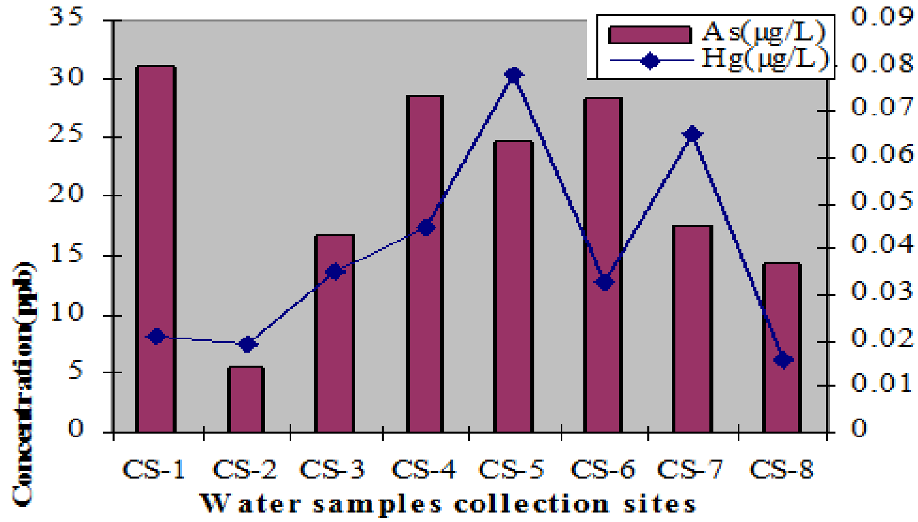

Fig.6. Arsenic and mercury concentration(ppb) in drinking water collected from different localities in control area

3.2 Use of multivariate statistical techniques for the source identification, distribution pattern, classification of point sources and effects of pollutants i.e. heavy metals Cr, Mn ,Zn, Cd, Pb, Ni, Cu and Co) on the soil and ground water quality.

The mean values of metal concentrations of the effluents of different industries has been presented in the Table 17 while statistical summary of selected metal concentration in different industrial effluents has been presented in Table 18. These data represent a total of 36 samples that correspond to 12 industries. From the data on metal distribution in industrial effluents, it is clear that Cd, Pb and Ni are the dominant metals with high mean concentration of Mn 6.849 mg/L followed by Pb 2.440 mg/L, Ni 0.479 mg/L, Cd 0.192 mg/L and then Cr 0.100 mg/L respectively. The order of distribution is Mn>Pb>Ni>Cd. The mean values of metal concentration of the effluents from different down steam points and ground water have been presented in the Table 19, 20, while the statistical summary of metal concentration in the three media (effluents from different down stream points, soil and water) from the polluted area is given in the table 21.

Table – 17 Mean concentrations of heavy metal (mg/L) in the effluents of different industries

Site	*Cr*	*Mn*	*Zn*	*Cd*	*Pb*	*Ni*	*Cu*	*Co*
GI-1	0.001	1.452	0.059	0.013	1.147	0.684	0.098	0.012
GI-2	0.016	3.909	0.077	0.031	3.949	0.286	0.313	0.431
PM-1	0.002	0.573	0.052	0.011	1.484	0.702	0.108	0.007
PM-2	0.004	0.081	0.081	0.015	1.62	0.701	0.114	0.012
TI-1	0.006	25.24	0.039	0.015	1.992	0.701	0.106	0.018
TI-2	0.006	0.436	0.043	0.023	2.308	0.63	0.116	0.014
RI	1.125	0.028	0.016	2.048	0.663	0.14	0.014	0.014
GF	0.008	0.475	0.041	0.022	2.687	0.548	0.173	0.016
WM	0.011	31.45	0.043	0.026	2.839	0.488	0.199	0.015
PI	0.008	6.749	0.111	0.034	2.943	0.459	0.203	0.033
P*l*	0.007	4.945	0.277	0.028	3.558	0.302	0.218	0.183
PEPSI	0.015	0.884	0.045	0.032	4.095	0.111	0.26	0.516

Table – 18 Statistical summary of selected metals concentrations in different industrial effluents (*n* =36)

Metals	*Industies*			
	Minimum	**Maximum**	**Mean**	**Std. Deviation**
Cr(mg/L)	0.001	1.125	0.1007	0.322
Mn(mg/L)	0.028	31.450	6.849	10.578
Zn(mg/L)	0.016	0.277	0.073	0.068
Cd(mg/L)	0.011	2.048	0.1912	0.585
Pb(mg/L)	0.663	4.095	2.440	1.102
Ni(mg/L)	0.111	0.702	0.479	0.221
Cu(mg/L)	0.014	0.313	0.160	0.083
Co(mg/L)	0.007	0.516	0.106	0.179

Industries:
Industries
GI-------Ghee Industry
PM------ Pharmaceutical Industry
TI-------- Textile Industry
RI--------Rubber Industry
GF--------Glass Factory
WM-------Woolen Mill
PI--------Paper Industry
P*l*--------Plastic Industry
PEPSI

Table – 19 Mean concentrations of heavy metal (mg/L) in the effluents of different down stream points

Site	*Cr*	*Mn*	*Zn*	*Cd*	*Pb*	*Ni*	*Cu*	*Co*
MBS-1	0.003	0.02	0.039	0.012	1.213	0.685	0.099	0.014
MBS-2	0.007	3.26	0.05	0.029	3.924	0.227	0.214	0.207
MS	0.007	14.24	0.046	0.031	3.275	0.395	0.1 83	0.038
DSC-1	0.011	3.549	0.063	0.028	3.757	0.313	0.222	0.202
DSC-2	0.007	84.81	0.063	0.032	3.166	0.391	0.22	0.082
DSC-3	0.013	7.319	0.034	0.03	3.389	0.345	0.242	0.089
DSC-4	0.017	1.147	0.03	0.038	4.328	0.078	0.247	0.647
DSC-5	0.017	1.452	0.03	0.04	4.662	0.029	0.259	0.776
DSC-6	0.017	1.221	0.039	0.037	4.621	0.204	0.247	0.715
DSC-7	0.016	1.083	0.03	0.035	4.148	0.18	0.24	0.574

Table – 20 Mean concentrations of heavy metal (mg/L) in drinking water from different sites in polluted area

Site	*Cr*	*Mn*	*Zn*	*Cd*	*Pb*	*Ni*	*Cu*	*Co*
GI-1	0.006	4.439	0.517	0.009	1.04	0.628	0.127	0.073
PM-1	0.003	2.073	0.128	0.013	1.616	0.713	0.096	0.016
PM-2	0.005	0.172	0.186	0.016	1.811	0.74	0.089	0.013
RI	0.007	0.479	0.082	0.019	2.241	0.654	0.13	0.015
TI-2	0.008	0.275	0.088	0.024	2.558	0.553	0.137	0.015
TTC	0.012	6.793	0.199	0.032	3.535	0.203	0.235	0.071
GF	0.009	0.482	0.067	25	2.774	0.54	0.196	0.015
WM	0.011	0.496	0.19	0.029	2.893	0.491	0.179	0.016
MS	0.006	1.258	0.042	0.047	4.951	0.021	0.279	0.825
DSC-1	0.013	4.973	0.034	0.045	4.969	0.002	0.26	0.9
DSC-2	0.008	3.768	0.926	0.044	5.497	0.194	0.758	1.144
DSC-3	0.046	79.85	0.0803	0.0803	0.0803	0.08	0.08	0.08
DSC-4	0.009	2.427	0.108	0.043	4.704	0.001	0.25	0.796

From the data it is clear that with downstream points the metal distribution follows the same order as in case of the different industrial effluents. The highest mean concentration was of Mn 11.810 mg/L followed by Pb 3.748 mg/L and Ni 0.542 mg/L respectively while Co mean concentration exceeded the Cu and Cd concentration that is 0.734mg/L .The order of distribution is Mn>Pb>Ni>Co>Cu>Cd. Chromium mean concentration in case of effluents from different industries as well as different down stream points was found low that was 0.100 mg/L and 0.015 mg/L respectively. In soil samples from polluted area along downstream points at increasing distances from the point sources, Mn mean concentration was found that is 130.452 mg/L followed by Pb 5.680 mg/L,Co 1.286 mg/L,Zn 0.685 mg/l,Cu 0.507 mg/L, Cd 0.157 mg/L and Ni 0.152 mg/L respectively. The order of distribution is Mn>Pb>Co>Zn>Cu>Cd>Ni. The ground water owing to high mean concentration of Mn in the effluent has high Mn contents of 8.268 mg/L followed by Pb 2.974 mg/L, Cd 1.954 mg/L, Ni 0.371 mg/L, Co 0.306 mg/L Cu 0.217 mg/L and Zn 0.204 mg/L, respectively. The order of distribution is n>Pb>Cd>Ni>Co>Cu>Zn. The obvious sources of dominant metals Mn,Pb Ni,Co in these effluents are their respective compounds which are used in the industries for various purposes i.e. as catalysts, modifiers and dyers, etc. The downstream dilution was also noticed from our results in case of effluents and soil samples at increasing distances from the point sources.

Table – 21 Statistical summary of selected metals concentrations in the effluents, soil, and drinking water samples from polluted (*n* =30 each)

	Effluents				*Soil*				*Drinking water*			
Element	**Minimum**	**Maximum**	**Mean**	**Std. Deviation**	**Minimum**	**Maximum**	**Mean**	**Std. Deviation**	**Minimum**	**Maximum**	**Mean**	**Std. Deviation**
Cr(mg/L)	0.003	0.043	0.015	0.012	0.040	0.068	0.053	0.009	0.003	0.046	0.011	0.010886
Mn(mg/L)	0.020	84.810	11.810	25.999	84.743	159.710	130.452	23.858	0.172	79.850	8.268	21.61151
Zn(mg/L)	0.025	0.123	0.051	0.028	0.281	2.937	0.685	0.803	0.034	0.926	0.204	0.25039
Cd(mg/L)	0.012	0.052	0.032	0.012	0.032	0.591	0.157	0.227	0.009	25.000	1.954	6.924504
Pb(mg/L)	1.213	4.662	3.748	1.016	4.321	6.304	5.68	0.608	0.080	5.497	2.974	1.674047
Ni(mg/L)	0.029	1.953	0.542	0.572	0.007	0.388	0.152	0.1286	0.001	0.740	0.371	0.290853
Cu(mg/L)	0.026	2.183	0.440	0.632	0.341	0.640	0.507	0.097	0.080	0.758	0.217	0.176431
Co(mg/L)	0.014	3.038	0.734	0.894	1.057	1.534	1.286	0.148	0.013	1.144	0.306	0.431395

The mean values of metal concentration in stream, soil and ground water from different sites have been presented in table 22,23 while the statistical summary of mean metals concentration in different streams water, soil and ground water samples from the control area have been given in the table 24.

Table – 22 Mean concentrations of heavy metal (mg/L) in water from different streams in relatively less polluted area

Site	*Cr*	*Mn*	*Zn*	*Cd*	*Pb*	*Ni*	*Cu*	*Co*
CS-1	0.067	0.048	0.001	0.051	0.726	0.034	0.013	0.090
CS-2	0.305	0.102	0.007	0.089	1.054	0.088	0.012	0.158
CS-3	0.181	0.063	0.006	0.062	0.695	0.057	0.015	0.109
CS-4	0.038	0.051	0.001	0.047	0.624	0.016	0.012	0.058
CS-5	0.306	0.108	ND	0.092	1.118	0.098	0.011	0.151
CS-6	0.128	0.024	ND	0.02	0.358	0.034	0.006	0.063
CS-7	0.018	0.038	ND	0.047	0.643	0.01	0.011	0.068
CS-8	0.109	0.047	0.001	0.055	0.756	0.042	0.014	0.087

Table – 23 Mean concentrations of heavy metal (mg/L) in drinking water from different sites in relatively less polluted area

Site	*Cr*	*Mn*	*Zn*	*Cd*	*Pb*	*Ni*	*Cu*	*Co*
CS-1	0.172	0.066	0.092	0.015	0.233	0.009	0.002	0.002
CS-2	0.002	0.033	0.02	0.043	0.682	0.013	0.01	0.082
CS-3	0.034	0.029	0.017	0.03	0.63	0.036	0.009	0.089
CS-4	0.09	0.031	0.003	0.035	0.499	0.004	0.007	0.076
CS-5	0.289	0.077	0.008	0.088	1.01	0.092	0.01	0.147
CS-6	0.264	0.106	0.411	0.105	1.141	0.088	0.006	0.128
CS-7	0.272	0.079	0.011	0.103	0.826	0.088	0.009	0.117
CS-8	0.212	0.069	0.002	0.071	0.827	0.077	0.017	0.121

Table – 24 Statistical summary of selected metals concentrations in the stream water, soil and drinking water samples from control area (*n* =30 each)

	Stream Water				*Soil*				*Drinking water*			
Element	**Minimum**	**Maximum**	**Mean**	**Std. Deviation**	**Minimum**	**Maximum**	**Mean**	**Std. Deviation**	**Minimum**	**Maximum**	**Mean**	**Std. Deviation**
Cr(mg/L)	0.018	0.306	0.144	0.112	0.043	0.773	0.256	0.234	0.018	0.306	0.167	0.113
Mn(mg/L)	0.024	0.108	0.060	0.0299	0.861	7.384	3.148	2.009	0.024	0.108	0.061	0.028
Zn(mg/L)	0.000	0.007	0.002	0.003	0.334	1.811	0.672	0.474	0.000	0.007	0.070	0.140
Cd(mg/L)	0.020	0.092	0.058	0.023	0.083	0.148	0.111	0.0216	0.020	0.092	0.061	0.035
Pb(mg/L)	0.358	1.118	0.747	0.243	1.677	2.560	2.006	0.312	0.358	1.118	0.731	0.288
Ni(mg/L)	0.010	0.098	0.047	0.032	0.254	0.582	0.359	0.123	0.010	0.098	0.051	0.039
Cu(mg/L)	0.006	0.015	0.012	0.003	0.014	0.025	0.018	0.004	0.006	0.015	0.009	0.004
Co(mg/L)	0.058	0.158	0.098	0.039	0.239	0.378	0.27	0.043	0.058	0.158	0.095	0.045

The overall mean metal concentration in the three media is quite low compared to the polluted area. Highest Pb mean concentration was found in case of stream water 0.747 mg/L which can be attributed to the discharge of effluents from service stations in the area, followed by Cr which can be attributed to the natural enrichment due to weathering. The other mean metals concentration in these cases was found low. Soil samples showed reasonably high mean metal concentration compared to stream water which clearly indicate the sources of metals by the adjacent soil matrix.Mn mean concentration in soil was 3.148 mg/L followed by Pb 2.006 mg/L ,Zn 0.672 mg/L ,Ni 0.359 mg/l and Cr 0.256mg/L respectively. In ground water samples the mean metals concentration compared to stream water and corresponding soil was found low with the exception of Pb 0.731 mg/L which can be attributed to the service stations ,natural enrichment process, wood and low grade coal combustion in homes. Comparison was also done between mean metal concentration in the ground water sample from the polluted area and the corresponding metal levels in the samples from the background area control area as well as with the WHO safe limits. From the figure 7 and 4 it is clear that some metals like Cr, is higher in mean concentration in ground water sample from control area than the polluted area as well as WHO safe limits while Zn and Pb were found higher than the WHO safe limits but lower than the corresponding metals levels in the polluted area. This can be attributed to the metal enrichment depending on individual metal soil chemistry.

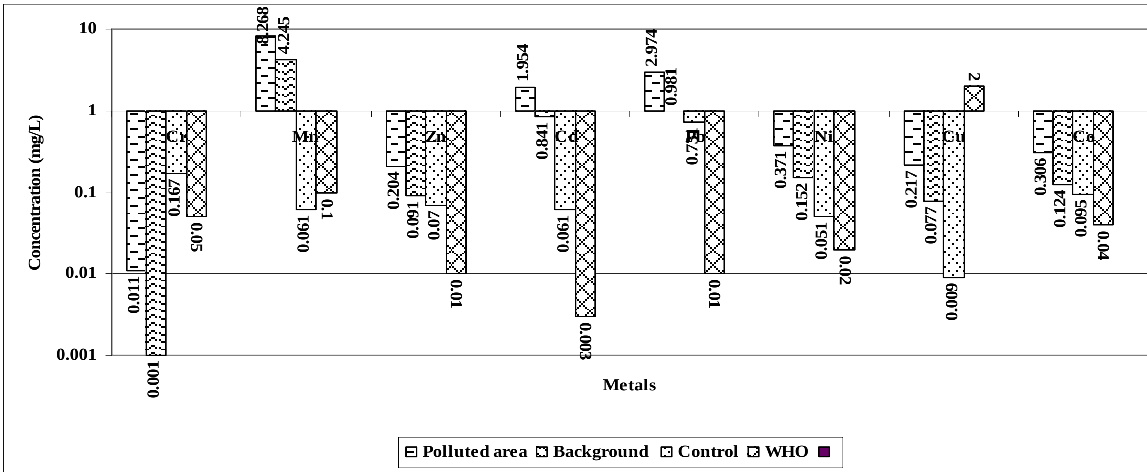

Fig.7 Comparison average metal level in ground water based on present study vs Background level ,Controle and WHO safe limits

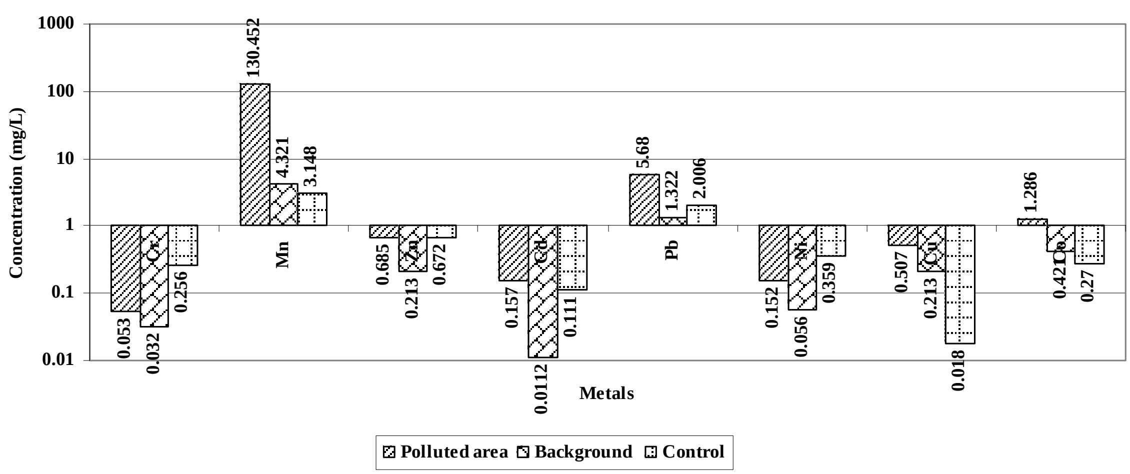

Fig.8 Comparison of average metal level in soil based on present study vs Background level, Control samples

The statistical comparison of the pollution of different industrial effluents using one way ANOVA (Table 25) showed no statistical difference (p=0.658) which indicate that all these industries contribute equally to the mean metals concentrations in the main effluents stream . Cluster analysis using complete linkage method classified various industries into two broad groups and a minor group (Dendogram in figure 9).

Table – 25 ANOVA table for comparison of Industries with regards to selected metals pollution

Source of Variation	*Sum of Squares*	*df*	*Mean Square*	*F*	*p-value*
Between Industries	154.312	11	14.028	0.781	0.658
Within industries	1508.282	84	17.956		
Total	1662.594	95			

The first broad group comprised of industries(TI-2,GF,PM-1,PM-2,GI-1,PEPSI and RI) the second group of industries(GI-2,PI,and P*l*) and the third minor group comprised of(TI-1 and WM)The statistical correlation study pertaining to metal-to metal relationship in the three media was conducted on mutual inclusive basis. It should be kept in mind that each downstream collection point was considered as separate pollution source of soil and ground water of the nearest location.

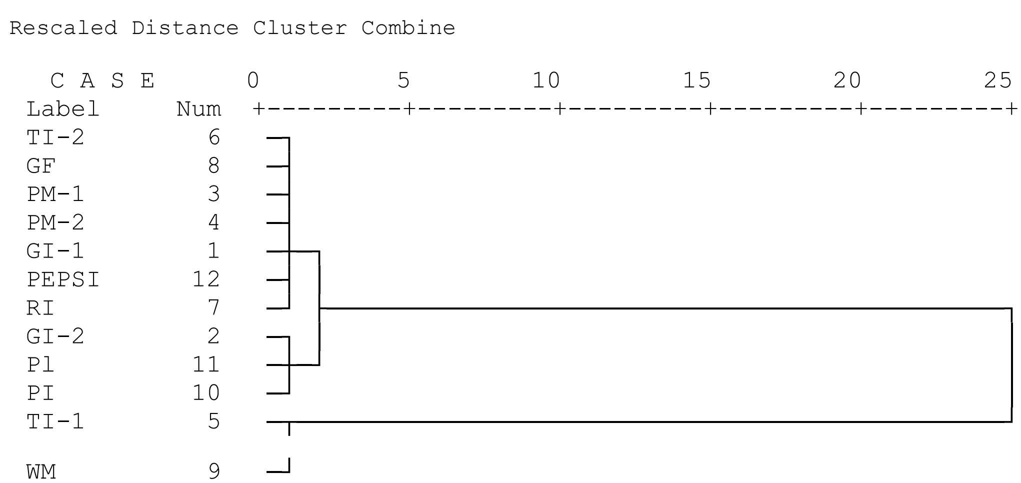

Fig. 9 Dendogram of selected metals in different industrial effluents using complete linkage Method

In order to know about the effect of these effluents on the surrounding soil and ground water correlation study between metals was undertaken which was further supported by principal components analysis. In case of effluents samples from different downstream points, the correlation coefficient evaluation yielded r value ≥0.492 or =-0.492 as significant at p<0.001 revealing that there was a significant correlation between Pb and Cr(r=0.597) and Pb and Cd (r=0.685) in the effluents from different downstream points as shown in the table 26

Table – 26 Linear correlation coefficient matrix for selected metals in the effluents samples form different downstream points (*n*=30)

	Cr	***Mn***	***Zn***	***Cd***	***Pb***	***Ni***	***Cu***	***Co***
Cr								
Mn	0.873							
Zn	0.953	0.913						
Cd	-0.033	-0.459	-0.213					
Pb	0.597	0.245	0.410	0.685				
Ni	0.844	0.897	0.938	-0.388	0.125			
Cu	0.869	0.985	0.916	-0.435	0.266	0.901		
Co	0.942	0.906	0.956	-0.123	0.486	0.901	0.934	

*r-values≥0.492 or =-0.492 are significant at P<0.05

For soil matrix the correlation study showed positive relationship between pairs of metals (Table 27) like Cd and Mn(r=0.553) Ni and Mn(r=0..629) Cu and Mn(r=0.580) Cu and Cd(r= 0.706) Co and Cr (0.617) Co and Zn(r=0.656) and Co and Cu (0.658) Cd concentration related to Cr in the effluent samples and to Cu in the soil samples indicates high dependent concentration levels of metals in the two media . Third correlation aspect of metals pair was found in ground water (table 28) showing that there is significant correlation between Pb and Mn(r= 0.492) Ni and Pb(r=0.596). A cross correlation study between effluents and soil multiple correlation showed that in effluent soil system Cr and Zn (r=0.650) Cd and Cr (r= 0.669, Cd and Mn (r=0.763) Cd and Ni (r=0.664) Cu and Cr (r=0717) Cu and Zn (r=0.691) and Co and Ni (r=0.680) are strongly correlated . In case of effluent and water system the correlation between Zn and Pb (r=0.771) Cu and Zn (r=0.640) and Cu and Ni (r=0.639) were found to be positive.

Table – 27 Linear correlation coefficient matrix for selected metals in the soil samples form different downstream points (*n*=30)

	Cr	*Mn*	*Zn*	*Cd*	*Pb*	*Ni*	*Cu*	*Co*
Cr								
Mn	0.720							
Zn	0.074	0.534						
Cd	0.852	0.553	-0.038					
Pb	0.074	0.112	-0.172	0.126				
Ni	0.534	0.629	0.383	0.242	0.296			
Cu	0.924	0.580	0.132	0.706	-0.052	0.535		
Co	0.617	745	0.656	0.391	-0.263	0.417	0.658	

*r-values≥0.492 or =-0.492 are significant at P<0.05

Table – 28 Linear correlation coefficient matrix for selected metals in the drinking water samples form different localities in polluted area (*n*=30)

	Cr	*Mn*	*Zn*	*Cd*	*Pb*	*Ni*	*Cu*	*Co*
Cr								
Mn	0.973							
Zn	-0.171	-0.113						
Cd	-0.053	-0.106	-0.164					
Pb	-.0391	-0.492	0.206	-0.036				
Ni	-0.430	-0.344	0.036	0.173	-0.596			
Cu	-0.168	-0.200	0.742	-0.034	0.742	-0.435		
Co	-0.092	-0.124	0.362	-0.202	0.842	-0.738	0.781	

*r-values≥0.492 or =-0.492 are significant at P<0.05

Correlation study conducted for soil water system showed a strong positive correlation between various pairs of metals including Cu, Mn, Cd, Zn, Ni , Cr,and Co. The study based on metal to metal correlation was further sustained by linear regression data in the table 23, which list significant linear regression equations in terms of pairs of metals for three media . For finding the source identification of metals concentration in the three media and interpretation of correlation study principle components analysis using varimax normalized rotation for the three media was conducted which is given in tables (30,31,32).

Table – 29 Significant correlation and linear regression analysis for effluents, soil and water samples from polluted area (n=99)

Matrix	*Regression equation*	*Correlations (r)*
Effluents	[Pb]=51.025[Cr]+2.978	0.597
	[Pb]=58.649[Cr]+1.898	0.685
Soil	[Co]=10.739[Cr]+0.718	0.517
	[Cu]=0.0023{Mn]0.200	0.580
	[Co]=0.121[Zn]+1.204	0.656
	[Cu]=0.301[Cd]+0.460	0.706
	[Co]=1.007[Cu]+0.776	0.658
Water	[Pb]= 0.038[Mn]+3.289	0.492
	[Ni]=-0.104[Pb]+0.679	0.596

It should be noted that significant correlation means the existence of a strong relationship between two metals while incase of regression significant results indicates the high dependence of one metal over the other. PCA was applied to extract factor loading in each media. In case of effluents PCA extracted two factors together, embodying 96% of total variance. The contribution by the two factors is 72.506% and 23.238% respectively. Principal component loading for soil sample extracted three factors. The %age of total variance being 86% the contribution of each factor being 42.586% and 28.755% and 14.460% towards the total variance respectively. Pricinple component loading for ground water extracted three components with % age of total variance of 87% with the contribution of each factor being 52.941%,1 9.498% and 14.866% respectively.

Table – 30 Principal Component loadings (Varimax Normalization) for metals in the effluents samples form different downstream points (*n*=30)

	Factor 1	*Factor 2*
Cr	0.941	0.294
Mn	0.971	-0.138
Zn	0.978	0.093
Cd	-0.316	0.924
Pb	0.350	0.910
Ni	0.945	-0.158
Cu	0.976	-0.114
Co	0.969	0.177
Eigen values	5.80	1.859
% total variance	72.506	23.238
Cumul. %	72.506	95.743

Table –31 Principal Component loadings (Varimax Normalization) for metals in the drinking water samples form different localities (*n*=30)

	Factor 1	*Factor 2*	*Factor 3*
Cr	0.021	0.412	0.034
Mn	-0.034	0.414	0.116
Zn	-0.151	-0.027	0.686
Cd	0.065	-.0111	-0.336
Pb	0.345	-0.139	-0.170
Ni	-0.368	-0.218	0.197
Cu	0.146	-0.036	0.318
Co	0.311	0.018	0.022
Eigen values	3.407	2.300	1.158
% total variance	42.586	28.755	14.480
Cumul. %	42.586	71.341	85.821

Table –32 Principal Component loadings (Varimax Normalization) for metals in the soil samples form different downstream points (*n*=30)

	Factor 1	*Factor 2*	*Factor 3*
Cr	0.328	-0.087	-0.002
Mn	0.063	0.248	0.127
Zn	-0.231	0.515	-0.042
Cd	0.363	-0.208	-0.029
Pb	-0.061	-0.041	0.736
Ni	-0.040	0.258	0.410
Cu	0.305	-0.053	-0.092
Co	0.067	0.285	-0.228
Eigen values	4.235	1.560	1.189
% total variance	52.941	19.498	14.866
Cumul. %	52.941	72.440	87.306

Discussion

In order to find out the contribution of different industries toward metals pollution in the main effluent stream, statistical comparison which compared different industries in terms of metals as variables yielded no significant difference between different industries with the p=0.0.658.This indicate that these industries contribute equally in terms of selected metals pollution. The cluster analysis using complete linkage method was followed in order to put industries of equal metal pollution efficiencies, grouped industries into two broad groups and a minor group. From the data it is clear that Mn ,Pb,Cd,Co are the dominant elements in the effluents soil and ground water their concentration is higher in case of soil samples compared to water samples as indicated in the previous studies(109,110)

This study also reveals moderately high concentration in effluents and low concentration in water samples. The order of metals distribution in the three media is Soil>effluents>water.

The effluents stream accumulate a large influx of metals in the surrounding soil in the vicinity through which it passes by, which causes the contamination of the ground water of the area nearby. Our observation is also supported by the mean metals concentration of the ground water in polluted area and metal concentration in water from background area and control area as indicated in figure 7.The order of distribution of mean metals concentration in the effluents samples is Mn>Pb>Ni>Co>Cu>Cd while small variation was observed in case of soil samples where the distribution order was Mn.Pb.Co>Zn>Cu>Cd>Ni. Ni and Zn, Co and Cu and Cu and Cd have changed their ranking positions this could be explained on the basis of possible chemical exchange process among atoms under given prevailing conditions of pH and temperature (111).This high concentration level of metals in soil samples in the polluted area was compared with the soil samples from the background and control area.This clearly supported our view that soil sample in the vicinity of the polluted stream accumulates high concentration of metals like Mn.Pb,Ni,Cd,Co and Zn than the WHO limits. In case of control soil, samples only Mn and Pb were found to have high mean concentration which can be attributed to the weathering of rocks natural enrichment or other physical and chemical processes. The metal to metal correlation study in the effluent data showed that the mean concentration of Pb,Cr and Cd mutually depends on each other. Incase of soil strong correlation was observed between Cd,Mn,Ni,Cu,Zn,Co.It indicates that their compounds are used in various industries for various purposes . Cd showed a strong correlation to Cu, Mn in the soil media while to Cr and Pb in the effluent media . In ground water strong correlation was noticed in Pb and Mn(r=0.492)Ni and Pb (r=0.596) This indicate the ground water system is influenced by relation between these metals pairs A cross correlation study between effluents and soil multiple correlation showed that in effluent soil system Cr and Zn (r=0.650) Cd and Cr (r= 0.669, Cd and Mn (r=0.763) Cd and Ni (r=0.664) Cu and Cr (r=0717) Cu and Zn (r=0.691) and Co and Ni (r=0.680) are strongly correlated . In case of effluent water system the correlation between Zn and Pb (r=0.771) Cu and Zn (r=0.640) and Cu Ni (r=0.639) were found to be positive. Correlation study conducted for soil water system showed a strong positive correlation between various pairs of metals including Cu, Mn, Cd, Zn, Ni , Cr,and Co. It can be pointed out from the results that the soil system rich in these metals can substantially affect the quality of ground water. Our metal to metal correlation was further supported by linear regression analysis interms of linear regression equations (table 29) which supports the correlation co-efficient analysis earlier described in terms of correlation dependence of various metals pairs like Pb-Cr,Pb-Cd,Cd-Mn,Ni-Mn,Cu-Cd,Co-Cr, Co-Zn Pb-Mn and Ni-Pb etc. The PCA which reduces a large number of variable into a new set of variables based on their mutual dependence. PCA using varimax normalized rotation was used for factor loading in the three media. In case of effluents the factor analysis extracted two factors embodying together 96% of total variance.The contribution of the first factor was 72.506%which shows high loading for Zn,Cu,Mn,Co,Ni,Cr, with significant loading for Pb which indicate the use of these chemicals in the various industries under study. Factor 2 contributed for 23.238% of toal variance showed maximum loading for Cd,Pb,Cr and significant loadings for Co,Mn,Ni ,Cu manifesting common source of these chemicals in various industries. In case of soil samples(table 32) three factors were extracted with a total variance of 86% with the contribution of the first factor 42.586% of the total variance showed maximum loadings for Ni,Pb,Co and significant loadings for the Cu and Zn probably originating in the soil from the effluents along with other factors such as soil texture,natural enrichment process etc. Factor 2 contributed 28.755% of the total variance with maximum loadings for Mn,Cr,Ni and significant loadings for Cd and Pb which can be attributed to the effluents. Factor 3 contributed 14.480% of the total variance with the loadings for Zn Cd,Cu and significant loadings for Ni,Mn and Pb originating from the industrial effluents which contaminate the adjacent soil. The PCA factor loading for ground water (table 31) also extracted three factors with a total variance of 87 % the contribution of the first factor 52.941% to the total variance with maximum loadings for Cd,CuCr and siginificant loadings for the Zn showing water soluble metals from the soil and effluents. Factor 2 contributed 19.498% to the total variance showed maximum loading for Zn,Co,Ni, which mainly originate from industrial effluents. Factor 3 contributed 19.866% of the total variance with maximum loading for Pb,Ni and significant for Co and Mn is assumed to originate from the soil contaminated by effluents. The correlation and principal component analysis study of the results indicate that the soil and the ground water in the surrounding of effluent stream is contaminated by the effluents. Our study is in good agreement with the earlier studies (112-113).

3.3 Evaluation of the effects of wastewater irrigation on the phytovailability of metals in the agricultural soil and their uptake by the food crops and its associated human health risk.

3.3.1 Soil fractionation

Table-33 summarizes different fractions of heavy metal concentrations in soil samples collected from wastewater irrigated, background and control sites. The data show that the phytoavailable fraction of Zn in the polluted soil was 40.94 mg/kg which was significantly higher as compared to background (10.08 mg/kg) and control soils (4.1 mg/kg). Phytoavailable Cd concentration was 0.87 mg/kg, 0.11 mg/kg and 0.1 mg/kg in wastewater irrigated, background and control soils, respectively. Pb phytoavailable concentration was 0.4mg/kg in wastewater irrigated, 0.30 mg/kg in background and 0.13 mg/kg in control soils. Similarly, Ni bioavailable concentration was 10.54 mg/kg, 3.54 mg/kg and 1.26 mg/kg in wastewater irrigated, background and control soils, respectively. In wastewater irrigated soil, the Cu phytoavailable concentration was 20.84 mg/kg, while13.03 mg/kg in background soil and 4.69 mg/kg in control soil. Furthermore, the Cr phytoavailable concentration was 1.65 mg/kg in the wastewater irrigated soil, 1.28 mg/kg in background and 0.2 mg/kg in control soils. Mn available concentration was 37.46 mg/kg in the wastewater irrigated soil, 18.08

mg/kg in background and 7.62 mg/kg in control soil. However, the total metal contents of the soil of the selected areas are also given in Table-34.

Table – 33 Mean values (mg/kg) of different fractions of heavy metals in soils collected from study areas

Fractions	***Zn***		***Cd***		***Pb***		***Ni***		***Cu***		***Cr***		***Mn***	
Polluted soil														
Water soluble + Exchangeable	15.50	(24.21)	0.06	(0.50)	0.21	(1.40)	5.12	(9.42)	8.32	(21.68)	0.31	(1.02)	12.56	(10.53)
Pb displaceable	14.92	(23.31)	0.03	(0.25)	0.11	(0.73)	4.11	(7.57)	7.12	(18.56)	0.08	(0.26)	14.1	(11.82)
Acid soluble	10.52	(16.43)	0.78	(6.50)	0.32	(2.13)	1.31	(2.41)	5.40	(14.07)	1.26	(4.24)	10.8	(9.06)
Organically bound	8.11	(12.66)	0.02	(0.16)	0.05	(0.33)	0.72	(1.34)	0.93	(2.42)	8.32	(27.72)	7.9	(6.62)
Mn-oxide occluded	2.42	(3.78)	0.54	(4.59)	5.61	(37.41)	10.3	(18.92)	0.11	(0.28)	6.72	(22.47)	6.4	(5.37)
Fe-oxide occluded	5.34	(8.34)	5.54	(46.24)	2.60	(14.17)	4.51	(7.87)	4.00	(10.42)	3.2	(10.71)	6.2	(5.20)
Residual	6.42	(10.03)	5.01	(41.81)	6.10	(40.66)	28.2	(49.24)	11.7	(30.50)	10	(32.84)	60	(50.32)
Background soil														
Water soluble + Exchangeable	1.91	(5.39)	0.01	(0.16)	0.07	(0.64)	2.09	(4.44)	0.42	(1.68)	0.10	(0.33)	3.45	(3.95)
Pb displaceable	4.75	(13.41)	0.03	(0.49)	0.01	(0.09)	1.2	(2.55)	6.4	(25.64)	0.08	(0.26)	8.32	(9.52)
Acid soluble	3.42	(9.65)	0.07	(1.15)	0.22	(2.05)	0.25	(0.53)	6.21	(24.87)	1.10	(3.61)	6.31	(7.23)
Organically bound	7.21	(20.36)	0.12	(1.90)	0.01	(0.09)	0.52	(1.4)	0.11	(0.44)	6.31	(21.22)	6.31	(7.23)
Mn-oxide occluded	0.35	(0.98)	0.32	(5.26)	2.40	(22.41)	12.03	(25.57)	0.05	(0.20)	5.23	(17.59)	6.32	(7.24)
Fe-oxide occluded	4.72	(34.76)	2.22	(36.53)	0.77	(7.24)	1.92	(4.08)	1.99	(7.97)	2.91	(9.76)	5.91	(6.760
Residual	12.31	(34.76)	3.31	(54.44)	7.20	(67.41)	29.02	(61.71)	9.23	(36.98)	14	(47.09)	50	(57.25)
Control soil														
Water soluble+ Exchangeable	0.58	(2.54)	0.02	(0.35)	0.04	(0.60)	1.09	(3.33)	0.19	(1.17)	0.05	(0.23)	1.97	(3.51)
Pb displaceable	2.20	(9.62)	0.03	(0.53)	0.07	(1.12)	0.09	(0.27)	4.45	(27.43)	0.02	(0.08)	0.33	(0.58)
Acid soluble	1.32	(5.77)	0.05	(0.89)	0.02	(0.32)	0.08	(0.24)	0.05	(0.31)	0.75	(3.26)	5.32	(9.49)
Organically bound	3.32	(14.51)	0.11	(1.97)	0.15	(2.42)	0.10	(0.30)	0.07	(0.43)	2.33	(10.09)	1.21	(2.16)
Mn-oxide occluded	0.07	(0.30)	0.81	(14.56)	1.22	(19.56)	8.55	(26.17)	0.03	(0.18)	6.51	(28.02)	5.98	(10.67)
Fe-oxide occluded	4.52	(19.76)	0.32	(5.73)	0.55	(8.82)	0.53	(1.65)	0.93	(5.73)	3.42	(14..81)	6.32	(11.28)
Residual	10.22	(44.68)	4.22	(75.89)	4.20	(67.20)	22.23	(68.04)	10.20	(62.88)	10	(43.32)	34	(6.07)

Table – 34 Mean concentration of total metals (mg/kg) in soil samples from different areas

Soil type	*Zn*	*Mn*	*Cr*	*Cu*	*Cd*	*Pb*	*Ni*
Polluted soil	64.02	119.23	30.45	38.36	13.22	18.34	50.07
Background soil	35.41	87.33	30.43	24.96	6.68	13.02	44.32
Control soil	22.87	56.01	21.67	16.22	5.78	6.78	32.86

3.2 Heavy metals in food crops

Heavy metals in the edible parts of food crops grown on wastewater irrigated soil, background and control areas along with WHO/FAO permissible limits are given in the Table-35 and 36.

The maximum permissible limits for Zn, Cd, Pb, Ni, Cu, Cr and Mn are 100, 0.1, 0.3, 67,73,2.3 and 5000, respectively on dry weight basis. Zn concentrations were ranged from 38.38-296.29 mg/kg in food crops grown on wastewater irrigated soil, 32.23-95.44 mg/kg in background and 30.53-89.34 mg/kg in control. *Brassica rapa, Spinacia oleracae* L*, Pisum sativum, Hebiscus esculantum,Corriandum sativum, portulaca oleracae, Daucus carota, Mentha viridis* and *Solanum tuberosum* accumulated significantly higher concentration of Zn as compared to background and control areas. The Zn concentrations in these food plants were exceeded the permissible limits set by WHO/FAO. Cd concentrations were ranged from 0.04-0.20 mg/kg in wastewater irrigated food crops, 0.01-0.07 mg/kg in background and in 0.01-0.06mg/kg control. Cd concentrations in *Mentha viridis, Allium sativum, Portulaca oleracae, Solanum tuberosum* and P*isum sativum* were exceeded the permissible limit set by WHO and FAO. Similarly, the concentrations of Pb were ranged from 0.1-0.28 mg/kg, in wastewater irrigated food crops, 0.07-0.25 mg/kg in background and 0.06-0.24mg/kg in control. Pb concentrations were found in *Hebiscus escluantus, B.oleracae botrytis, Corriandum sativum, Mentha viridis, Pisum staivum, Brassica rapa* and *Malva neglecta* plants higher than permissible limit. Ni concentrations were ranged from 29.55-66.46 mg/kg in food crops grown in wastewater irrigated soil, 18.24-58.26 mg/kg in background and

17.47-56.65 mg/kg in control. Cu concentrations were ranged from 36.22-78.72 mg/kg in wastewater irrigated food crops, 20.21-66.34 mg/kg in background and 18.22-63.42 mg/kg in control. Only in two species such as S*olanum tuberosum* and P*ortulaca olerace*, Cu concentrations were exceeded the permissible limit. Cr concentrations were ranged from 0.98-2.10 mg/kg in wastewater irrigated food crops, 0.79-1.92 mg/kg in background and 0.77-1.75mg/kg in control. Mn concentrations were ranged from 61.86-156.24 mg/kg in food crops grown on wastewater irrigated soil, 16.14-102.22 mg/kg in background and 13.03-98.56 mg/kg in control.

Table– 35 Mean metal concentrations (mg/kg) in food crops irrigated with wastewater

S. No	*Vegetables*	*Zn*	*Cd*	*Pb*	*Ni*	*Cu*	*Cr*	*Mn*
1	*Brassica rapa*	108.43(6.341)	0.06(0.011)	0.26(0.006)	58.44(3.112)	55.98(3.221)	2.10(0.011)	135.46(7.432)
2	*Spinacia oleracae* L.	194.23(6.231)	0.07(0.003)	0.14(0.011)	63.46(3.054)	36.22(2.302)	1.98(0.013)	134.88(6. 334)
3	*B. oleracae Botrytis*	74.14(3.442)	0.10(0.008)	0.28(0.013)	50.64(3.012)	48.42(2.443)	1.82(0.009)	75.74(3.223)
4	*Pisum sativum*	122.54(7.234)	0.11(0.005)	0.27(0.012)	53.43(2.056)	54.73(3.543)	1.53(0.011)	91.98(5.221)
5	*Lycopersicum Esculantum*	98.65(4.342)	0.06(0.011)	0.24(0.014)	66.48(4.405)	62.53(4.421)	2.20(0.012)	144.14(6.004)
6	*B. Compestris*	81.376(4.221)	0.04(0.007)	0.22(0.007)	46.72(2.001)	52.62(3.214)	1.77(0.008)	150.44(5.554)
7	*Hebiscus Esculantus*	118.41(6.201)	0.20(0.013)	0.26(0.005)	54.12(2.475)	54.76(2.012)	1.55(0.011)	74.22(3.221)
8	*B.oleracae Capitita*	68.51(3.225)	0.07(0.006)	0.10(0.015)	52.54(3.117)	61.24(3.226)	1.63(0.013)	61.868(2.234)
9	*Triticum aesativum* L *(grain).*	70.43(3.421)	0.04(0.005)	0.18(0.004)	50.44(3.044)	45.56(3.441)	1.28(0.007)	107.16(5.332)
10	*Mentha vridis*	72.55(3.761)	0.12(0.006)	0.27(0.011)	28.32(2.213)	66.46(4.006)	1.93(0.007)	119.68(5.330)
11	*Coriandum sativum*	192.54(7.131)	0.09(0.011)	0.28(0.013)	46.38(2.305)	65.45(3.043)	0.93(0.003)	156.24(6.003)
12	*Oryza sativa* L.*(grain)*	78.43(3.112)	0.08(0.013)	0.24(0.009)	56.56(5.621)	65.33(4.421)	0.78(0.003)	66.72(3.453)
13	*Lactuca sativum*	67.13(3.221)	0.06(0.008)	0.16(0.003)	45.65(3.104)	58.65(4.047)	1.45(0.006)	144.54(6.437)
14	*Portulaca oleracae*	166.44(7.320)	0.11(0.014)	0.13(0.016)	52.34(3.227)	75.15(5.310)	0.98(0.005)	70.2(3.435)
15	*Allium sativum*	79.22(3.110)	0.12(0.004)	0.13(0.014)	32.33(2.108)	60.65(3.221)	1.65(0.011)	145.96(7.342)
16	*Allium*	76.26(3.005)	0.09(0.003)	0.25(0.004)	55.54(3.005)	67.54(4.430)	1.75(0.007)	104.06(5.392)
17	*Daucus carota*	146.44(6.403)	0.08(0.006)	0.13(0.006)	49.31(3.452)	54.44(3.227)	2.01(0.013)	148.84(6.226)
18	*Malva neglecta*	288.47(7.224)	0.04(0.005)	0.26(0.005)	29.55(1.143)	61.76(3.114)	1.73(0.014)	87.42(3.675)
19	*Solanum tuberosum*	296.26(6.113)	0.12(0.011)	0.22(0.011)	61.54(3.531)	78.72(4.531)	2.11(0.008)	96.38(3.455)
20	*Zea Mays* L	38.38(2.107)	0.05(0.003)	0.21(0.015)	46.57(2.143)	46.34(2.114)	1.49(0.009)	87.48(3.402)
	WHO/ FAO guidelines 2001	100	0.1	0.3	67	73	2.30	500
	Background values(mean)	56	0.03	0.07	29	40	0.331	70

Figures in parenthesis indicate standard deviation

Table – 36 Mean metal concentrations (mg/kg) in food crops collected from control area

S.No	*Vegetables*	*Zn*	*Cd*	*Pb*	*Ni*	*Cu*	*Cr*	*Mn*
1	*Brassica rapa*	88.54(3.230)	ND	0.23(0.011)	53.44(2.436)	18.22(1.321)	1.12(0.001)	73.24(3.120)
2	*Spinacia oleracae* L.	72.45(3.176)	0.02(0.004)	0.19(0.006)	50.67(2.443)	31.43(2.213)	1.53(0.012)	88.14(3.407)
3	*B. oleracae Botrytis*	64.43(3.305)	ND	0.20(0.012)	37.43(2.036)	35.65(2.432)	0.92(0.003)	25.24(2.508)
4	*Pisum sativum*	64.41(2.334)	0.02(0.006)	0.09(0.003)	41.65(2.304)	63.42(3.541)	0.77(0.006)	50.68(2.341)
5	*Lycopersicum Esculantum*	65.64(3.4003)	0.01(0.003)	0.21(0.022)	56.65(3.162)	39.56(3.430)	1.43(0.015)	85.44(3.234)
6	*B. Compestris*	54.43(2.641)	0.05(0.005)	0.15(0.005)	28.46(2.441)	41.56(3.441)	1.62(0.017)	23.56(2.430)
7	*Hebiscus Esculantus*	68.54(3.103)	1.05(0.011)	0.23(0.013)	44.67(2.031)	37.57(2.113)	1.66(0.016)	22.86(1.421)
8	*B.oleracae Capitita*	46.33(2.110)	ND	0.17(0.008)	38.54(2.044)	52.33(3.172)	0.83(0.009)	19.22(1.008)
9	*Triticum aesativum* L *(grain).*	52.22(2.032)	ND	0.08(0.004)	40.44(2.401)	18.436(1.165)	1.44(0.021)	75.66(3.634)
10	*Mentha vridis*	44.45(2.436)	0.06(0.004)	0.24(0.011)	23.74(1.126)	22.54(1.045)	1.74(0.031)	89.78(3.231)
11	*Coriandum sativum*	84.67(5.334)	ND	0.09(0.002)	38.67(2.301)	53.65(3.078)	1.22(0.034)	95.24(4.342)
12	*Oryza sativa* L.*(grain)*	30.54(1.223)	0.03(0.007)	0.11(0.006)	56.44(4..034)	43.44(3.334)	0.88(0.005)	98.56(4.643)
13	*Lactuca sativum*	56.67(2.110)	ND	0.06(0.004)	45.66(2.334)	33.21(2.013)	1.75(0.014)	33.82(2.433)
14	*Portulaca oleracae*	74.41(3.043)	0.07(0.005)	0.08(0.014)	21.65(1.186)	46.32(2.22)	1.11(0.017)	28.02(2.411)
15	*Allium sativum*	52.44(2.451)	0.04(0.006)	0.12(0.006)	24.75(1.102)	51.55(4.353)	1.30(0.054)	30.99(2.113)
16	*Allium*	56.71(3.704)	0.01(0.006)	0.06(0.013)	39.53(3.423)	49.16(3.125)	1.54(0.044)	26.38(2.332)
17	*Daucus carota*	64.56(3.112)	0.03(0.011)	0.05(0.008)	30.32(2.006)	34.63(3.005)	1.32(0.061)	32.82(2.113)
18	*Malva neglecta*	89.34(5.647)	ND	0.13(0.004)	17.47(1.156)	45.65(2.541)	0.78(0.005)	43.55(3.231)
19	*Solanum tuberosum*	72.41(3.193)	0.06(0.004)	0.19(0.007)	49.64(2.431)	50.45(3.3002)	1.65(0.009)	13.03(1.112)
20	*Zea Mays* L	28.55(2.314)	ND	0.06(0.004)	32.38(2.158)	26.55(2.032)	1.32(0.011)	36.08(2.430)
	WHO/ FAO guidelines 2001	**100**	**0.1**	**0.3**	**67**	**73**	**2.30**	**500**

Figures in parenthesis indicate standard deviation

3.3.3 Heavy metals transfer from soil to plants

Table – 37 summarizes the metal transfer factor (MTF) values for selected metals in different food crops collected from the study areas. The MTF for plants irrigated with wastewater were ranged from 0.59-4.62, 0.003-0.015, 0.005-0.015, 0.56-1.32, 0.40-0.82, 0.944-2.05, 0.05-0.072, 0.51- 1.31 for Zn, Cd, Pb, Ni, Co Cu, Cr and Mn, respectively. Zn transfer factor was highest (4.62) for S*olanum tuberosum* followed by *Malva neglecta* (4.50), S*pinacia oleracae* L *(*3.03), *Corriandum staivum* (3.00), *Portulaca oleracae* (2.59) and *Daucus carota* (2.28). The trend of MTF for heavy metals in different food crops species grown on wastewater irrigated soil was in order of Zn>Cu>Ni>Mn>Co>Cr>Pb>Cd.

In case of vegetables collected from background and control areas the MTF for Zn, Cd, Pb, Ni, Co, Cu, Cr and Mn were ranged from 1.12-3.9, 0.001-0.18, 0.007-0.035, 0.54-1.76, 0.56-1.13, 1.12-3.90, 0.03-0.08, 0.23-1.75, respectively. Highest MTF value (3.90) for Zn was found in *Malva neglecta* followed by B*rassica rapa* (3.87) C*orriandum sativum* (3.70), *Portulaca oleracae* (3.25), S*pinacia oleracae* L (3.16) and *Solanum tuberosum* (3.16). The highest MTF value (3.9) for Cu was found in *Pisum sativum* followed by *Corriandum sativum* (3.30), *B.oleracae capitita* (3.22), *Allium* (3.03) *Allium sativum* (3.17) and *Solanum tuberosum* (3.11). No significant difference was observed in the trends of MTF for heavy metals in food crops grown in background and control areas.

Table – 37 MTF for heavy metals in vegetables grown in wastewater irrigated soil

Vegetable	*Zn*	*Cd*	*Pb*	*Ni*	*Cu*	*Cr*	*Mn*
Brassica rapa	1.693	0.004	0.014	1.167	1.459	0.068	1.136
Spinacia oleracae L.	3.033	0.005	0.007	1.267	0.944	0.065	1.131
B. oleracae Botrytis	1.158	0.007	0.015	1.011	1.262	0.059	0.635
Pisum sativum	1.914	0.008	0.014	1.067	1.426	0.050	0.771
Lycopersicum Esculantum	1.540	0.004	0.013	1.327	1.630	0.072	1.208
B. Compestris	1.271	0.003	0.011	0.933	1.371	0.058	1.261
Hebiscus Esculantus	1.849	0.015	0.014	1.080	1.427	0.050	0.622
B.oleracae Capitita	1.070	0.005	0.005	1.049	1.596	0.053	0.518
Triticum aesativum L *(grain).*	1.100	0.003	0.009	1.007	1.187	0.042	0.898
Mentha vridis	1.133	0.009	0.014	0.565	1.732	0.063	1.003
Coriandum sativum	3.006	0.006	0.015	0.926	1.706	0.030	1.310
Oryza sativa L.*(grain)*	1.225	0.006	0.013	1.129	1.703	0.025	0.559
Lactuca sativum	1.048	0.004	0.008	0.911	1.528	0.047	1.212
Portulaca oleracae	2.599	0.008	0.011	1.045	1.959	0.032	0.588
Allium sativum	1.237	0.009	0.007	0.645	1.581	0.054	1.224
Allium	1.191	0.006	0.013	1.109	1.760	0.057	0.872
Daucus carota	2.287	0.005	0.007	0.984	1.419	0.066	1.248
Malva neglecta	4.505	0.003	0.014	0.590	1.610	0.056	0.733
Solanum tuberosum	4.627	0.009	0.011	1.229	2.052	0.069	0.808
Zea Mays L	0.599	0.003	0.011	0.930	1.208	0.048	0.733

3.3.4 Cluster analysis

Cluster analysis (CA) using complete linkage method was applied to classify the vegetables of similar nature on the basis of metals as variables into different groups. In case of wastewater irrigated and control, CA classified the food crops into 6 groups as shown in Table 38,39 and Figure 10,11.

Table – 38 Classification of food crops grown on wastewater irrigated soil using cluster analysis

Group No.	*Food Crops*
1	*Brasssica compestress ,Allium sativum*, *Lactuca sativum*, *B. rapa*, *Lycopersicum esculantum*
2	*Triticum aesativum* L, *Allium*, *Mentha viridis,B. oleracae botrytis, B.oleracae capitita*, *Zea mays* L
3	*Oryza sativa* L
4	*Pisum sativum*, *Hebiscus esculantum*, *Portulaca oleracae*
5	*Spinacia oleracae L,Corriandum sativum*, *Daucus carota*
6	*Malva neglecta,Solanum tuberosum*

Table – 39 Classification of food crops grown on control soil using cluster analysis

Group No.	*Food Crops*
1	B.*oleracae botrytis,Hebiscus esculantum*, *Daucus carota, Lactuca sativum, B.oleracae capitita,Allium*, *B.compestress*, *Allium staivum*
2	*Solanum tuberosum*
3	*Portulaca oleracae, Malva neglecta,Pisum sativum*
4	*Zea Mays* L
5	*Spincia oleracae* L, *Lycpersicum esculantum,B.Rapa, Corriandum sativum*
6	*Triticum aesativum*, *mentha viridis*, *Oryza sativa* L.

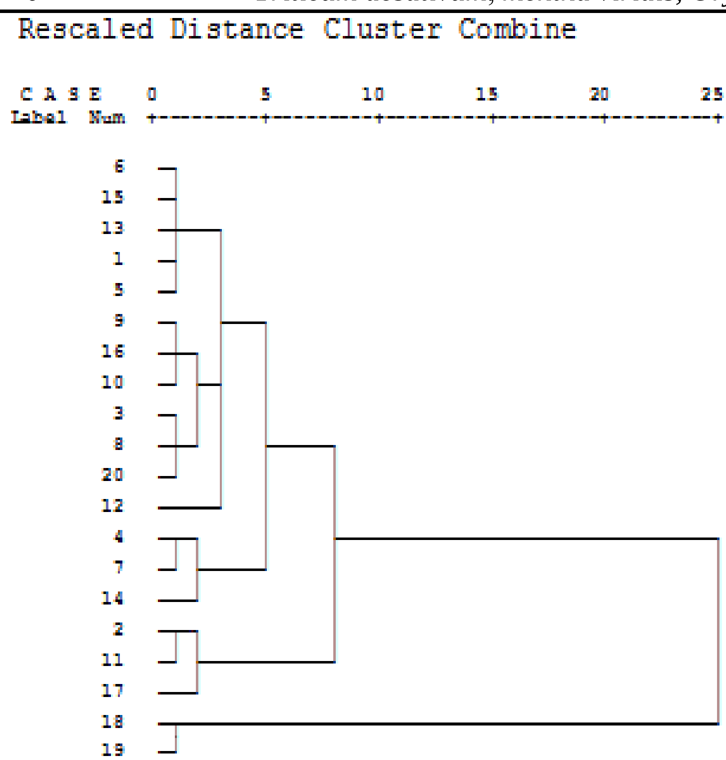

Fig 10 Dendogram for the classification of food crops grown on wastewater irrigated soil

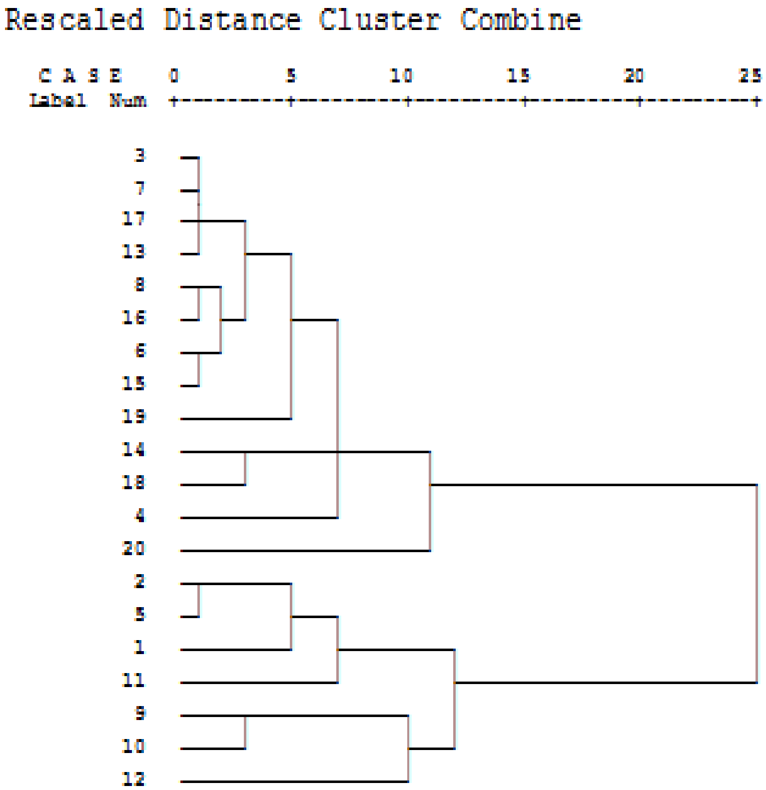

Fig. 11 Dendogram for the classification of food crops grown in control area.

3.3.5 Daily intake of metal (DIM) through food and human health risk

The estimated Daily intake of Metals (DIM) and Health Risk Index (HRI) values are given in the Tables 40 and 41 both for children and adults. The data indicate that the DIM values for metals were higher for vegetables obtained from wastewater irrigated area as compared to control areas. The highest intake of Cd, Pb and Cr was found for all these vegetables, while lowest intake for Zn, Ni, Cu and Mn.

Incase of wastewater irrigated area, the HRI for Zn, Cd, Pb, Ni, Cu, Cr and Mn were ranged from 7.6E-2 to 1.0E-1,5.8E-2 to 1.1E-2 , 9.8E-3 to1.1E-2,9.6E-1 to 4.1 E-1, 5.7E-1 to 2.6E-1 ,4.2E-4 to 1.5E-4 and 9.3E1 to 0 1.4, respectively for adults and from 9.4E-2 to 1.1E-1 ,3.5E-2 to 1.7 E-2 ,3.8 E-2 to 1.8 E-2 ,9.8E-1 to 4.0 E-1 ,5.6E-1 to 2.5E-1 4.1 E-4 to 1.4E-4 and 9.7E-1 to 1.4, respectively for children. In case of control area, the HRI for Zn, Cd, Pb, Ni, Cu, Cr and Mn were ranged from 8.6E-2 to 2.7E-2,8.7E-3 to 3.0E-1,9.4E-3 to 1.2E-2,8.2E-1 to 4.1E-1,4.6E-1 to 1.3E-1, 3.4E-4 to 1.4E-4 and 9.5E-1 to 1.2E-1, respectively for adults, while ranged from 8.5E-2 to 2.7E-2,8.5E-3 to 1.1E-2,9.2E-3 to 1.0 E-2, 8.0E-1 to 2.4E-1,3.8E-1 to 1.3E-1,3.3E-4 to 1.4E-1 and 9.3E-1 to 1.2 E-1, respectively for children.

Table – 40 DIM and HRI for individual heavy metals caused by the consumption of different selected vegetables grown on waste water irrigated soil

Vegetables Individuals		***Zn***	***Cd***	***Pb***	***Ni***	***Cu***	***Cr***	***Mn***
Brassica rapa	DIM	3.1E-2	1.7E-5	7.5E-5	1.7E-2	1.6E-2	6.1E-4	3.9E-2
Adults	HRI	1.0E-1	1.7E-2	1.8E-2	8.5E-1	4.0E-1	4.0E-4	1.3
	DIM	3.1E-2	1.7-E5	7.4E-5	1.6E-2	1.6E-2	6.0E-4	3.8E-2
Children	HRI	1.0E-1	1.7E-2	1.8E-2	8.3E-1	4.0E-1	4.0E-4	1.2
Spinacia oleracae L	DIM	5.6E-2	2.0E-5	9.8E-5	1.8E-2	1.0E-2	5.7E-4	3.9E-2
Adults	HRI	1.8E-1	2.0E-2	2.4E-2	9.2E-1	2.6E-1	3.8E-4	1.3
Children	DIM	5.5E-2	2.0E-5	9.7E-5	1.8E-2	1.0E-2	5.6E-4	3.8E-2
	HRI	1.8E-1	2.0E-2	2.4E2	9.0E-1	2.5E-1	3.7E-4	1.28
B. oleracae botrytis	DIM	2.1E-2	3.7E-5	8.1E-5	1.4E-2	1.4E-2	5.3E-4	2.2E-2
Adults	HRI	7.1E-1	3.7E-2	2.0E-2	7.3E-1	3.5E-1	3.5E-4	7.3E-1
Children	DIM	2.1E-2	3.7E-5	8.0E-5	1.4E-2	1.3E-2	5.2E-4	2.1E-2
	HRI	7.0E-2	3.7E-2	2.0E-2	7.2E-1	3.4E-1	3.4E-4	7.2E-1
Pisum sativum	DIM	3.5E-2	3.2E-5	1.0E-4	1.5E-2	1.5E-2	4.4E-4	2.6E-2
Adults	HRI	1.1E-1	3.2E-2	2.6E-2	7.7E-1	3.9E-1	2.9E-4	8.9E-1
Children	DIM	3.5E-2	3.1E-5	1.0E-4	1.5E-2	1.5E-2	4.3E-4	2.6E-2
	HRI	1.1E-1	3.1E-2	2.6E-2	7.6E-1	3.9E-1	2.9E-4	8.7E-1
Lycopersicum	DIM	2.8E-2	1.7E-5	1.8E-4	1.9E-2	1.8E-2	6.4E-4	4.1E-2
Esculantum	HRI	9.5E-2	1.7E-2	4.6E-2	9.6E-1	4.5E-1	4.2E-4	1.3
Adults	DIM	2.8E-2	1.7E-5	1.8E-4	1.9E-2	1.7E-2	6.2E-4	4.1E-2
Children	HRI	9.4E-2	1.7E-2	4.5E-2	9.5E-1	4.4E-1	4.1E-4	1.31
B. Compestris	DIM	2.3E-2	1.1E-5	6.4E-5	1.3E-2	1.5E-2	5.1E-	4.3E-2
Adults	HRI	7.8E-2	1.1E-2	1.6E-2	6.8E-1	3.8E-1	3.4E-4	1.4
Children	DIM	2.3E-2	1.1E-5	6.2E-5	1.3E-2	1.5E-2	5.0E-4	4.3E-2
	HRI	7.7E-2	1.1E-2	1.5E-2	6.6E-1	3.7E-1	3.3E-4	1.4
Hebiscus Esculantus	DIM	3.4E-2	5.8E-5	7.59E-5	1.5E-2	1.5E-2	4.5E-4	2.1E-2
Adults	HRI	1.1E-1	5.8E-2	1.8E-2	7.8E-1	3.9E-1	3.0E-4	7.2E-1
Children	DIM	3.3E-2	5.7E-5	7.4E-5	1.5E-2	1.5E-2	4.4E-4	2.1E-2
	HRI	1.1E-1	5.7E-2	1.8E-2	7.7E-1	3.9E-1	2.9E-4	7.0E-1
B. oleracae capitita	DIM	1.9E-2	2.0E-5	8.7E-5	1.5E-2	1.7E-2	4.7E-4	1.8E-2
Adults	HRI	6.6E-2	2.0E-2	7.1E-3	7.6E-1	4.4E-1	3.1E-4	6.0E-1
Children	DIM	1.9E-2	2.0E-5	8.5E-5	1.5E-2	1.7E-2	4.6E-4	1.7E-2
	HRI	6.5E-2	2.0E-2	2.1E-2	7.5E-1	4.3E-1	3.1E-4	5.8E-1
Triticum aestivum L	DIM	2.0E-2	1.1E-5	5.2E-5	1.4E-2	1.3E-2	3.7E-4	3.1E-2
Adults	HRI	6.8E-2	1.1E-2	1.3E-2	7.3E-1	3.3E1	2.4E-4	1.0
Children	DIM	2.0E-2	1.1E-5	5.1E-5	1.4E-2	1.3E-2	3.6E-4	3.0E-2

	HRI	6.7E-2	1.1E-2	1.2E-2	7.2E-1	3.2E-1	2.4E-4	1.0
Mentha vridis	DIM	2.1E-2	4.6E-5	7.8E-5	8.2E-3	1.9E-2	5.6E-4	3.4E-2
Adults	HRI	7.0E-2	4.6E-2	1.9E-2	4.1E-1	4.8E-1	3.7E-4	1.1
Children	DIM	2.0E-2	4.0E-5	7.7E-5	8.0E-3	1.9E-2	5.5E-4	3.4E-2
	HRI	6.9E-2	4.5E-2	1.9E-2	4.0E-1	4.7E-1	3.6E-4	1.1
Coriandum sativum	DIM	5.5E-2	2.6E-5	8.1E-5	1.3E-2	1.9E-2	2.7E-4	4.5E-2
Adults	HRI	1.8E1	2.6E-2	2.0E-2	6.7E-1	4.7E-1	1.8E-4	1.5
Children	DIM	5.5E-2	2.5E-5	8.0E-5	1.3E-2	1.8E-2	2.6E-4	4.4E-2
	HRI	1.8E-1	2.5E-2	2.0E-2	6.6E-1	4.6E-1	1.7E-4	1.4
Oryza sativa L	DIM	2.2E-2	5.8E-5	6.9E-5	1.6E-2	1.9E-2	2.2E-4	1.9E-2
Adults	HRI	7.6E-2	5.8E-2	1.7E-2	8.2E-1	4.7E-1	1.5E-4	6.4E-1
	DIM	2.2E-2	5.7E-5	6.8E-5	1.6E-2	1.8E-2	2.2E-4	1.9E-2
Children	HRI	7.4E-2	5.7E-2	1.7E-2	8.0E-1	4.6E-1	1.4E-4	6.3E-1
Lactuca sativum	DIM	1.9E-2	1.7E-05	4.6E-5	1.3E-2	1.7E-2	4.2E-4	4.2E-2
Adults	HRI	6.5E-2	1.7E-2	1.1E-2	6.6E-1	4.2E-1	2.8E-4	1.4
Children	DIM	1.9E-2	1.7E-5	4.5E-5	1.3E-2	1.6E-2	4.1E-4	4.1E-2
	HRI	6.3E-2	1.7E-2	1.1E-2	6.5E-1	4.1E-1	2.7E-4	1.3
Portulaca oleracae	DIM	4.8E-2	3.7E-5	9.0E-5	1.5E-2	2.1E-2	2.8E-4	2.0E-2
Adults	HRI	1.6E-1	3.7E-2	2.2E-2	7.6E-1	5.4E-1	1.9E-4	6.8E-1
Children	DIM	4.7E-2	3.7E-5	8.8E-5	1.4E-2	2.1E-2	2.8E-4	2.0E-2
	HRI	1.5E-1	3.7E-2	2.2E-2	7.4E-1	5.3E-1	1.8E-4	6.6E-1
Allium sativum	DIM	2.3E-2	3.4E-5	1.5E-4	9.4E-3	1.7E-2	4.8E-4	4.2E-2
Adults	HRI	7.6E-2	3.4E-2	9.8E-3	4.7E-1	4.4E-1	3.2E-4	1.4
Children	DIM	2.2E-2	3.4E-5	1.5E-4	9.2E-3	1.7E-2	4.7E-4	4.1E-2
	HRI	7.5E-2	3.4E-2	3.7E-2	4.6E-1	4.3E-1	3.1E-4	1.3
Allium	DIM	2.2E-2	2.6E-5	7.2E-5	1.6E-2	1.9E-2	5.0E-4	3.0E-2
Adults	HRI	7.3E-2	2.6E-2	1.8E-2	8.0E-1	4.9E-1	3.4E-4	1.0
Children	DIM	2.1E-2	2.5E-5	7.1E-5	1.5E-2	1.9E-2	5.0E-4	2.9E-2
	HRI	7.2E-2	2.5E-2	1.7E-2	7.9E-1	4.8E-1	3.3E-4	9.7E-1
Daucus carota	DIM	4.2E-2	3.2E-5	3.7E-5	1.4E-2	1.5E-2	5.8E-4	4.3E-2
Adults	HRI	1.4E-1	3.2E-2	9.4E-3	7.1E-1	3.9E-1	3.9E-4	1.4
Children	DIM	4.1E-2	3.1E-5	3.7E-5	1.4E-2	1.5E-2	5.7E-4	4.2E-2
	HRI	1.3E-1	3.1E-2	9.2E-3	7.0E-1	3.8E-1	3.8E-4	1.4
Malva neglecta	DIM	8.3E-2	1.1E-5	7.5E-5	8.6E-3	1.7E-2	5.0E-4	2.5E-2
Adults	HRI	2.7E-2	1.1E-2	1.8E-2	4.3E-1	4.4E-1	3.3E-4	8.4E-1
Children	DIM	8.2E-2	1.1E-5	7.4E-5	8.4E-3	1.7E-2	4.9E-4	2.4E-2
	HRI	2.7E-1	1.1E-2	1.8E-2	4.2E-1	4.4E-1	3.3E-4	8.3E-1
Solanum tuberosum	DIM	8.6E-2	6.1E-5	1.5E-4	1.7E-2	2.2E-2	6.1E-4	2.8E-2
Adults	HRI	2.8E-1	6.1E-2	3.7E-2	8.9E-1	5.7E-1	4.0E-4	9.3E-1
Children	DIM	8.4E-2	6.0E-5	1.4E-4	1.7E-2	2.2E-2	6.0E-4	2.7E-2
	HRI	2.8E-1	6.0E-2	3.7E-2	8.7E-1	5.6E-1	4.0E-4	9.1E-1
Zea Mays L	DIM	1.1E-2	1.4E-5	6.1E-5	1.3E-2	1.3E-2	4.3E-4	2.5E-2
Adults	HRI	3.7E-2	1.4E-2	1.5E-2	6.7E-1	3.3E-1	2.8E-4	8.4E-1
Children	DIM	1.0E-2	1.4E-5	6.0E-5	1.3E-2	1.3E-2	4.2E-4	2.5E-2
	HRI	3.6E-2	1.4E-2	1.5E-2	6.6E-1	3.3E-1	2.8E-4	8.3E-1

Table – 41 DIM and HRI for individual heavy metals caused by the consumption of different selected vegetables grown on control area

Vegetables Individuals		*Zn*	*Cd*	*Pb*	*Ni*	*Cu*	*Cr*	*Mn*
Brassica rapa	DIM	2.5E-2	-	6.6E-5	1.5E-2	5.3E-3	3.2E-4	2.1E-2
Adults	HRI	8.5E-2	-	1.6E-2	7.7E-1	1.3E-1	2.1E-4	7.1E-1
Children	DIM	2.5E-2	-	6.5E-5	1.5E-2	5.2E-3	3.2E-4	2.0E-2
	HRI	8.4E-2	-	1.6E-2	7.6E-1	1.3E-1	2.1E-4	6.9E-1
Spinacia oleracae	DIM	2.1E-2	5.8E-6	5.5E-5	1.4E-2	9.1E-3	4.4E-4	2.5E-2
L	HRI	7.0E-2	5.8E-3	1.3E-2	7.3E-1	2.2E-1	2.9E-4	8.5E-1
Adults	DIM	2.0E-2	5.7E-6	5.4E-5	1.4E-2	8.9E-3	4.3E-4	2.5E-2
Children	HRI	6.9E-2	5.7E-3	1.3E-2	7.2E-1	2.2E-1	2.9E-4	8.4E-1
B.oleracae botrytis	DIM	1.8E-2	-	5.8E-5	1.0E-2	1.0E-2	2.6E-4	7.3E-3
Adults	HRI	6.2E-2	-	1.4E-2	5.4E-1	2.5E-1	1.7E-4	2.4E-1
Children	DIM	1.8E-2	-	5.7E-5	1.0E-2	1.0E-2	2.6E-4	7.2E-3
	HRI	6.1E-2	-	1.4E-2	5.3E-1	2.5E-1	1.7E-4	2.4E-1
Pisum sativum	DIM	1.8E-2	5.8E-6	2.6E-5	1.2E-2	1.8E-2	2.2E-4	1.4E-2
Adults	HRI	6.2E-2	5.8E-3	6.5E-3	6.0E-1	4.6E-1	1.4E-4	4.9E-1
Children	DIM	1.8E-2	5.7E-6	2.5E-5	1.1E-2	1.8E2	2.2E-4	1.4E-2
	HRI	6.1E-2	5.7E-3	6.4E-3	5.9E-1	4.5E-1	1.4E-4	4.8E-1
Lycopersicum	DIM	1.9E-2	2.9E-6	6.1E-5	1.6E-2	1.1E-2	4.1E-4	2.4E-2
Esculantum	HRI	6.3E-2	2.9E-3	1.5E-2	8.2E-1	2.8E-1	2.7E-4	8.2E-1
Adults	DIM	1.8E-2	2.8E-6	6.0E-5	1.6E-2	1.1E-2	4.0E-4	2.4E-2
Children	HRI	6.2E-2	2.8E-3	1.5E-2	8.0E-1	2.8E-1	2.7E-4	8.1E-1
B. Compestris	DIM	1.5E-2	1.4E-5	4.3E-5	8.2E-3	1.2E-2	4.7E-4	6.8E-3
Adults	HRI	5.2E-2	1.4E-2	1.0E-2	4.1E-1	3.0E-1	3.1E-4	2.2E-1
Children	DIM	1.5E-2	1.4E-5	4.2E-5	8.1E-3	1.1E-2	4.6E-4	6.7E-3
	HRI	5.1E-2	1.4E-1	1.0E-2	4.0E-1	2.9E-1	3.0E-4	2.2E-1
Hebiscus	DIM	1.9E-2	3.0E-4	6.6E-5	1.3E-2	1.0E-2	4.8E-4	6.6E-3
Esculantus	HRI	6.6E-2	3.0E-1	1.6E-2	6.5E-1	2.7E-1	3.2E-4	2.2E-1
Adults	DIM	1.9E-2	3.0E-4	6.5E-5	1.2E-2	1.0E-2	4.7E-4	6.5E-3
Children	HRI	6.5E-2	3.0E-1	1.6E-2	6.3E-1	2.6E-1	3.1E-4	2.1E-1
B.oleracae capitita	DIM	1.3E-2	-	4.9E-5	1.1E-2	1.5E-2	2.4E-4	5.5E-3
Adults	HRI	4.4E-2	-	1.2E-2	5.6E-1	3.8E-1	1.6E-4	1.8E-1
Children	DIM	1.3E-2	-	4.8E-5	1.1E-2	1.4E-2	2.3E-4	5.4E-3
	HRI	4.4E-2	-	1.2E-2	5.5E-1	3.7E-1	1.5E-4	1.8E-1
Triticum aestivum	DIM	1.5E-2	-	2.3E-5	1.1E-2	5.3E-3	4.1E-4	2.2E-2
L	HRI	5.0E-2	-	5.8E-2	5.8E-1	1.3E-1	2.7E-4	7.3E-1
Adults	DIM	1.4E-2	-	2.2E-5	1.1E-2	5.2E-3	4.1E-4	2.1E-2
Children	HRI	4.9E-2	-	5.7E-3	5.7E-1	1.3E-1	2.7E-4	7.2E-1
Mentha vridis	DIM	1.2E-2	1.7E-5	6.9E-5	6.9E-3	6.5E-3	5.0E-4	2.6E-2
Adults	HRI	4.3E-2	1.7E-2	1.7E-2	3.4E-1	1.6E-1	3.3E-4	8.7E-1
Children	DIM	1.2E-2	1.7E-5	6.8E-5	6.7E-3	6.4E-3	4.9E-4	2.5E-2
	HRI	4.2E-2	1.7E-2	1.7E-2	3.3E-1	1.6E-1	3.3E-4	8.5E-1
Coriandum sativum	DIM	2.4E-2	-	2.6E-5	1.1E-2	1.5E-2	3.5E-4	2.7E-2
Adults	HRI	8.2E-2	-	6.5E-3	5.6E-1	3.9E-1	2.3E-4	9.2E-1
Children	DIM	2.4E-2	-	2.5E-5	1.1E-2	1.5E-2	3.4E-4	2.7E-2
	HRI	8.0E-2	-	6.4E-3	5.5E-1	3.8E-1	2.3E-4	9.0E-1

Oryza sativa L	DIM	8.8E-3	8.7E-6	3.2E-5	1.6E-2	1.2E-2	2.5E-4	2.8E-2
Adults	HRI	2.9E-2	8.7E-3	8.0E-3	8.2E-1	3.1E-1	1.7E-4	9.5E-1
Children	DIM	8.7E-3	8.5E-6	3.1E-5	1.6E-2	1.2E-2	2.5E-4	2.8E-2
	HRI	2.9E-2	8.5E-3	7.8E-3	8.0E-1	3.1E-1	1.6E-4	9.3E-1
Lactuca sativum	DIM	1.6E-2	-	1.7E-5	1.3E-2	9.6E-3	5.0E-4	9.8E-3
Adults	HRI	5.4E-2	-	4.3E-3	6.6E-1	2.4E-1	3.4E-4	3.2E-1
Children	DIM	1.6E-2	-	1.7E-5	1.3E-2	9.4E-3	5.0E-4	9.6E-3
	HRI	5.4E-2	-	4.2E-3	6.5E-1	2.3E-1	3.3E-4	3.2E-1
Portulaca oleracae	DIM	2.1E-2	2.0E-5	2.3E-5	6.3E-3	1.3E-2	3.2E-4	8.1E-3
Adults	HRI	7.2E-2	2.0E-2	5.8E-3	3.1E-1	3.3E-1	2.1E-4	2.7E-1
Children	DIM	2.1E-2	2.0E-5	2.2E-5	6.1E-3	1.3E-2	3.1E-4	8.0E-3
	HRI	7.0E-2	2.0E-2	5.7E-3	3.0E-1	3.3E-1	2.1E-4	2.6E-1
Allium sativum	DIM	1.5E-2	1.1E-5	3.4E-5	7.3E3	1.5E-2	3.7E-4	9.0E-3
Adults	HRI	5.0E-2	1.1E-2	8.7E-3	3.6E-1	3.7E-1	2.5E-4	3.0E-1
Children	DIM	1.4E-2	1.1E-5	3.4E-5	7.0E-3	1.4E-2	3.7E-4	8.8E-3
	HRI	4.9E-2	1.1E-2	8.5E-3	3.5E-1	3.6E-1	2.4E-4	2.9E-1
Allium	DIM	1.6E-2	2.9E-6	1.7E-5	1.1E-2	1.4E-2	4.4E-4	7.6E-3
Adults	HRI	5.5E-2	2.9E-3	4.3E-3	5.7E-1	3.5E-1	2.9E-4	2.5E-1
Children	DIM	1.6E-2	2.8E-6	1.7E-5	1.1E-2	1.4E-2	4.4E-4	7.5E-3
	HRI	5.4E-2	2.8E-3	4.2E-3	5.6E-1	3.5E-1	2.9E-4	2.5E-1
Daucus carota	DIM	1.8E-2	8.7E-6	1.4E-5	8.8E-3	1.0E-2	3.8E-4	9.5E-3
Adults	HRI	6.2E-2	8.7E-3	3.6E-3	4.4E-1	2.5E-1	2.5E-4	3.1E-1
Children	DIM	1.8E-2	8.5E-6	1.4E-5	8.6E-3	9.9E-3	3.7E-4	9.3E-3
	HRI	6.1E-2	8.5E-3	3.5E-3	4.3E-1	2.4E-1	2.5E-4	3.1E-1
Malva neglecta	DIM	2.6E-2	-	3.7E-5	5.0E-3	1.3E-2	2.2E-4	1.2E-2
Adults	HRI	8.6E-2	-	9.4E-3	2.5E-1	3.3E-1	1.5E-4	4.2E-1
Children	DIM	2.5E-2	-	3.7E-5	4.9E-3	1.3E-2	2.2E-4	1.2E-2
	HRI	8.5E-2	-	9.2E-3	2.4E-1	3.2E-1	1.4E-4	4.1E-1
Solanum tuberosum	DIM	2.1E-2	1.7E-5	5.5E-5	1.4E-2	1.4E-2	4.8E-4	3.7E-3
Adults	HRI	7.0E-2	1.7E-2	1.3E-2	7.2E-1	3.6E-1	3.2E-4	1.2E-1
Children	DIM	2.0E-2	1.7E-6	5.4E-5	1.4E-2	1.4E-2	4.7E-4	3.7E-3
	HRI	6.9E-2	1.7E-2	1.3E-2	7.0E-1	3.6E-1	3.1E-4	1.2E-1
Zea Mays L	DIM	8.3E-3	-	1.7E-5	9.4E-3	7.7E-3	3.8E-4	1.0E-2
Adults	HRI	2.7E-2	-	4.3E-3	4.7E-1	1.9E-1	2.5E-4	3.5E-1
Children	DIM	8.1E-3	-	1.7E-5	9.2E-3	7.5E-3	3.7E-4	1.0E-2
	HRI	2.7E-2	-	4.2E-3	4.6E-1	1.8E-1	2.5E-4	3.4E-1

Discussions

Continuous application of wastewater leads to the enrichment of soil with heavy metals. Oxidation state, phase and form of heavy metals strongly affect their bioavailability. Chemical extraction techniques provide a well established mean of identification and characterization of different fractions of heavy metals in soil (114-116). The data in Table-33 and fig. 12 indicate that metal bioavailable fraction was higher in wastewater irrigated soil as compared to background and control soils. Zn, Cu and Mn have shown high concentrations in the available pool in the present study and can be attributed to the reduction in soil pH into moderately acidic conditions as well as increase in organic contents due to continuous use of wastewater.

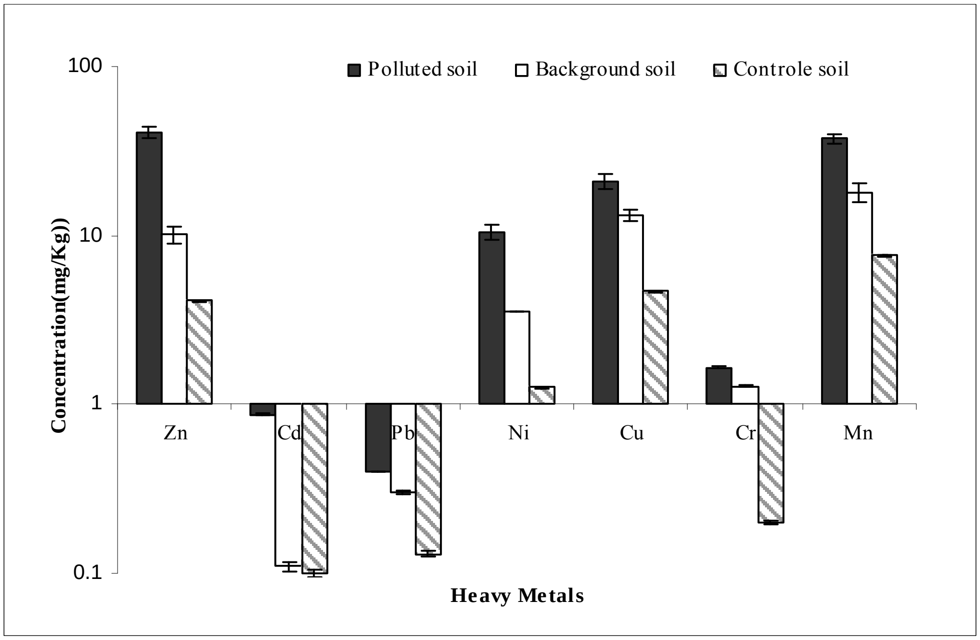

Fig 12 Phytoavailable concentrations of different heavy metals in soils collected from wastewater irrigated, background and control areas (error bars indicate standard deviation)

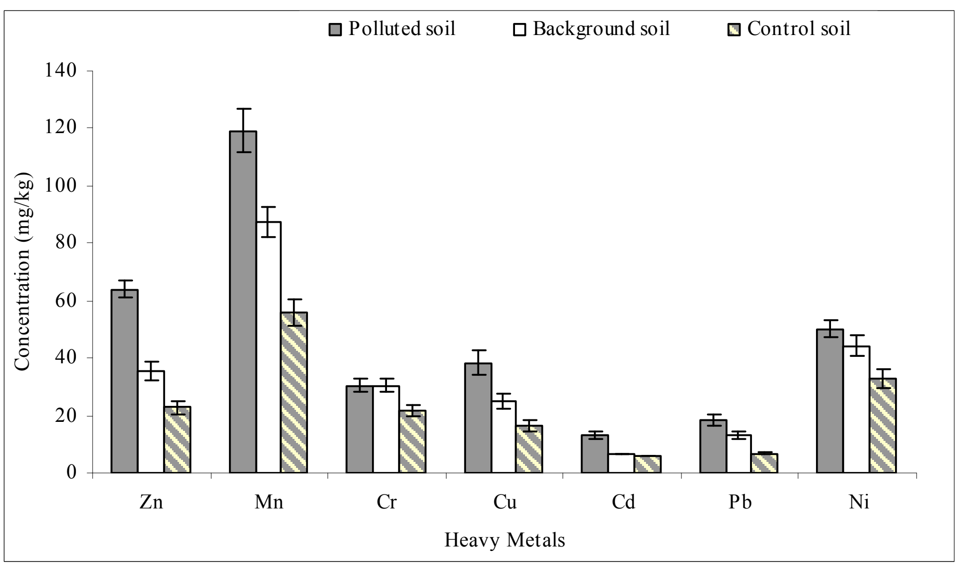

Fig. 13 Total heavy metals content of soils collected from wastewater irrigated, background and control areas (error bars indicate standard deviation)

Long-term application of wastewater resulted an increase in organic carbon and reduction in soil pH which might result in the remobilization of metal pool to more mobile fraction. Based on the fractionation study, the metals can be arranged in the decreasing order of bioavailability Cu>Zn>Ni>Cd>Cr>Pb. The data in Table-34 and fig.13 also show that the total metal concentrations, were higher in wastewater irrigated soil as compared to background and control soils. The heavy metals accumulation by food crops can cause a serious health concern due to potential public health risks. In this study, the contamination of soil with heavy metals was due to wastewater irrigation and possible atmospheric deposition. One way ANOVA was used to compare the metal concentrations in wastewater irrigated soil with the control and background sites. The data show a significantly higher concentration ($p \geq 0.001$) in wastewater irrigated soil as compared to control, indicating that heavy metal concentrations were increased due to application of wastewater. These results are in agreement with the previous studies (117-118). Though there was a grade variation in the heavy metal concentrations of the wastewater irrigated, background and control soils but were found within permissible limits set by WHO/FAO except for Zn.

Previous studies (119,120) indicated that the vegetables grown on wastewater irrigated soil accumulated high concentration of heavy metals. The present study also indicates that higher concentrations of metals accumulated in vegetables grown on wastewater irrigated soil. All the plants grown on wastewater irrigated soil were contaminated with these heavy metals. In most of the food crops, Zn concentration exceeded the permissible limits set by WHO/FAO as indicated by fig.14. Other heavy metals such as Cd, Pb, Ni, Cu, Cr and Mn were found within permissible limits.

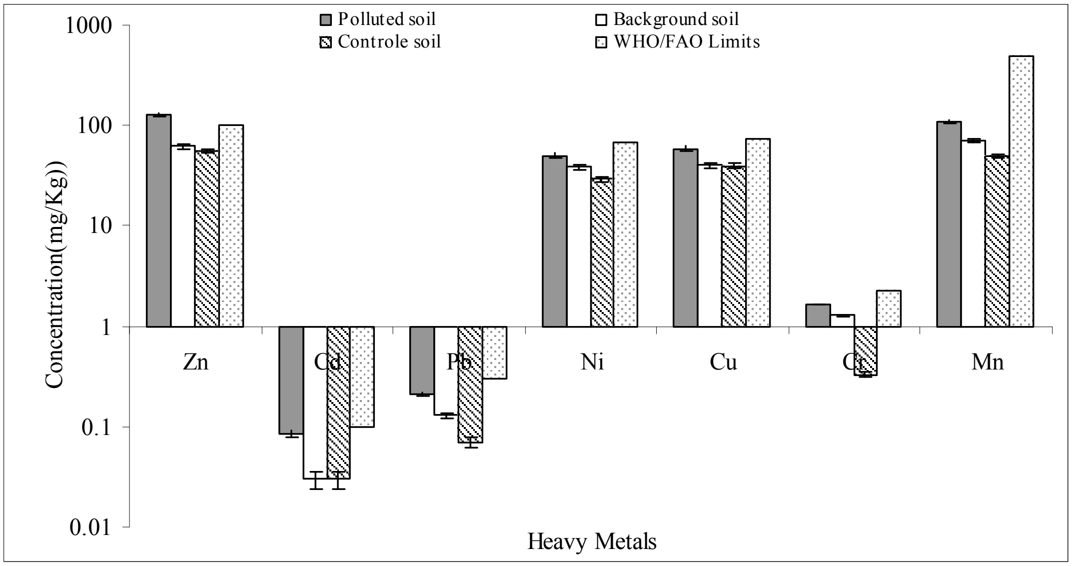

Fig 14Comparative plot of mean heavy metals concentration of 20 food crops from wastewater irrigated, background, and control area Vs WHO/FAO safe limits (error bars indicate standard deviation)

In case of food crops grown in background and control areas, these heavy metal concentrations were found within the limits set by WHO/FAO. Using ANOVA to know the differences in vegetables based on their metal contents it showed no statistical difference (p=0.99). In order to classify the vegetables of similar nature cluster analysis (CA) was applied that grouped the vegetables into 6 groups in case of polluted, background and control areas.

Soil to plant transfer factor is the key component of human exposure to metals through food chain. In order to investigate HRI for selected metals, it is essential to asses MTF. MTF varied greatly for metals in different vegetables and was found higher for Zn, Ni and Mn (Table-37).The high MTF values were found for Zn, Cu Ni and Mn for leafy vegetables. MTF values were lower than those reported in the literature for food crops (121). The decrease in MTF values with increasing total metal concentrations in soil indicated an inverse relationship between transfer factor and total metal concentrations as reported for vegetables (122).

For assessing health risk associated with any chemical pollutant, it is necessary to estimate the level of exposure by quantifying the route of exposure of pollutant to target organism. Among different pathways of human exposure, food chain is one of the most important routes. In the study area food crops were contaminated with the heavy metals and consumption of these contaminated food crops can cause human health risks. The food crops were sold in the urban market therefore, the average metal concentrations were used for the calculation of HRI. The data indicate that HRI values were >1; for most of the other metals except Mn, particularly for plants grown on wastewater irrigated soil. For some food crops, HRI was found to be higher like *Brassica rapa*, S*pinacia oleracae* L, *Lycopersicum esculantum*, *B.Compestress*, *Mentha viridis, Corrinadum sativum* , *Lactuca sativum* and *Allium sativum*. These vegetable consumption poses a possible health risk regarding Mn intake, while safe in respect of other metals. HRI values for metals were >1 incase of vegetable grown on control area and found to be risk free and generally assumed to be safe.

The oral reference dose for Zn, Cd, Pb, Ni, Cu, Cr and Mn are 3E-1, 1E-1, 4E-3, 2E-2 4E-2 1.5E0, and 3.3E-2 mg/kg/day, respectively (112). The estimated dietary intake of Zn, Cd, Pb, Ni, Cu, and Cr were below the tolerable limits. DIM values for metals through consumption of vegetables in case of wastewater irrigated and control areas were less than the tolerable limits. The daily intake values for metals both for adults and children through consumption of vegetables were less than the limits of RfD limits set by US-EPA IRIS. The findings regarding DIM and HRI in this study suggest that *B.oleracae botrytis Pisum sativum*, *Hebiscus esculanmtum*, *Triticum aesativum* L*, oryza sativa L*, *Portulavca oleracae* ,A*llium, Daucus acrota, Malva neglecta* , *B.oleracae capitita, Solanum tubersoum* and *zea mays* L grown on wastewater irrigated soil were nearly free of any risk but a few species *B.*

rapa, Spinacia oleracae L, *lycopersicum esculantum*, *Mentha virids*, C*orriandum sativum*, and *Lactuca sativa* pose risk with regard to Mn pollution. In case of background and control areas these vegetable were totally risk free.

3.4 Effect of consumption of food crops, meat and milk on the blood metal composition of humans in polluted and less polluted areas

3.4.1 Distribution of heavy metals in forage grass

Forage grass is the main fodder crop of the majority of cattle in the study areas. Mean concentrations of metals in forage grass are given in Table 42. Their concentration were within normal ranges. Cu, Zn, Cr, Ni, Pb and Mn concentrations were in the range of 13.7-25, 158.00-185.00, 17.30-29.40, 8.00-16.70, 49.00-88 and 49.00-88.00 (µg/g) respectively. While the transfer coefficient values for Cu, Zn, Cr, Ni, Pb and Mn were ranged from 0.65-0.72, 0.45-0.51, 0.62-0.81, 0.25-0.32, 0.19-0.29 and 0.56-0.76 respectively

Table 42 Metal concentrations in fodder grass (µg/g) and plant soil transfer coefficient values

Metals	***Normal ranges***	***Transfer factor***	***Fodder grass values from study area***	***Transfer coefficient values from study area***
Cu	5-20	0.0-0.1	13.7-25(22)	0.65-0.72
Zn	1-100	0.1-10	158-185(167)	0.45-0.51
Cr	0.03-14	0.01-0.1	17.3-29.4(25.4)	0.62-0.81
Ni	0.02-5	0.01-1.0	8-16.7(15)	0.25-0.32
Pb	5-10	0.01-0.2	49-88(82)	0.19-0.29
Mn	5-25	0.01-0.1	32-44(38)	0.56-0.76

3.4.2 Distribution of heavy metals in blood samples of males and females of different age groups

Mean concentration of metals in blood of the individuals from polluted and control areas is given in Table 43-58 while basic statistical distribution parameters of the selected trace metals are given in Table-59 and 60. From the Table 59 it is clear that the mean concentrations of Cu Zn, Cr, Ni, Pb, Mn and Fe in male children's blood samples collected from control area were 1.32, 5.97, 0.45, 0.08, 0.01, 1.57, 290.90 µg/L, while in female children these values were 0.29, 3.63, 0.17, 0.03, 0.06, 1.55 and 369.55 µg/L, respectively. In adolescent male, mean concentrations of Cu Zn, Cr, Ni, Pb, Mn and Fe were 1.48, 6.73, 0.48, 0.06, 0.03, 1.39 and 304.71 µg/L, while in female these values were 1.00, 12.04 0.31, 0.01, 0.05, 1.82 and 359.73 µg/L, respectively. In case of male adults, the mean concentrations of Cu, Zn, Cr, Ni, Pb, Mn and Fe were 1.35, 7.84, 0.33, 0.12, 0.03, 1.50 and 310.11 µg/L, while in female these values were 0.18, 8.32, 0.26, 0.02,0.18,1.82 and 378.26 µg/L, respectively.

Table – 43 Distributions of metals concentrations in male children's blood from polluted area

Individuals	*Cu(µg/L)*	*Zn(µg/L)*	*Cr(µg/L)*	*Ni(µg/L)*	*Pb(µg/L)*	*Mn(µg/L)*	*Fe(µg/L)*
CM-1	1.25	16.54	0.02	0.02	0.07	1.88	423.684
CM-2	3.24	10.41	0.01	0.07	0.06	1.68	358.687
CM-3	2.48	14.21	ND	ND	0.01	0.94	238.541
CM-4	4.56	12.58	0.02	ND	ND	1.49	289.679
CM-5	4.26	17.56	0.16	0.01	ND	0.94	519.643
CM-6	0.12	0.14	ND	0.03	0.01	2.08	369.24
CM-7	0.97	7.58	0.08	0.01	0.01	1.58	477.215
CM-8	7.12	10.45	ND	0.04	0.01	2.41	510.248
CM-9	0.87	17.54	0.12	ND	ND	1.94	482.34
CM-10	0.32	0.12	0.1	0.01	ND	2.04	358.246

- ND: Not detected

Table – 44 Distributions of metals concentrations in male children's blood from control areas

Individuals	***Cu(μg/L)***	***Zn(μg/L)***	***Cr(μg/L)***	***Ni(μg/L)***	***Pb(μg/L)***	***Mn(μg/L)***	***Fe(μg/L)***
CM-1	1.45	3.69	0.68	0.04	0.03	1.84	314.811
CM-2	0.14	3.21	0.32	0.15	ND	1.74	405.872
CM-3	2.15	16.71	1.5	0.41	0.02	1.23	235.832
CM-4	1.56	3.21	0.36	0.03	0.02	1.13	348.712
CM-5	0.12	12.54	0.23	0.01	0.01	1.09	213.411
CM-6	1.25	3.24	0.48	0.1	0.04	1.62	325.642
CM-7	1.24	11.45	0.33	0.03	0.02	2.1	245.86
CM-8	1.24	3.21	0.15	ND	ND	1.45	303.54
CM-9	3.54	1.23	0.32	0.03	ND	1.65	316.872
CM-10	0.49	1.25	0.13	0.06	0.01	1.87	198.471

***** Each value is the mean of seven readings

Table – 45 Distributions of metals concentrations in adolescent male blood from polluted areas

Individuals	*Cu(µg/L)*	*Zn(µg/L)*	*Cr(µg/L)*	*Ni(µg/L)*	*Pb(µg/L)*	*Mn(µg/L)*	*Fe(µg/L)*
ADM-1	1.56	25.04	1.8	ND	ND	1.72	423.012
ADM-2	4.42	33.74	ND	0.02	0.24	3.96	324.159
ADM-3	2.94	21.74	0.18	ND	0.08	3.74	421.021
ADM-4	3.14	21.74	0.18	0.02	0.2	3.68	508.121
ADM-5	1.72	24.82	0.1	0.16	ND	3.92	211.843
ADM-6	7.14	17.12	0.3	0.02	0.02	5.16	325.571
ADM-7	3.16	33.08	0.7	0.02	0.06	2.96	596.358
ADM-8	8.42	29.5	0.28	0.2	ND	1.32	498.451
ADM-9	2.24	17.38	1.68	0.02	ND	2.6	509.001
ADM-10	2.46	0.66	0.84	0.02	ND	2.9	438.561

Table – 46 Distribution of metals concentrations in adolescent male blood from control areas

Individuals	*Cu(µg/L)*	*Zn(µg/L)*	*Cr(µg/L)*	*Ni(µg/L)*	*Pb(µg/L)*	*Mn(µg/L)*	*Fe(µg/L)*
ADM-1	1.94	1.42	0.36	0.01	ND	1.34	356.71
ADM-2	0.96	9.33	0.87	0.05	0.07	1.11	320.422
ADM-3	0.17	12.34	0.12	ND	0.01	1.98	428.681
ADM-4	1.55	1.54	ND	0.04	0.03	1.75	347.981
ADM-5	1.71	6.42	0.42	0.11	0.05	1.2	301.632
ADM-6	0.12	11.23	0.16	ND	0.01	2.17	345.971
ADM-7	1.47	1.25	0.22	ND	ND	0.85	428.751
ADM-8	4.21	6.22	0.73	0.24	0.02	1.25	124.465
ADM-9	1.84	7.44	0.48	0.04	0.04	1.24	125.021
ADM-10	0.84	10.08	0.72	0.13	0.07	1.01	267.512

***** Each value is the mean of seven readings

Table –47 Distributions of metals concentrations in adults male blood from polluted areas

Individuals	*Cu(µg/L)*	*Zn(µg/L)*	*Cr(µg/L)*	*Ni(µg/L)*	*Pb(µg/L)*	*Mn(µg/L)*	*Fe(µg/L)*
AM-1	7.08	0.99	0.27	0.03	0.18	4.41	357.153
AM-2	4.5	46.29	0.72	0.03	0.24	6.24	507.962
AM-3	5.94	32.28	0.09	ND	0.03	4.8	467.189
AM-4	10.35	58.95	1.62	0.03	0.21	6.21	503.62
AM-5	5.61	4.62	0.03	ND	0.15	4.38	581.244
AM-6	3.03	41.07	0.27	ND	0.21	ND	368.951
AM-7	2.34	37.05	0.27	ND	ND	7.2	384.153
AM-8	13.53	31.05	0.24	0.3	ND	6.93	462.058
AM-9	14.16	56.1	0.21	0.03	0.03	6.12	531.246
AM-10	3.75	1.08	1.05	0.06	0.24	7.62	358.12

Table – 48 Distributions of metals concentrations in adults male blood from control areas

Individuals	*Cu(µg/L)*	*Zn(µg/L)*	*Cr(µg/L)*	*Ni(µg/L)*	*Pb(µg/L)*	*Mn(µg/L)*	*Fe(µg/L)*
AM-1	2.62	7.52	0.19	0.06	0.08	1.06	431.571
AM-2	1.45	2.58	0.09	0.04	0.03	1.62	245.946
AM-3	0.61	9.77	0.48	0.04	ND	2.00	248.655
AM-4	1.46	14.86	0.14	ND	0.02	2.66	276.483
AM-5	1.17	9.14	0.91	0.74	0.07	1.31	299.523
AM-6	1.53	8.24	0.32	0.15	0.05	1.21	241.143
AM-7	0.12	1.45	0.15	0.01	ND	1.24	364.892
AM-8	0.87	12.56	0.14	ND	0.04	1.87	268.583
AM-9	0.12	1.54	0.17	0.14	ND	1.08	415.871
AM-10	3.58	10.75	0.72	0.04	0.04	0.98	308.412

*Each value is the mean of six readings

Table – 49 Distributions of metals concentrations in old age male blood from polluted areas

Individuals	*Cu(μg/L)*	*Zn(μg/L)*	*Cr(μg/L)*	*Ni(μg/L)*	*Pb(μg/L)*	*Mn(μg/L)*	*Fe(μg/L)*
OAM-1	12.25	87.7	0.05	ND	ND	7.45	269.99
OAM-2	7.25	50.35	0.45	0.05	ND	9.2	212.023
OAM-3	12.9	37.95	0.7	0.05	0.35	13.4	268.954
OAM-4	24.25	39.2	1.85	ND	ND	7.4	348.982
OAM-5	34.35	34.45	1.6	0.05	ND	8.4	287.182
OAM-6	3.75	49.35	18.4	0.05	0.1	8.4	502.211
OAM-7	13.4	49.25	0.35	0.1	ND	11.55	284.586
OAM-8	21.05	43.35	0.1	0.05	0.2	8.25	506.351
OAM-9	2.4	29.35	1.6	0.05	0.05	6.25	506.782

Table – 50 Distributions of metals concentrations in old age male blood from control areas

Individuals	*Cu(μg/L)*	*Zn(μg/L)*	*Cr(μg/L)*	*Ni(μg/L)*	*Pb(μg/L)*	*Mn(μg/L)*	*Fe(μg/L)*
OAM-1	2.15	14.89	0.32	ND	0.15	1.64	247.983
OAM-2	0.15	11.54	0.22	ND	0.02	0.95	204.922
OAM-3	0.25	1.59	0.32	0.02	0.01	2.05	315.781
OAM-4	1.62	8.33	0.54	0.09	0.08	1.42	425.413
OAM-5	0.12	11.25	0.15	0.08	0.01	1.4	254.872
OAM-6	1.13	18.42	1.04	0.15	0.06	1.7	467.165
OAM-7	1.21	10.11	0.28	ND	ND	8.8	410.84
OAM-8	0.01	14.56	0.22	0.07	0.01	1.85	265.473
OAM-9	0.14	3.21	0.26	0.13	ND	1.07	465.253
OAM-10	1.25	1.54	0.35	ND	0.08	1.32	417.847

*Each value is the mean of six readings

Table – 51 Distributions of metals concentrations in female children's blood from polluted area

Individuals	*Cu(µg/L)*	*Zn(µg/L)*	*Cr(µg/L)*	*Ni(µg/L)*	*Pb(µg/L)*	*Mn(µg/L)*	*Fe(µg/L)*
CF-1	0.86	20.41	0.15	0.04	ND	0.76	405.283
CF-2	5.21	5.89	0.08	0.01	0.04	1.32	358.456
CF-3	4.21	7.89	0.24	ND	ND	1.07	368.95
CF-4	0.89	15.21	0.04	0.03	0.01	0.75	530.942
CF-5	1.42	10.66	0.02	0.04	ND	1.64	507.687
CF-6	1.87	10.24	0.78	ND	ND	2.08	463.104
CF-7	1.45	0.12	0.08	ND	0.04	1.36	510.874
CF-8	2.86	0.32	0.05	0.01	ND	1.24	502.314

Table – 52 Distributions of metals concentrations in female children's blood from control area

Individuals	*Cu(µg/L)*	*Zn(µg/L)*	*Cr(µg/L)*	*Ni(µg/L)*	*Pb(µg/L)*	*Mn(µg/L)*	*Fe(µg/L)*
CF-1	0.135	1.404	ND	0.081	0.009	1.206	487.652
CF-2	0.225	2.889	0.387	0.009	ND	1.539	406.582
CF-2	0.189	1.305	0.225	ND	0.009	1.422	409.841
CF-3	0.117	2.286	0.108	ND	0.117	1.287	394.121
CF-4	0.135	1.413	0.009	ND	0.18	0.513	426.716
CF-5	0.135	2.889	0.216	0.072	0.009	0.819	542.214
CF-6	0.234	1.395	0.405	0.009	0.018	0.936	245.353
CF-7	0.333	1.125	0.216	0.036	0.27	1.935	378.212
CF-8	0.108	1.125	ND	0.045	ND	1.962	287.946
CF-9	0.207	10.107	0.081	0.009	ND	1.872	237.41
CF-10	1.116	10.008	ND	ND	ND	1.881	248.962

*Each value is the mean of seven readings

Table – 53 Distribution of metals concentrations in adolescent female blood from polluted areas

Individuals	*Cu(µg/L)*	*Zn(µg/L)*	*Cr(µg/L)*	*Ni(µg/L)*	*Pb(µg/L)*	*Mn(µg/L)*	*Fe(µg/L)*
ADF-1	12.615	15.54	0.105	0.135	ND	3.165	387.14
ADF-2	2.385	34.71	0.21	0.015	ND	1.26	538.943
ADF-3	3.87	15.675	0.135	ND	0.075	2.505	533.405
ADF-4	5.535	21.78	ND	ND	ND	2.76	528.485
ADF-5	2.835	20.535	ND	0.03	0.12	1.29	264.285
ADF-6	1.47	16.305	1.86	0.015	ND	2.64	452.36
ADF-7	0.72	21.84	0.18	0.72	0.075	1.065	479.543
ADF-8	11.91	8.67	ND	0.06	0.015	1.845	264.12

Table –54 Distribution of metals concentrations in adolescent female blood from control areas

Individuals	*Cu(µg/L)*	*Zn(µg/L)*	*Cr(µg/L)*	*Ni(µg/L)*	*Pb(µg/L)*	*Mn(µg/L)*	*Fe(µg/L)*
ADF-1	1.25	11.45	0.26	ND	0.07	2.04	235.842
ADF-2	1.54	11.47	0.15	0.01	0.05	2.41	325.144
ADF-3	1.23	12.54	0.26	0.01	0.06	1.55	365.214
ADF-4	1.45	14.87	0.13	0.01	0.12	1.08	324.154
ADF-5	1.25	11.54	1.24	0.01	0.05	0.58	271.453
ADF-6	1.45	13.21	0.13	0.02	0.07	1.54	419.582
ADF-7	1.25	11.47	0.45	0.01	0.04	1.78	456.257
ADF-8	0.12	11.11	0.25	0.01	0.01	1.64	417.146
ADF-9	0.23	11.25	0.09	0.01	ND	2.87	401.018
ADF-10	0.21	11.47	0.1	0.01	0.08	2.68	381.476

*Each value is the mean of six readings

Table – 55 Distributions of metals concentrations in adults female blood from polluted areas

Individuals	*Cu(μg/L)*	*Zn(μg/L)*	*Cr(μg/L)*	*Ni(μg/L)*	*Pb(μg/L)*	*Mn(μg/L)*	*Fe(μg/L)*
AF-1	3.476	32.758	0.044	ND	ND	5.588	3487.64
AF-2	1.342	22.55	0.0462	0.55	0.132	3.41	412.01
AF-3	7.062	44.088	0.022	ND	ND	4.048	456.368
AF-4	5.434	45.056	0.308	ND	ND	4.422	421.71
AF-5	5.434	22.77	0.154	ND	ND	3.124	487.424
AF-6	1.914	27.632	0.154	0.022	0.264	3.454	247.684
AF-7	11.88	23.298	0.044	0.066	0.132	3.85	267.31
AF-8	1.056	22.572	0.374	0.022	ND	3.696	357.424
AF-9	3.432	40.502	0.506	ND	ND	3.96	421.361
AF-10	3.872	22.77	0.154	ND	ND	3.586	289.154

Table – 56 Distributions of metals concentrations in adults female blood from control areas

Individuals	*Cu(μg/L)*	*Zn(μg/L)*	*Cr(μg/L)*	*Ni(μg/L)*	*Pb(μg/L)*	*Mn(μg/L)*	*Fe(μg/L)*
AF-1	0.14	11.2	0.09	0.1	0.07	2.41	320.473
AF-2	0.22	10.01	0.24	0.02	0.04	1.84	384.122
AF-3	0.12	10.05	0.22	ND	1.47	1.67	387.656
AF-4	0.25	10.01	0.15	ND	0.04	1.49	348.144
AF-5	0.13	10.02	1.25	0.08	0.07	1.75	406.983
AF-6	0.24	10.12	0.18	0.01	0.07	1.85	423.873
AF-7	0.13	10.32	0.08	ND	ND	1.56	410.252
AF-8	0.21	10.12	0.17	ND	ND	2.09	408.567
AF-9	0.14	0.12	0.11	0.01	0.01	2.41	308.401
AF-10	0.21	1.24	0.12	ND	0.05	1.11	384.15

*Each value is the mean of six readings

Table – 57 Distributions of metals concentrations in old age female blood from polluted areas

Individuals	*Cu(μg/L)*	*Zn(μg/L)*	*Cr(μg/L)*	*Ni(μg/L)*	*Pb(μg/L)*	*Mn(μg/L)*	*Fe(μg/L)*
OAF-1	13.92	81.36	0.56	0.2	0.04	4.32	368.91
OAF-2	6.32	66.16	1.4	0.04	0.12	5.92	596.358
OAF-3	11.76	43	0.48	ND	0.04	7.92	502.11
OAF-4	30.32	53.84	0.24	ND	ND	7.04	384.124
OAF-5	5.8	54.16	0.12	ND	ND	6.56	203.841
OAF-6	8.44	39.24	ND	ND	ND	5.6	284.153
OAF-7	5.8	1.44	0.52	ND	ND	6.08	560.21
OAF-8	29.72	42.84	ND	ND	ND	7.56	345.68
OAF-9	16.92	41.72	0.04	ND	ND	6.08	278.423
OAF-10	14.44	1.92	0.48	0.52	ND	10.52	541.301

Table – 58 Distributions of metals concentrations in old age female blood from control areas

Individuals	*Cu(μg/L)*	*Zn(μg/L)*	*Cr(μg/L)*	*Ni(μg/L)*	*Pb(μg/L)*	*Mn(μg/L)*	*Fe(μg/L)*
OAF-1	0.45	1.42	0.08	0.0224	0.008	0.0016	387.652
OAF-2	0.15	10.12	0.09	0.056	0.0016	0.0048	341.102
OAF-3	0.13	0.15	0.1	0.0192	ND	0.0016	401.235
OAF-4	0.15	1.3	0.07	0.0096	ND	ND	436.252
OAF-5	0.12	1.45	ND	0.0048	ND	ND	456.32
OAF-6	0.15	10.12	0.08	ND	ND	ND	472.652
OAF-7	0.26	11.23	ND	0.0208	ND	ND	248.651
OAF-8	0.32	11.54	0.09	ND	ND	ND	287.262
OAF-9	0.46	10.23	0.17	0.0016	ND	ND	289.231
OAF-10	0.13	10.11	0.15	0.0192	0.0208	ND	287.43

*Each value is the mean of six readings

In old age male, mean concentrations of Cu Zn, Cr, Ni, Pb, Mn and Fe were 0.80, 9.54, 0.37, 0.05, 0.04, 2.22 and 347.55 μg/L, while in female these values were 0.23, 6.78, 0.08, 0.06, 0.04, 1.17 and 318.78 μg/L, respectively. From the Table 60 it is clear that the mean concentrations of Cu Zn, Cr, Ni, Pb, Mn and Fe in male children' blood samples collected from polluted area were 2.52, 10.71, 0.05, 0.02, 0.02, 1.70 and 402.75 µg/L, while in female children these values were 2.35, 8.84, 0.18, 0.02, 0.01, 1.28 and 455.95 µg/L, respectively.

In adolescent male Cu Zn, Cr, Ni, Pb, Mn and Fe mean concentrations were 3.72, 22.48, 0.61 , 0.05, 0.06 , 3.20 and 425.60 µg/L and in female these values were 5.17, 19.38, 0.31, 0.122, 0.04, 2.07 and 431.04 µg/L, respectively. In case of male adults, mean concentrations of Cu, Zn, Cr, Ni, Pb, Mn and Fe were 7.03, 30.95, 0.48, 0.05, 0.13, 5.39 and 452.17) µg/L, while in female these values were 4.49, 30.40, 0.18, 0.07, 0.05, 3.91 and 684.81 µg/L, respectively. In old age male, Cu Zn, Cr, Ni, Pb, Mn and Fe mean concentrations were 14.62, 46.77, 2.79 , 0.04, 0.07, 8.92 and 354.12 µg/L, while in female these values were 14.34, 42.57, 0.38, 0.08, 0.02, 6.76 and 406.51 µg/L, respectively. Comparison between mean metal concentrations of males and females of different age groups and reference values (123,124) are also given in the Fig. 15, 16, 17 and 18 (No clear reference value is available for Cr).

Table-59 Statistical parameters of metal concentrations (µg/L) in blood of people of different age groups from Peshawar

Individuals		***Cu***	***Zn***	***Cr***	***Ni***	***Pb***	***Mn***	***Fe***
n =70	Mean	2.52	10.71	0.05	0.02	0.02	1.70	402.75
Children (male)	Range	(0.12-7.12)	(0.12-17.56)	(0-0.16)	(0-0.07)	(0-0.07)	(0.94-2.41)	(238.54-519.64)
	Std. Deviation	0.065	1.473	0.008	0.002	0.005	0.079	15.645
n =65	Mean	3.72	22.48	0.61	0.05	0.06	3.20	425.61
Adolescent(male)	Range	(1.57-8.42)	(0.66-33.74)	(0-1.82)	(0-0.210)	(0-0.24)	(1.32-5.16)	(211.84-596.37)
	Std. Deviation	0.015	2.085	0.026	0.005	0.004	0.069	12.750
n =63	Mean	7.03	30.95	0.48	0.05	0.013	5.39	452.17
Adults(male)	Range	(2.34-14.16)	(0.99-58.95)	(0.031-1.62)	(0-0.31)	(0-0.24)	(0-7.62)	(357.15-581.24)
	Std. Deviation	0.016	2.065	0.068	0.002	0.004	0.010	18.568
n =55	Mean	14.62	46.77	2.79	0.04	0.20	8.92	354.12
Old age (male)	Range	(2.48-34.35)	(29.35-87.72)	(0.05-18.68)	(0-0.12)	(0-0.35)	(6.25-13.43)	(212.02-506.782)
	Std. Deviation	1.067	3.093	0.0178	0.0004	0.004	1.044	18.467
n =70	Mean	2.35	8.84	0.18	0.02	0.01	1.28	455.95
Children (female)	Range	(0.86-5.21)	(0.12-20.41)	(0.02-0.78)	(0-0.04)	(0-0.04)	(0.75-2.08)	(358.45-530.94)
	Std. Deviation	0.010	1.048	0.052	0.007	0.008	0.043	16.8260
n =65	Mean	5.17	19.38	0.31	0.12	0.04	2.07	431.04
Adolescent(female)	Range	(0.72-12.61)	(8.67-34.71)	(0-1.86)	(0-0.72)	(0-0.12)	(1.05-3.16)	(264.12-538.94)
	Std. Deviation	0.0179	1.144	0.020	0.006	0.001	0.0135	14.655
n =63	Mean	4.49	30.40	0.18	0.07	0.05	3.91	684.81
Adults(female)	Range	(1.5-11.88)	(22.55-45.05)	(0.-0.55)	(0-0.64)	(0-0.72)	(3.12-5.58)	(247.68-348.64)
	Std. Deviation	0.0468	2.304	0.004	0.007	0.004	0.015	15.217
n =55	Mean	14.34	42.57	0.38	0.08	0.12	6.76	406.51
Old age (female)	Range	(5.81-0.76)	(1.44-81.36)	(0-1.4)	(0-0.53)	(0-0.12)	(4.32-10..52)	(203.84-596.36)
	Std. Deviation	1.0282	2.0279	0.005	0.0012	0.0002	0.018	15.417

Table-60 Statistical parameters of metal concentrations (µg/L) in blood of people of different age groups from lower Dir

Individuals		***Cu***	***Zn***	***Cr***	***Ni***	***Pb***	***Mn***	***Fe***
n =70	Mean	1.32	5.97	0.45	0.09	0.02	1.57	290.90
Children (male)	Range	(0.12-3.54)	(1.23-16.71)	(0.13-1.5)	(0-0.41)	(0-0.04)	(1.09-2.10)	(198.47-405.87)
	Std. Deviation	0.012	0.0164	0.001	0.002	0.003	0.039	15.644
n =65	Mean	1.48	6.73	0.41	0.06	0.03	1.39	304.71
Adolescent(male)	Range	(0.12-4.21)	(1.25-12.34)	(0-0.87)	(0-0.24)	(0-0.07)	(0.85-2.17)	(124.46-428.75)
	Std. Deviation	0.059	0.159	0.002	0.007	0.006	0.002	17.212
n =63	Mean	1.35	7.84	0.33	0.12	0.03	1.50	310.11
Adults(male)	Range	(1.2-3.58)	(1.45-14.86)	(0.09-0.91)	(0-0.74)	(0-0.08)	(0.98-2.66)	(241.14-431.57)
	Std. Deviation	0.078	0.641	0.082	0.023	0.008	0.013	13.363
n =55	Mean	0.80	9.54	0.37	0.05	0.04	2.22	347.55
Old age (male)	Range	(0.01-2.15)	(1.54-18.42)	(0.15-1.04)	(0-0.15)	(0-0.15)	(0.95-8.8)	(204.92-204.92)
	Std. Deviation	0.016	0.564	0.057	0.007	0.009	0.036	19.868
n =70	Mean	0.30	3.63	0.17	0.03	0.06	1.55	369.55
Children (female)	Range	(0.12-1.24)	(1.25-1.12)	(0-0.45)	(0-0.09)	(0-0.30)	(0.57-2.18)	(237.41-542.214)
	Std. Deviation	0.021	0.091	0.068	0.007	0.002	0.015	12.366
n =65	Mean	1.00	12.04	0.31	0.01	0.06	1.82	359.73
Adolescent(female)	Range	(0.12-1.54)	(11.11-14.87)	(0.09-1.24)	(0-0.02)	(0-0.12)	(0.58-2.87)	(235.84-456.26)
	Std. Deviation	0.070	1.871	0.045	0.004	0.004	0.011	16.926
n =63	Mean	0.18	8.32	0.26	0.02	0.18	1.82	378.26
Adults(female)	Range	(0.12-0.25)	(0.12-11.20)	(0.08-1.25)	(0-0.10)	(0-1.47)	(1.11-2.41)	(308.40-423.87)
	Std. Deviation	0.051	1.405	0.0351	0.006	0.045	0.040	39.625
n =55	Mean	0.23	6.77	0.05	0.01	0.24	1.17	318.78
Old age (female)	Range	(0.12-0.46)	(0.15-11.54)	(0-0.17)	(0-0.01)	(0-0.1)	(0.56-1.84)	(248.65-472.65)
	Std. Deviation	0.003	0.031	0.004	0.000	0.006	0.002	11.665

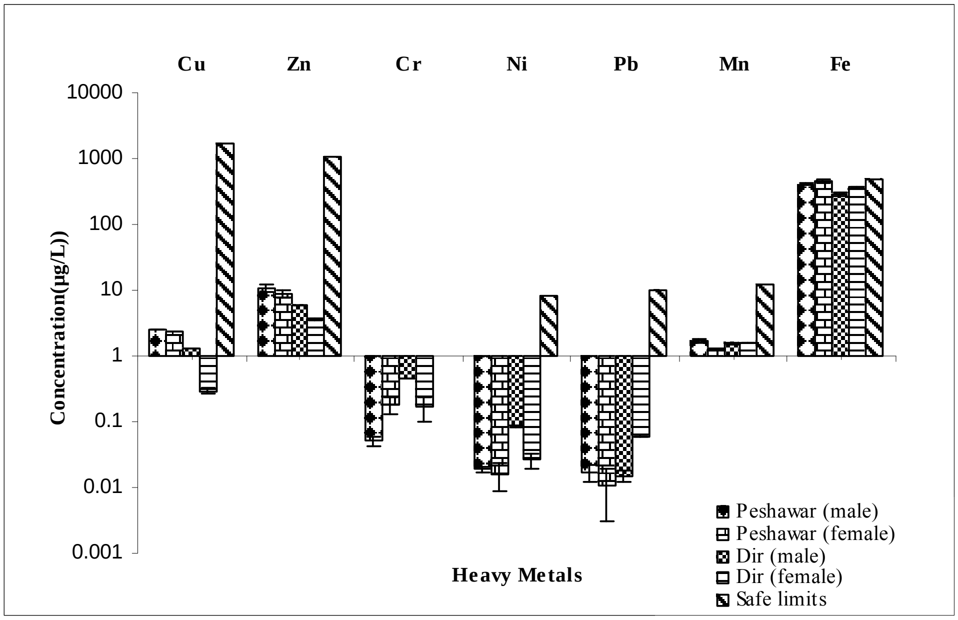

Fig.15 Comparative plot of blood metal concentrations of children male and female from the study areas and with the reference values

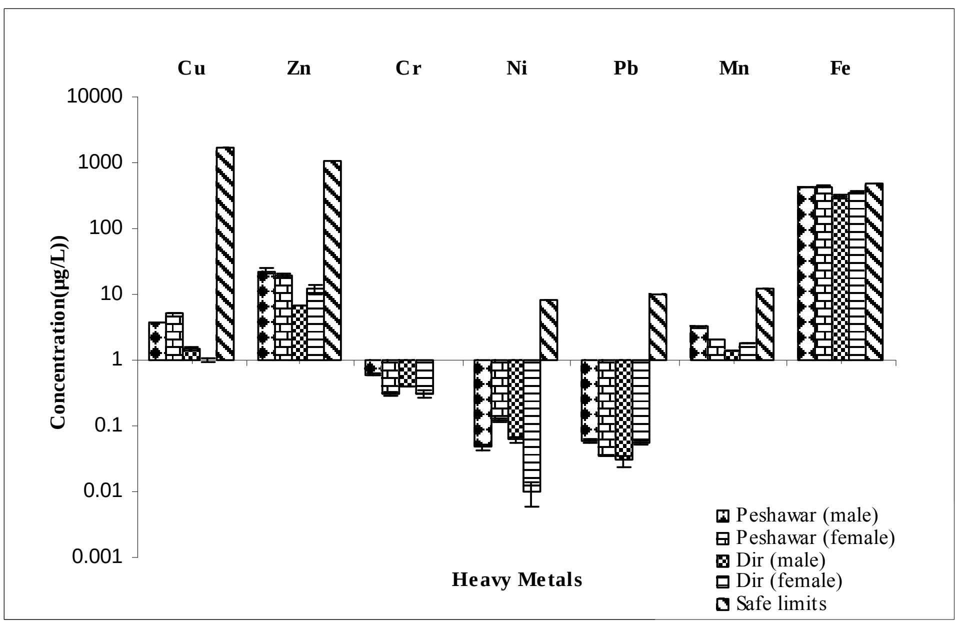

Fig.16 Comparative plot of blood metal concentrations of adolescent male and female from the study areas and with the reference values

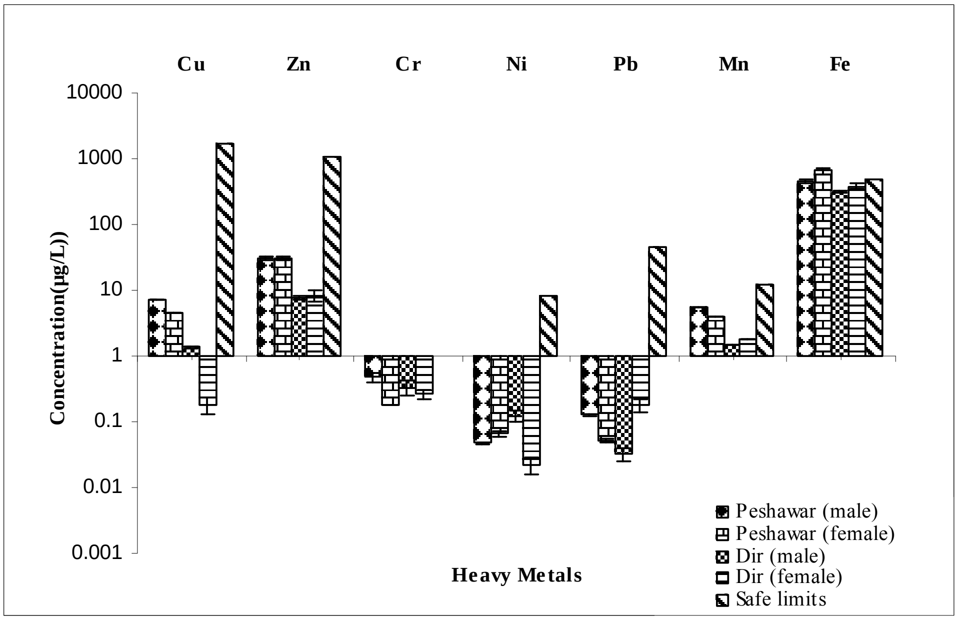

Fig.17 Comparative plot of blood metal concentrations of adult male and female from the study areas and with the reference values

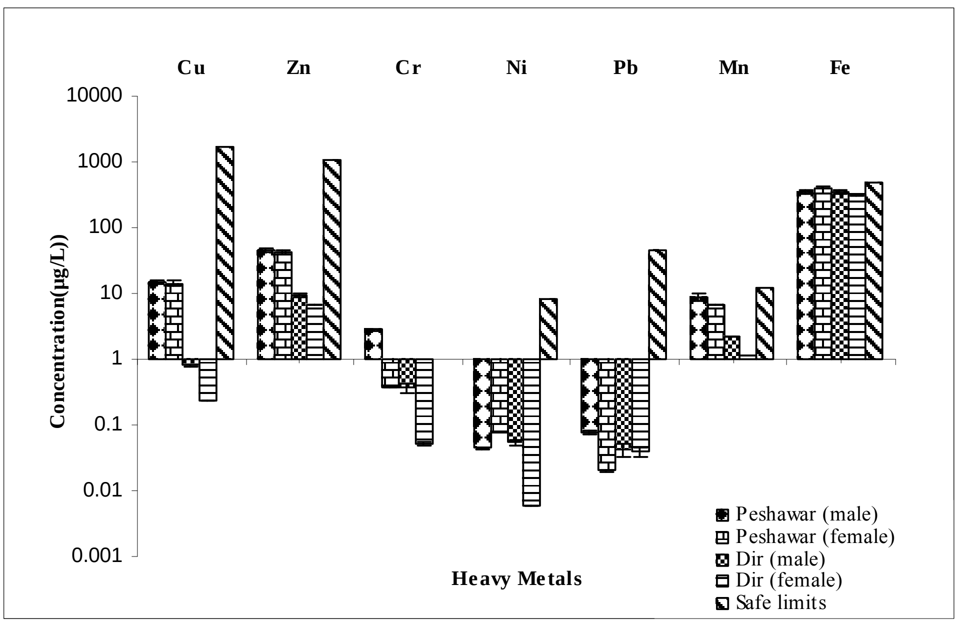

Fig.18 Comparative plot of blood metal concentrations of old age male and female from the study areas and with the reference values

3.4.3 Distribution of heavy metals in meat and milk samples

The statistical parameters of metal concentrations in meat and milk samples collected from contaminated and control areas are presented in Table 61 . In meat samples collected from control area, the mean concentrations of Cu, Zn, Cr, Ni, Pb, Mn and Fe were 68.21, 18.68, 3.91, 0.07, 12.18 and 29.00 μg/L, respectively, while in milk samples these were 9.96, 0.49, 45.94, 0.036 and 26.24 μg/L, respectively. In case of meat samples collected from polluted area Cu, Zn, Cr, Ni, Pb, Mn and Fe mean concentrations were 91.56, 2.26, 7.34, 0.04, 53.13 and 55.07 μg/L, respectively, while in milk samples these were 14.89, 0.58, 8.44, 0.30, and 37.45 μg/L, respectively.

Table -61 Statistical parameters of metal concentrations (μg/L) in meat and milk samples collected from different areas in Peshawar and lower Dir

Location/Sample		*Cu*	*Zn*	*Cr*	*Ni*	*Pb*	*Mn*
Dir	Mean	68.28	18.68	3.91	0.10	12.18	29.00
Meat (*n* =20)	Range	(35.43-169.55)	(0.784-2.37)	(3.380-15.24)	(0.06-0.16)	(13.69-59.93)	(4.322-22.56)
	Std. Deviation	12.435	0.014	0.022	0.001	3.241	1.152
Dir	Mean	9.96	0.49	5.94	0.04	5.34	26.24
Milk (*n* =24)	Range	(8.347-12.66)	(0.354-1.27)	(25.635-73.00)	(0.165-0.93)	(0.01-9.23)	(17.753-47.57)
	Std. Deviation	1.352	0.004	5.448	0.026	0.056	2.113
Peshawar	Mean	91.57	45.26	7.34	0.74	53.13	55.07
Meat(*n* =20)	Range	(37.353-120.42)	(1.355-2.77)	(4.899-8.57)	(0.024-0.05)	(4.636-81.78)	(15.812-5.80)
	Std. Deviation	6.983	0.085	0.113	0.003	4.230	4.036
Peshawar	Mean	14.88	0.88	8.44	0.300	13.23	37.45
Milk (*n* =26)	Range	(7.658-22.69)	(0.399-0.78)	(36.473-49.80)	(0.225-0.38)	(0.12-17.34)	(29.836-42.57)
	Std. Deviation	2.532	0.095	5.038	0.079	1.234	3.723

3.4.4 Statistical Analysis

NOVA (A multivariate statistical technique) was applied to find-out the difference between the blood metal concentrations of different age groups of polluted and control area, as well as within the same area and between male and female participants of the study area. Comparing male children from the two areas, a significant difference was found for Cr ($p = 0.006$) and Fe ($p = 0.007$) concentrations, while in female children there was a significant difference for Cu ($p = 0.001$) and Zn ($p = 0.001$) concentrations. No significant variation was noted for the concentrations of Mn, Pb and Ni. Comparing the metal concentrations of adolescent's blood samples of the polluted and control areas, a significant difference for Cu ($p = 0.013$), Zn ($p = 0.000$), Mn ($p = 0.000$) and Fe ($p = 0.024$) concentrations, while in females a significant variation for Cu ($p = 0.012$) and Zn ($p = 0.008$) concentrations was observed. Adult males were found to be significantly different with respect to Cu ($p = 0.001$), Zn ($p = 0.004$), Pb ($p = 0.010$), Mn ($p = 0.000$) and Fe ($p = 0.001$) concentrations and in female adults significant variation in Cu ($p = 0.000$), Zn ($p = 0.000$) and Mn ($p = 0.000$) concentrations was noticed. Old age male of the two areas were significantly different with respect to of Cu ($p = 0.001$), Zn ($p = 0.000$) and Mn ($p = 0.000$) concentrations and in female significant variation in Cu ($p = 0.000$), Zn ($p = 0.000$) and Mn ($p = 0.000$) concentrations were found. We also compared the metal concentrations in the blood samples of different age groups within the same area, significant variation was found in the concentrations of some metals. In order to find out which group have significantly higher concentration of a particular metal than the other we applied post-hoc test that is the extended form of MNOVA. The results showed that Zn concentration was relatively higher in different age groups compared to Cu and Mn concentrations. A higher statistical variation in Cu concentrations was observed between the old age people as compared to adults, adolescent and children which indicated that old age people have accumulated higher concentrations of metal compared to other age groups. Pb concentration was found higher in old age's blood samples (p = 0.008) as compared to adults, adolescent and children. Mn concentration was also found significantly different in different age groups of the same area, with higher concentration in the old age followed by adults , adolescent and children respectively. For other metals i.e Cr, Ni, Fe no any significant variations were found ($p>0.05$). Comparing female subjects of different age groups of the same area, these were found significantly different in Cu (p = 0.011), Zn (p = 0.000) and Mn (p = 0.001) concentrations. A Comparison of the male and female subjects of different age groups also revealed no any significant differences between blood's metal concentrations of children and adolescent while adults male and female were found significantly different in their Cu concentrations. Old age males and female subjects were found to be different in Mn (p = 0.008) concentration. In order to find out the effects of the food crops, meat and milk consumption on the blood we statistically correlated the metal concentration in both the media . Data showed some positive correlation between the metal pairs in case of foods and blood i.e. Between Cu and Zn (r = 0.591), Mn and Cu (r = 0.412) Ni and Pb (r = 0.408) , Cr and Ni (r = 0.419) while a negative correlation was also found between Cu and Cr (r = -0.583) Mn and Pb (r = -0.580) Zn and Cr (r = 0.460) Cu and Pb (r = -0.523) and Zn and Pb (r = 0.431). Meat and milk samples collected from the two areas were also found to have statistically different concentration of metals.

3.4.5 Cluster Analysis

Cluster analysis using hierarchal cluster method was applied in order to classify the individuals from polluted and control areas into groups based on their mean metal concentrations in their blood. This classified individuals from both the areas into four groups the data is given in Table 62 and figure 19.

Table – 62 Classification of individuals from polluted and control areas based on their mean metals concentration in their blood

Group	*Individuals*
1	Male children, adolescent and adults from control areas
2	Female children, adolescent, adults and old age and old age males from control and polluted area
3	Children, adolescent and adults males and female children and adolescent from polluted area
4	Adults females from the polluted

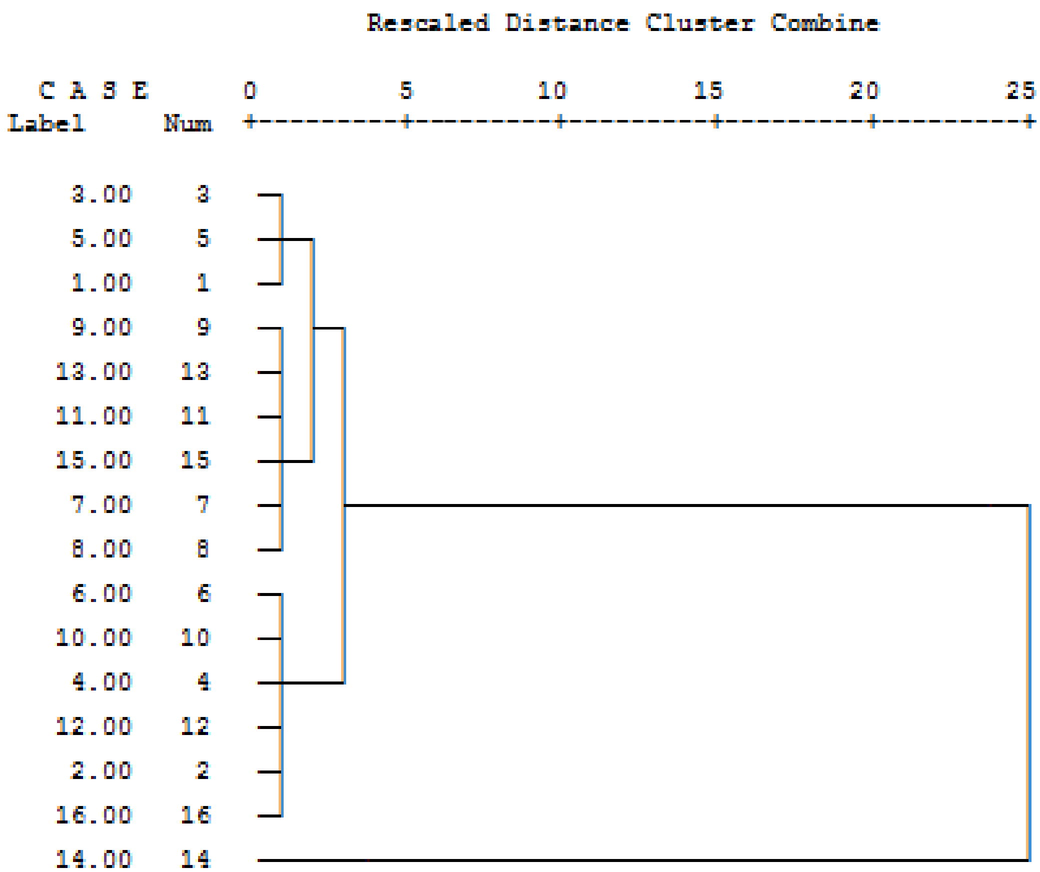

Fig.19 Dendogram for the classification of individual from the polluted area and control area based on the metals as variables

Discussions

Transfer factor is a convenient way of quantifying relative differences in bioavailability of metals to plants (125). In this study, the transfer co-efficient were found higher for Cu, Zn, Mn and Cr. This is due to high mobility and phytoavailability of these metals, which is a reflection of their relatively poor sorption in soils. In contrast, metals such as Ni, and Pb have low transfer coefficients because they are strongly bound, usually to the soil colloids(126). The results of our study (Table-42) are in good agreement with the earlier two hypotheses which clearly indicated high concentrations of Zn, Cu, and Mn in plants and high transfer coefficient values as compared to Ni and Pb. In case of control samples, which is generally free from anthropogenic contamination, the metal concentrations and their transfer co-efficients were found very low. High concentrations of Cu, Cr, Pb and Mn were observed in milk samples. Buffalo milk was found to have high concentrations of metals as compared to cow's milk which may be ascribed to the high fat content in buffalo's milk, which helps in metal retention due to the formation of bioactive (lipophilic) complexes(130).

Large variation in the minimum, maximum and mean metal concentrations was observed in the blood samples collected from both study areas. Higher mean concentrations were found for Cu, Zn and Mn as compared to Cr, Ni, and Pb and this is in good agreement with the mean metal concentrations in different food crops from polluted and background areas (data given in Table-35,36) . Most metals showed random distribution as shown by large standard deviation values. In case of the polluted and control areas, the order of distribution of trace metals were found as Zn>Cu>Mn>Cr>Ni>Pb. The concentrations of the Zn, Cu and Mn in the blood samples from the polluted area was found nearly two folds higher as compared to control area, indicating the large input of the selected metals due to consumption of food crops, meat and milk contaminated with respective metals. This clearly indicated the effect of the food crops, milk and meat consumption on the metal composition of the blood. The gender-wise and age-wise distribution of trace metals in the blood of the subjects are also shown in Figures 15,16,17 and 18. It is obvious from the plots that overall concentrations of metals in the subjects from the polluted area were higher than the control. However, their concentrations were found within the safe limits and may not pose any risk. Random distribution of trace metal concentrations was noticed in the blood of males and females subjects. Significant differences in concentrations were observed for Cu, Zn and Mn in the blood samples from two areas as well as between different age groups. To find out food crops, meat and milk as the possible sources of contamination of the human blood along with the other sources, correlation study was also performed between the metal concentrations in food crops, meat milk and blood. Strong correlation was observed between Cu and Zn, followed by Mn-Zn , Pb-Ni, Cr-Ni and Ni-Cr metal pairs, while Cr and Pb was found to be negatively correlated with Cu, Zn and Mn . The correlation study further strengthened by the linear regression analysis which gives the dependence of different metal pairs in the form of equations given in the Table-63. Cluster analysis also classified the individuals from both the areas into four groups based on their mean metals concentrations in their blood. Individuals having nearly the same total metal concentrations fall in the same group. The correlations and regression study clearly indicate that the consumption of metal contaminated food increased the concentrations of metals in the blood as compared to metal concentrations in the food crops and blood collected from the control area. Statistical comparison also revealed that old age males and females have accumulated higher concentrations of the these metals in their blood as compared to adults, adolescents and children which may be due to slow accumulation of these metals in their bodies. In a few cases of the polluted area, the participants had a variety of health risk. Irritation of the skin with black rashes was the symptoms which may be attributed to exposure to Pb Zn and Cr concentrations(128,129).

Table 63 Significant linear correlation for selected metals in food crops and blood samples collected form different localities in polluted and control areas.

Matrix	*Regression Equation*	*Correlations (r)*
Food Crops and Blood	Cu=66.738+0.585[Zn]	0.591
	Zn=25.443+0.645[Cu]	0.587
	Cr=1.325-0.0495[Cu]	-0.538
	Cr=1.325-0.248[Pb]	-0.429
	Ni=26.851+0.429[Cr]	-0.419
	Cr=26.851+0.760[Pb]	0.488
	Pb=0.250-991[Mn]	-0.598
	Pb=0.250-0.665[Zn]	-0.431
	Mn=50.994+803[Zn]	0.612
	Cr=0.873-0.532[Mn]	-0.330
	Ni=61.580-0.964[Cr]	-0.402
	Ni=61.580+0.662[Pb]	0.412

r-Values ≥ 0.330 or r = - 0.330 are significant at $p < 0.05$

3.5 Anthropometric measurements for the nutritional status of the individuals from the study areas

In the present study anthropometric parameters such as age, height, weight, Mid upper arm circumference (MUAC), Wrist circumference (WC), Body mass index (BMI), frame size, Basal metabolic rate (BMR), standard daily allowance (SDA) for life style and total energy requirements were measured for the determination of nutritional status of the individuals from the study areas. The data has been provided in the tables 64-67. From the Table 64 it is clear that fro the individuals male from the polluted area the minimum age of 14 years and maximum of 73 years for adolescent, adults and old age with the median on of 22 and standard deviation of 19.59 wer recorded. Maximum height of 179 cm among old age and minimum of 149cm among adolescent with the median of 23 and standard deviation of 7.93 were found. Among males lower weight 0f 46 Kg and higher of 95 Kg for old age with median of 24 and standard deviation of 10.24 were noticed. Lower MUAC of 22 cm and higher of 34cm with the median 25 and standard deviation of 2.85 were recorded for adolescent and adults respectively. Wrist circumference with the lower value of 14cm and high of 20 cm with the median 26 and standard deviation of 5.70 were found fro adolescent and old age males repectively.Higher BMI of 32 and lower of 15 with the median of 27 and standard deviation of 17.27,lower frame size o f 8.29 for old age and higher of 11.33 with the median 28 and standard deviation of 3.04 were found for the old age males. Higher values of BMR 2280Cal/Kh/24 hours and lower 1104 Cal/Kh/24 with the median 29 and standard deviation 245.45 and higher Specific Dynamic Activity SDA 10% 228 and lower of 110 with median 30 and standard deviation 24 were recorded for old age and adolescent males respectively Maximum value of allowance for the life style 2280 and lower of 662 with median 31 and standard deviation of 417 and total energy requirement /day of 4788 and lower 1876 with the median of 32 and standard deviation of648 were found for adolescent and old age respectively.

From the Table 65 it is clear that for the individuals females from the polluted area the minimum age of 14 years and maximum of 60 years for adolescent, adults and old age with the median on of 25 and standard deviation of 25.76 were recorded. Maximum height of 169 cm among adults and minimum of 140cm among the adults with the median of 26 and standard deviation of 7.98 were found. Among females lower weight of 36 Kg for adolescent and higher of 70 Kg for adults with median of 27 and standard deviation of 8.95 were noticed. Lower MUAC of 9.30 cm and higher of 19.40 cm with the median 28 and standard deviation of 1.92 were recorded for adolescent and adults respectively. Wrist circumference with the lower value of 13.30cm and higher of 18.40 cm with the median 29 and standard deviation of 1.28 were found for adolescent females. Higher BMI of 27.58 for old age and lower of 15.76 for adolescent with the median of 30 and standard deviation of 3.72, higher frame size o f 12.52 and lower of 8.09 for adults with the median 31 and standard deviation of 1.06 were found. Higher values of BMR 1512Cal/Kh/24 hours and lower 734.40 Cal/Kh/24 with the median 32 and standard deviation 193.42 and higher Specific Dynamic Activity SDA 10% 151 and lower of 73 with median 33 and standard deviation 19 were recorded for adults and adolescent females respectively. Maximum value of allowance for the life style 1318 and lower of 441 with median 34 and standard deviation of 224 and total energy requirement /day of 2767 and lower 1248 with the median of 35 and standard deviation of 370 were found for old age andadolsecent females respectively

From the Table 66 it is clear that for the individuals males from the control area the minimum age of 19 years and maximum of 67 years for adolescent, adults and old age with the median on of 27 and standard deviation of 14.84 were recorded. Maximum height of 179 cm among adolescent and minimum of 149cm among old age with the median of 28 and standard deviation of 8.13 were found. Among males lower weight of 45 Kg and higher of 72 Kg for adolescent with median of 29 and standard deviation of 7.73 were noticed. Lower MUAC of 20 cm and higher of 30cm with the median 30 and standard deviation of 2.46 were recorded for adolescent and adults respectively. Wrist circumference with the lower value of 15cm and high of 18.80 cm with the median 31 and standard deviation of 0.98 were found for adolescent and adults males respectively. Higher BMI of 28.30 for old age and lower

Table 64 BMI data for the individual males from Peshawar

Unique ID	*Age(Years)*	*Height(cm)*	*Weight(Kg)*	*MUAC(cm)*	*W.C(cm)*	*BMI*	*Frame size*	*BMR(Cal /Kg/24hrs)*	*SDA 10%*	*Allowance for life style*	*Total energy req/day*	*N-status*
ADM_1	14	169.00	56.00	24.00	18.00	19.61	9.39	1344	134	806	2285	Normal
ADM-2	14	161.00	46.00	23.20	15.50	17.75	10.39	1104	110	662	1878	Underweight
ADM-3	17	160.00	53.00	25.40	16.00	20.70	10.00	1272	127	763	2162	Normal
ADM-4	17	175.00	63.50	25.00	16.90	20.73	10.35	1524	152	914	2591	Normal
ADM-5	17	167.00	56.00	25.00	16.60	20.08	10.06	1344	134	806	2285	Normal
ADM-6	18	178.00	66.00	29.20	16.50	20.83	10.79	1584	158	950	2693	Normal
ADM-7	18	167.00	59.00	26.00	16.80	21.15	9.94	1416	142	849	2407	Normal
ADM-8	14	149.00	60.00	26.50	14.80	27.02	10.06	1440	144	864	2448	Overweight
ADM-9	15	157.00	48.00	25.00	17.00	19.47	9.23	1152	115	691	1958	Normal
ADM-10	17	172.00	50.00	22.00	16.00	16.90	10.75	1200	120	720	2040	Underweight
AM-1	22	174.00	69.00	28.50	18.00	22.79	9.66	1656	166	1656	3477	Normal
AM-2	19	154.00	57.00	34.00	17.80	24.03	8.65	1368	137	1368	2873	Normal
AM-3	21	175.00	74.00	29.00	18.00	24.16	9.72	1776	178	1776	3729	Normal
AM-4	20	160.00	60.00	25.00	17.00	23.44	9.41	1440	144	864	2448	Normal
AM-5	20	154.00	55.00	25.50	16.00	23.19	9.62	1320	132	792	2244	Normal
AM-6	23	170.00	66.00	29.50	18.00	22.84	9.44	1584	158	950	2693	Normal
AM-7	23	179.00	62.00	27.50	17.00	19.35	10.52	1488	149	893	2529	Normal
AM-8	22	166.00	50.00	24.50	15.50	18.14	10.70	1200	120	1200	2520	Underweight
AM-9	20	175.00	65.40	26.00	17.80	21.22	9.83	1560	156	1560	3276	Normal
AM-10	24	163.00	71.32	27.00	17.00	26.72	9.59	1704	170	1704	3578	Overweight
OAM-1	35	163.00	77.00	32.00	18.00	28.98	9.05	1848	185	1848	3881	Overweight
OAM-2	58	166.00	55.00	25.00	16.00	19.96	10.37	1320	132	792	2244	Normal
OAM-3	56	168.00	54.00	23.21	17.00	19.13	9.88	1296	129	778	2203	Normal
OAM-4	55	174.00	53.00	24.50	15.60	17.50	11.15	1272	127	763	2162	Underweight
OAM-5	65	169.00	58.00	27.50	17.00	20.31	9.94	1392	139	1392	2923	Normal
OAM-6	55	170.00	95.00	32.50	20.50	32.87	8.29	2280	228	2280	4788	Obese
OAM-7	60	156.00	54.00	27.50	16.20	22.19	9.63	1296	129	1296	2722	Normal
OAM-8	60	163.00	51.00	24.30	16.30	19.19	10.00	1224	122	1224	2570	Normal
OAM-9	60	179.00	50.00	24.00	15.80	15.60	11.32	1200	120	1200	2520	Underweight
OAM-10	73	170.00	54.00	27.50	16.00	18.68	10.62	1296	129	1296	2721	Normal

Continued------------Table 64

Min	14.00	149.00	46.00	22.00	14.80	15.60	8.29	1104.00	110	662	1876
Max	73.00	179.00	95.00	34.00	20.50	32.87	11.33	2280.00	228	2280	4788
Mean	31.73	166.76	59.58	26.52	16.82	21.49	9.95	1430.00	143	1122	2695
CV%	61.76	4.76	17.19	10.75	6.70	17.36	6.91	17.19	17	37	24
Sd	19.59	7.934	10.24	2.85	1.127	3.73	0.69	245.85	24	417	648
Range	59.00	30.00	49.00	12.00	5.70	17.27	3.04	1176.00	118	1618	2911
Median	22.00	23.00	24.00	25.00	26.00	27.00	28.00	29.00	30	31	32

Table 65 BMI data for the individual females from Peshawar

Unique ID	***Age(Years)***	***Height(cm)***	***Weight(Kg)***	***MUAC(cm)***	***W.C(cm)***	***BMI***	***Frame size***	***BMR(Cal /Kg/24hrs)***	***SDA 10%***	***Allowance for life style***	***Total energy req/day***	***N-status***
ADF_1	15	147.00	38.00	16.40	15.30	17.58	9.61	821	82.08	821	17248	Underweight
ADF-2	17	160.00	44.00	13.40	18.40	17.19	8.69	950	95.04	950	1996	Underweight
ADF-3	14	145.00	38.00	9.30	15.40	18.07	9.41	821	82.08	821	1724	Normal
ADF-4	20	144.00	47.00	15.00	17.40	22.66	8.27	1015	101.52	1015	2132	Normal
ADF-5	20	149.00	35.00	15.00	13.30	15.76	11.20	756	75.6	756	1588	Underweight
ADF-6	18	150.00	37.00	12.00	16.60	16.44	9.03	799	79.92	799	1678	Underweight
ADF-7	17	150.00	46.00	16.12	17.30	20.44	8.67	993	99.36	596	1689	Normal
ADF-8	16	146.00	34.00	15.00	16.00	15.95	9.12	734	73.44	440	1248	Underweight
ADF-9	18	146.00	50.00	12.00	15.00	23.45	9.73	1080	108	648	1836	Normal
ADF-10	18	156.00	46.00	16.12	15.00	18.90	10.40	993	99.36	596	1689	Normal
AF-1	22	164.00	51.00	15.10	14.00	18.96	11.71	1102	110.16	661	1872	Normal
AF-2	25	169.00	70.00	15.00	17.40	24.51	9.71	1512	151.2	907	2570	Normal
AF-3	24	150.00	42.00	13.40	16.40	18.66	9.15	907	90.72	544	1542	Normal
AF-4	27	147.00	54.00	19.40	17.60	24.99	8.35	1166	116.64	1166	2449	Normal
AF-5	35	149.00	51.00	12.30	16.40	22.97	9.08	1102	110.16	1102	2313	Normal
AF-6	30	140.00	50.00	14.30	17.30	25.51	8.09	1080	108	1080	2268	Overweight
AF-7	25	150.00	45.00	12.00	17.00	20.00	8.82	972	97.2	972	2041	Normal
AF-8	25	164.00	68.00	15.10	17.00	25.28	9.65	1469	146.88	881	2497	Overweight
AF-9	27	169.00	46.00	16.00	13.50	16.11	12.51	994	99.36	596	1689	Underweight
AF-10	24	169.00	48.00	15.00	16.40	16.80	10.30	1037	103.68	622	1762	Underweight
OAF-1	45	145.00	44.00	15.40	17.00	20.92	8.53	950	95.04	570	1616	Normal
OAF-2	46	145.00	58.00	12.00	16.40	27.58	8.84	1253	125.28	752	2129	Overweight
OAF-3	48	148.00	51.00	13.70	18.10	23.28	8.17	1102	110.16	1102	2313	Normal
OAF-4	45	150.00	46.00	15.00	16.20	20.44	9.26	994	99.36	994	2086	Normal
OAF5	55	146.00	58.00	15.00	17.30	27.21	8.43	1253	125.28	1253	2631	Overweight
OAF-6	150	150.00	61.00	15.00	17.40	27.11	8.62	1318	131.76	1317	2767	Overweight
OAF-7	60	150.00	42.00	12.00	17.10	18.66	8.77	907	90.72	907	1905	Normal
OAF-8	48	149.00	35.00	15.11	17.20	15.76	8.66	756	75.6	756	1587	Underweight
OAF-9	50	150.00	45.00	15.00	17.40	20.00	8.62	972	97.2	972	2041	Normal

Continued------------Table 65

Min	14.00	140.00	34.00	9.30	13.30	15.76	8.09	734.40	73	441	1248
max	150.00	169.00	70.00	19.40	18.40	27.59	12.52	1512.00	151	1318	2767
Mean	34.30	151.43	47.46	14.39	16.47	20.73	9.26	1025.28	102	852	1979
CV%	75.11	5.27	18.86	13.32	7.81	17.95	11.41	18.86	18	26	19
Sd	25.76	7.98	8.95	1.92	1.28	3.72	1.06	193.42	19	224	370
Range	136.00	29.00	36.00	10.10	5.10	11.82	4.43	777.60	78	877	1518
Median	25.00	26.00	27.00	28.00	29.00	30.00	31.00	32.00	33	34	35

of 16.73 for adolescent, adults with the median of 32 and standard deviation of 3.06,lower frame size o f 8.75 for adolescent and higher of 11.35 for adults with the median 33 and standard deviation of 0.66 were found. Higher values of BMR 1728Cal/Kh/24 hours and lower 1080 Cal/Kh/24 with the median 34 and standard deviation 185.54 for adolescent and higher Specific Dynamic Activity SDA 10% 173 and lower of 108 with median 35 and standard deviation 18 were recorded for adult males. Maximum value of allowance for the life style 1656 and lower of 648 with median 36 and standard deviation of 248 and total energy requirement /day of 3478 and lower 1836 with the median of 37 and standard deviation of 390 were found for adults and adolescent respectively.

From the Table 67 it is clear that for the individuals females from the control area the minimum age of 14 years and maximum of 71 years for adolescent, adults and old age with the median on of 26 and standard deviation of 17.64 were recorded. Maximum height of 167 cm among adults and minimum of 145 cm among the adolescent with the median of 27 and standard deviation of 20.41 were found. Among females lower weight of 35 Kg for adolescent and higher of 76 Kg for adults with median of 28 and standard deviation of 8.68 were noticed. Lower MUAC of 20.50 cm and higher of 33.50 cm with the median 29 and standard deviation of 2.87 were recorded for adolescent and adults respectively. Wrist circumference with the lower value of 14cm and higher of 20.50 cm with the median 30 and standard deviation of 1.16 were found for adolescent and adults females respectively. Higher BMI of 27.16 for adolescent and lower of 14.70 for adults with the median of 31 and standard deviation of 46.07, higher frame size o f 10.96 and lower of 2.81 for adolescent with the median 32 and standard deviation of 1.48 were found. Higher values of BMR 1641Cal/Kh/24 hours and lower 756 Cal/Kh/24 with the median 33 and standard deviation 187.56 and higher Specific Dynamic Activity SDA 10% 164 and lower of 76 with median 34 and standard deviation 19 were recorded for adults and adolescent females respectively.

Maximum value of allowance for the life style 1253 for old age and lower of 454 for adolescent with median 35 and standard deviation of 220 and total energy requirement /day of 2791 and lower 1285 with the median of 36 and standard deviation of 365 were found for adults and adolescent females respectively.

Table 66 BMI data for the individual males from Dir

Unique ID	*Age(Years)*	*Height(cm)*	*Weight(Kg)*	*MUAC(cm)*	*W.C(cm)*	*BMI*	*Frame size*	*BMR(Cal /Kg/24hrs)*	*SDA 10%*	*Allowance for life style*	*Total energy req/day*	*N-status*
ADM_1	20	164.00	52.00	22.00	16.11	19.33	10.25	1248	125	749	2122	Normal
ADM-2	19	164.00	45.00	20.00	15.00	16.73	10.93	1080	108	648	1836	Underweight
ADM-3	19	156.00	46.00	20.00	17.10	18.90	9.17	1104	110	662	1877	Normal
ADM-4	21	160.00	46.00	23.50	16.10	17.97	10.00	1104	110	662	1877	Underweight
ADM-5	20	172.00	72.00	28.20	18.00	24.34	9.55	1728	173	1037	2938	Normal
ADM-6	22	161.00	60.00	28.00	18.40	23.15	8.75	1440	144	864	2448	Normal
ADM-7	22	178.00	69.00	27.20	18.30	21.77	9.73	1656	166	994	2815	Normal
ADM-8	20	170.00	68.00	29.00	17.60	23.53	9.66	1632	163	979	2774	Normal
ADM-9	23	179.00	64.00	26.80	16.00	19.97	11.18	1536	154	922	2611	Normal
ADM-10	22	176.00	53.00	24.40	15.50	17.11	11.35	1272	127	763	2162	Underweight
AM-1	27	168.00	50.00	24.00	16.50	17.72	10.18	1200	120	1200	2520	Underweight
AM-2	26	167.00	48.00	22.00	16.00	17.21	10.44	1152	115	1152	2419	Underweight
AM-3	27	177.00	56.00	24.50	17.40	17.87	10.17	1344	134	1344	2822	Underweight
AM-4	25	173.00	53.00	24.50	16.60	17.71	10.42	1272	127	1272	2671	Underweight
AM-5	25	177.00	53.00	24.20	16.80	16.91	10.53	1272	127	1272	2671	Underweight
AM-6	27	161.00	51.00	24.00	15.30	19.67	10.52	1224	122	1224	2570	Normal
AM-7	25	176.00	60.00	25.50	16.40	19.37	10.73	1440	144	1440	3024	Normal
AM-8	32	168.00	69.00	25.50	18.80	24.44	8.94	1656	166	1656	3477	Normal
AM-9	35	170.00	66.00	30.00	18.40	22.84	9.23	1584	158	950	2693	Normal
AM-10	30	177.00	58.00	26.00	16.00	18.51	11.06	1392	139	835	2366	Normal
OAM-1	50	169.00	59.00	27.00	16.20	20.66	10.43	1416	142	849	2407	Normal
OAM-2	45	172.00	69.00	28.00	17.50	23.32	9.83	1656	166	994	2815	Normal
OAM-3	55	170.00	59.00	26.00	17.00	20.41	10.00	1416	142	849	2407	Normal
OAM-4	57	175.00	62.00	27.00	16.60	20.24	10.54	1488	149	893	2529	Normal
OAM-5	55	155.00	68.00	28.00	15.70	28.30	9.87	1632	163	979	2774	Overweight
OAM-6	52	149.00	53.00	26.00	16.00	23.87	9.31	1272	127	1272	2671	Normal
OAM-7	48	167.00	59.00	25.00	17.00	21.15	9.82	1416	142	1416	2974	Normal
OAM-8	56	168.00	62.00	26.00	17.20	21.97	9.77	1488	149	1488	3125	Normal
OAM-9	67	154.00	63.00	24.00	16.00	26.56	9.62	1512	151	1512	3175	Overweight
OAM-10	50	156.00	59.00	28.00	16.80	24.24	9.28	1416	142	1416	2974	Normal

Continued------------Table 66

Min	19.00	149.00	45.00	20.00	15.00	16.73	8.75	1080.00	108	648	1836
max	67.00	179.00	72.00	30.00	18.80	28.30	11.35484	1728.00	173	1656	3478
Mean	34.06	167.63	58.40	25.48	16.73	20.86	10.04416	1401.60	140	1076	2618
CV%	43.51	4.85	13.24	9.66	5.87	14.67	6.62793	13.23	13	26	15
Sd	14.82	8.13	7.73	2.46	0.98	3.06	0.66572	185.54	18	284	390
Range	48.00	30.00	27.00	10.00	3.80	11.57	2.604839	648.00	65	1008	1642
Median	27.00	28.00	29.00	30.00	31.00	32.00	33	34.00	35	36	37

Table 67 BMI data for the individual females from Dir

Unique ID	***Age(Years)***	***Height(cm)***	***Weight(Kg)***	***MUAC(cm)***	***W.C(cm)***	***BMI***	***Frame size***	***BMR(Cal /Kg/24hrs)***	***SDA 10%***	***Allowance for life style***	***Total energy req/day***	***N-status***
ADF_1	18	149.00	38.00	23.10	14.80	17.12	10.07	821	82.08	492	1395	Underweight
ADF-2	14	156.00	44.00	25.00	15.50	18.08	10.06	950	95.04	570	1616	Normal
ADF-3	14	159.00	38.00	20.50	14.50	15.03	10.96	821	82.08	492	1395	Underweight
ADF-4	17	157.00	53.00	28.20	16.00	21.50	9.81	1145	114.48	687	1946	Normal
ADF-5	17	151.00	35.00	22.00	14.50	15.35	10.41	756	75.6	454	1285	Underweight
ADF-6	14	149.00	41.00	24.00	14.00	18.47	10.64	886	88.56	531	1505	Normal
ADF-7	17	45.00	55.00	25.00	16.00	27.16	2.81	1188	118.8	713	2019	Overweight
ADF-8	18	145.00	45.00	27.00	17.00	21.403	8.53	972	97.2	583	1652	Normal
ADF-9	18	155.00	50.00	27.00	15.50	20.81	10.00	1080	108	648	1836	Normal
ADF-10	19	157.00	53.00	28.12	16.00	21.50	9.81	1145	114.48	687	1946	Normal
AF-1	28	150.00	55.00	28.60	16.80	24.44	8.93	1188	118.8	713	2019	Normal
AF-2	31	152.00	76.00	33.50	20.50	32.89	7.41	1642	164.16	985	2791	Obese
AF-3	21	151.00	42.00	23.70	15.00	18.42	10.07	907	90.72	544	1542	Normal
AF-4	28	158.00	54.00	29.00	15.00	21.63	10.53	1166	116.64	699	1983	Normal
AF-5	18	151.00	50.00	27.50	16.70	21.93	9.04	1080	108	648	1836	Normal
AF-6	19	155.00	45.00	24.00	15.00	18.73	10.33	972	97.2	583	1652	Normal
AF-7	34	150.00	68.00	33.00	16.70	30.22	8.98	1469	146.88	881	2497	Obese
AF-8	22	152.00	45.00	23.50	16.00	19.48	9.50	972	97.2	583	1652	Normal
AF-9	26	167.00	41.00	25.50	15.50	14.70	10.77	886	88.56	531	1505	Underweight
AF-10	19	150.00	46.00	25.00	16.00	20.44	9.37	994	99.36	596	1689	Normal
OAF-1	50	156.00	45.00	26.11	15.00	18.49	10.40	972	97.2	972	2041	Normal
OAF-2	52	163.00	58.00	27.80	15.50	21.83	10.52	1253	125.28	1253	2631	Normal
OAF-3	50	155.00	43.00	25.00	15.00	17.89	10.33	929	92.88	929	1950	Underweight
OAF-4	45	156.00	44.00	23.70	15.50	18.08	10.06	950	95.04	950	1996	Normal
OAF5	50	153.00	38.00	22.00	16.00	16.23	9.56	821	82.08	821	1724	Underweight
OAF-6	71	155.00	49.00	26.50	15.50	20.39	10.00	1058	105.84	1058	2223	Normal
OAF-7	50	155.00	46.00	25.00	15.00	19.15	10.33	994	99.36	994	2086	Normal
OAF-8	60	156.00	50.00	25.00	16.00	20.54	9.75	1080	108	1080	2268	Normal
OAF-9	55	154.00	49.00	25.00	15.00	20.66	10.27	1058	105.84	1058	2223	Normal
OAF-10	65	156.00	47.00	26.00	15.30	19.31	10.20	1015	101.52	1015	2131	Normal

Continued------------Table 67

Min	14.00	45.00	35.00	20.50	14.00	14.70	2.8125	756.00	76	454	1285
Max	71.00	167.00	76.00	33.50	20.50	271.60	10.96552	1641.60	164	1253	2791
Mean	32.00	150.60	48.10	25.83	15.69	28.54	9.64978	1038.96	104	758	1901
CV%	55.11	13.55	18.05	11.12	7.39	161.38	15.41659	18.05	18	29	19
Sd	17.64	20.41	8.68	2.87	1.16	46.07	1.487667	187.56	19	220	365
Range	57.00	122.00	41.00	13.00	6.50	256.90	8.153017	885.60	88	799	1505
Median	26.00	27.00	28.00	29.00	30.00	31.00	32	33.00	34	35	36

Table-68 Nutritional status of males and females from Peshawar

Serial No	*Nutritional Status*	*Percentage of males*	*Percentage of females*
1	Underweight	8	6
2	Normal	20	21
3	Overweight	2	1
4	Obese	0	2

Table-69 Nutritional status of males and females from Peshawar

Serial No	*Nutritional Status*	*Percentage of males*	*Percentage of females*
1	Underweight	5	6
2	Normal	21	21
3	Overweight	3	1
4	Obese	1	2

Tables 68 69 and figure 20-23 represent the percentage of nutritional status of males and females from Peshawar and Dir. It is clear from Table 68 figure 20 and 22 that incase of males from Peshawar 5 % were underweight 21% normal,3 % overweight and 1% obese while among the females 8% were underweight, 17% normal, 5% overweight and 0% obese.

While incase of individuals from Dir the data in Tables 69 and figure 21 and 23 it is clear that 8% were underweight, 20% normal, 2% overweight and 0% obese, in case of females 6% were underweight, 21% were normal 1% overweight, and 2% obese. If we compare the nutritional status of males from both the areas it can be inferred that more %age of males (3% more) in case of Peshawar were underweight as compared to Dir. Percentage of overweight (2%) and obese (0%) people in Dir was also lower as compared to Peshawar (3% and 1% respectively).It can be attributed to the strong daily activities in people of Dir that majority of them are farmers working whole the day in farms enjoying a pleasant weather. If we compare the females from the two areas lower percentage of underweight and higher percentage of normal were found in Dir as compared to Peshawar. The percentage of overweight females were also less incase of Dir .Interestingly 2% of females were found obese but this may be explained in term that most have large families comprising of wives of their sons and granddaughters which never allow them to do hard work as a tradition while expecting prayers from them only. The other females are usually busy in their household work keeping them normal and healthy. Figures 24, 25, 32 and 33 represent the age wise distribution of males and females from Peshawar and Dir. From figure 24 it is clear that in Peshawar 3 persons were 14 years of age, 17 of 26, 1 of 38, 7 of 62 and 2 were above 62. From Dir 2 persons were 19 years of age 15 of 29, 3 of 39, 1 of 48, 8 of 58 and 1 was more than 58. From figure 32 in case of females from Peshawar 1 female was 14 years of age ,19 of 42,9 of 69 and 1 was more than 69. From figure 33 from Dir 3 females were of 14 years age, 12 of 26, 5 of 37 1 of 49,6 of 60 and 3 were above 60. Figure 26, 27, 34 and 35 represent the height wise distribution of individuals from Peshawar and Dir. From figure 26 it is clear that 2 persons were of 149 cm height, 2 of 155, 5 of 161, 7 of 167, 7 of 173 and 9 were more than 173.Incase of males from Dir figure 27 shows that 1 was of 149 cm height, 2 of 155, 5 of 161, 4 of 167,10 of 173 and 10 were of more that 173. From figure 34 the females from peshawar1 was of 140 cm height, 4 of 146,18 of 152, 1 of 158,1 of 164 and 5 were of more than 164. Incase of female from Dir figure 35 1 female was of 45cm height the rest were more than 143cm height. Figure 28, 29, 36 and 37 represent the weight wise distribution of individuals from Peshawar and Dir .Figure 28

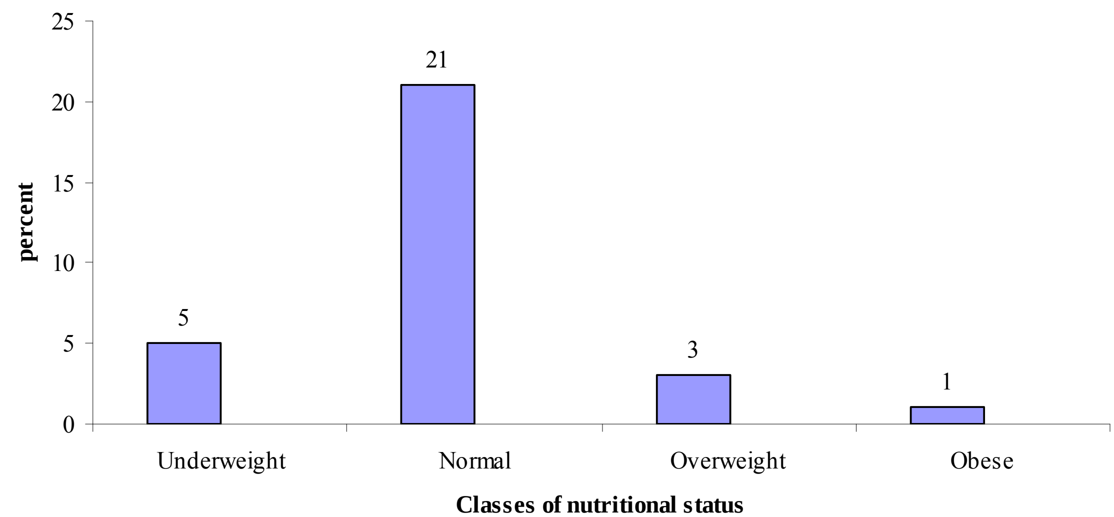

Fig.20 Nutritional status of males from Peshawar

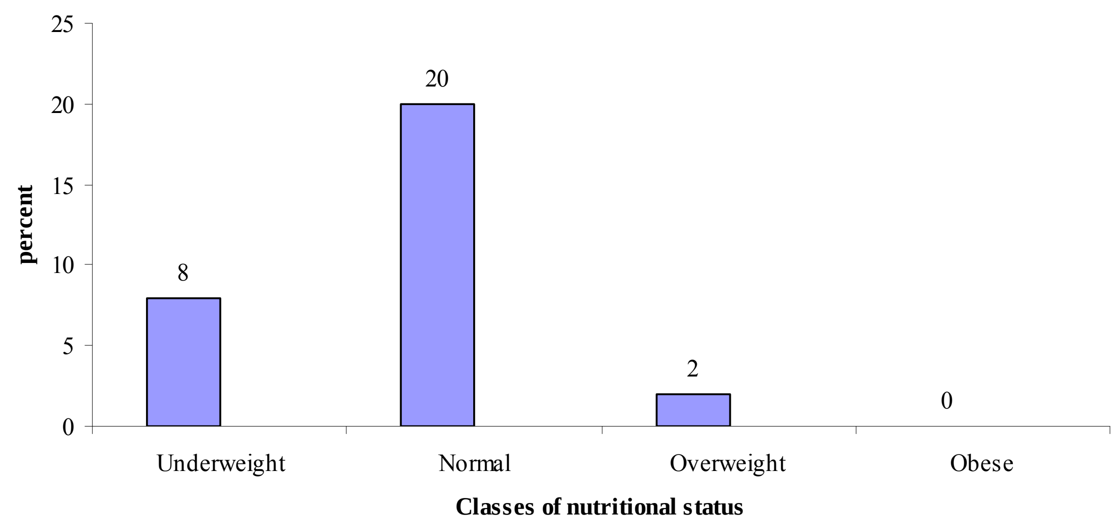

Fig.21 Nutritional status of males from Dir

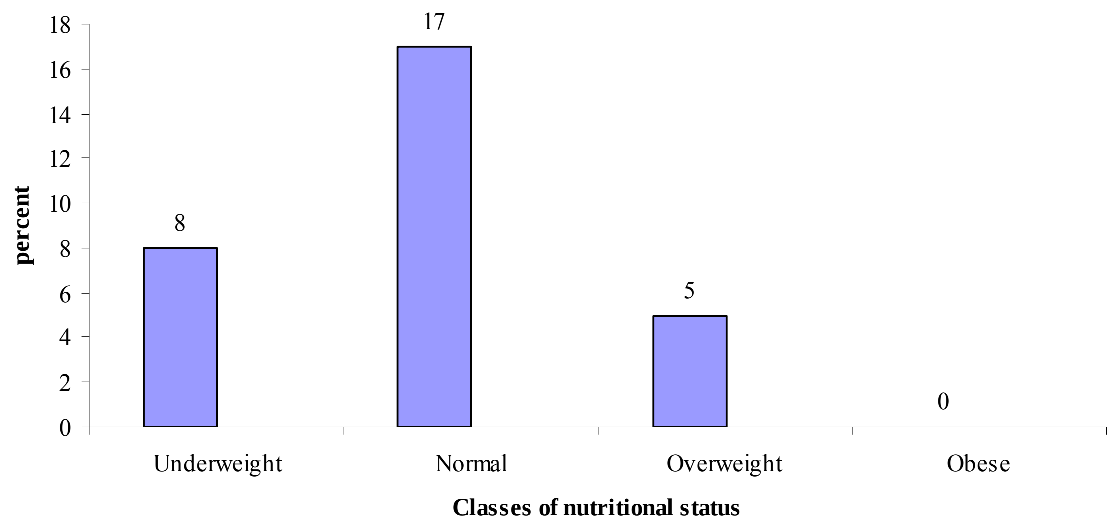

Fig.22 Nutritional status of female from Peshawar

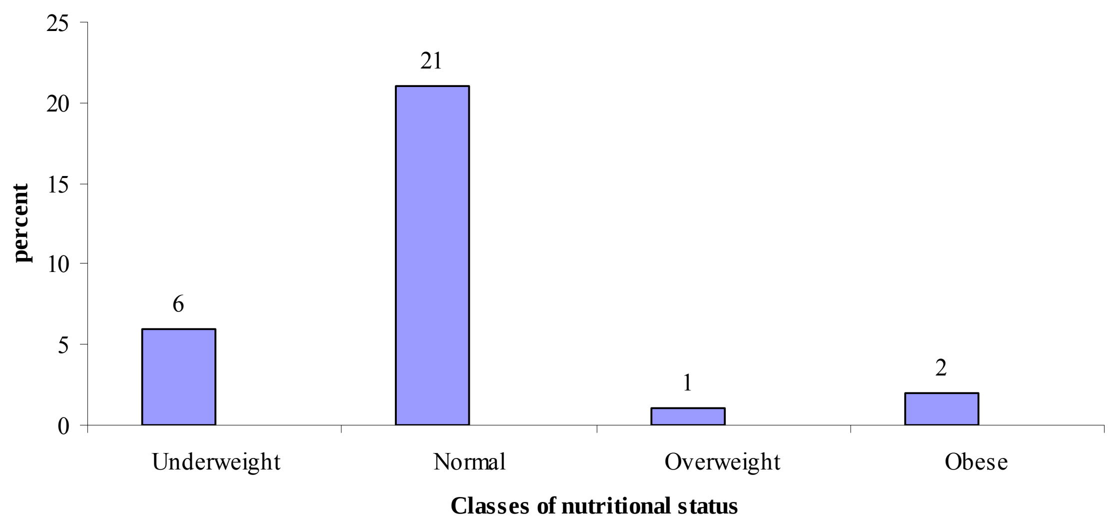

Fig.23 Nutritional status of female from dir

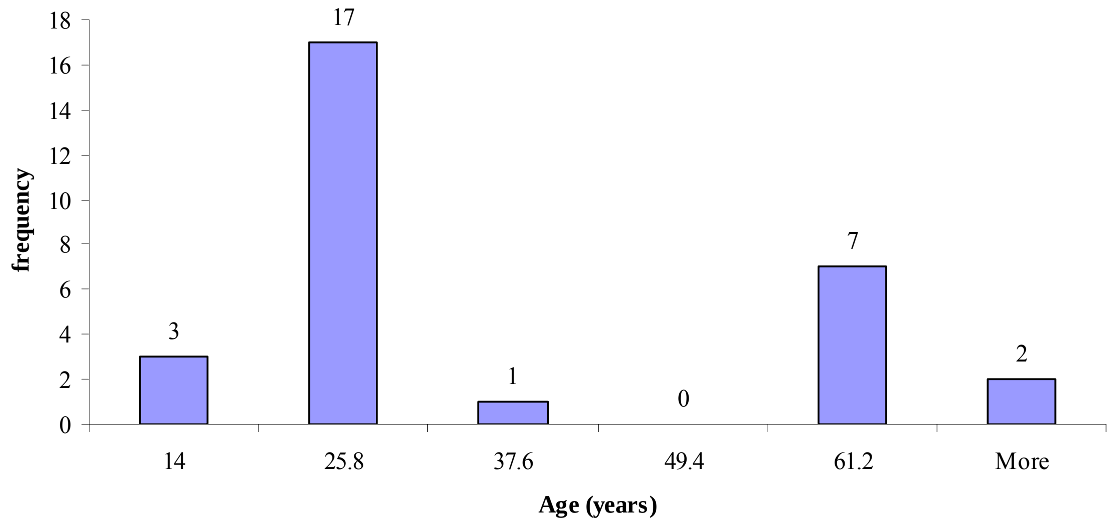

Fig 24 Frequency distribution of age (for males from Peshawar)

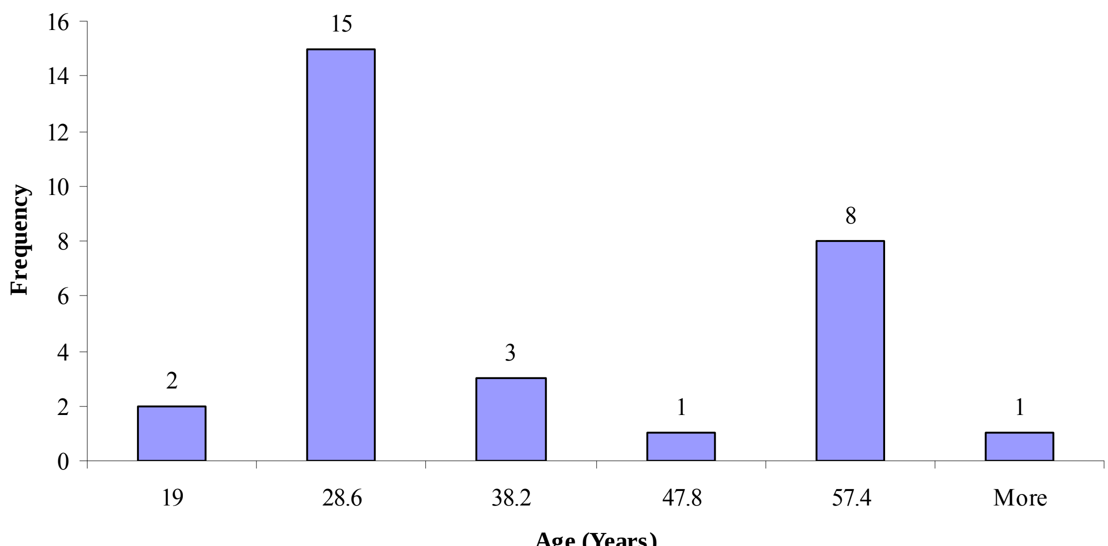

Fig. 25 Frequency distribution of age (for males from Dir)

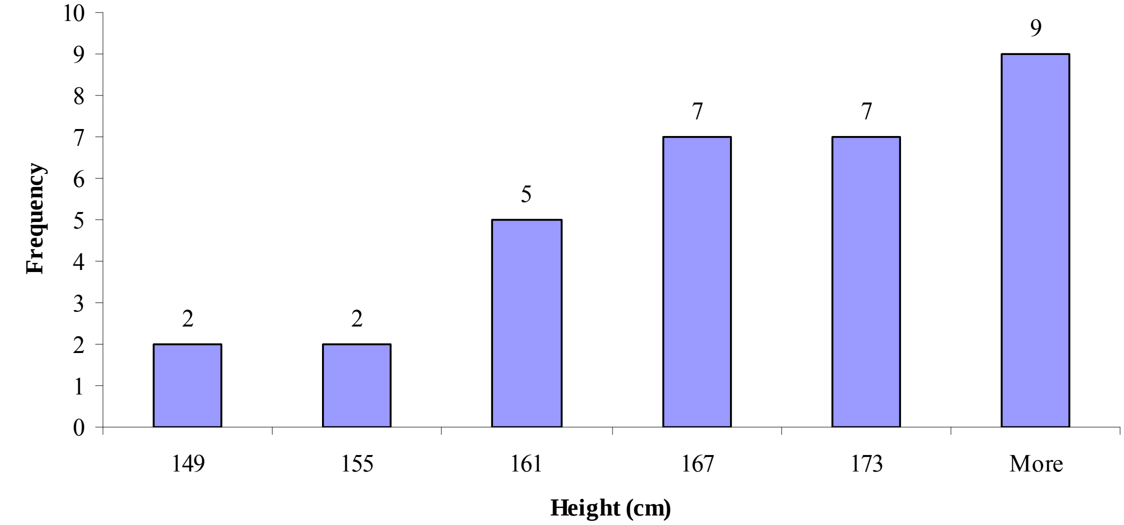

Fig.26 Frequency distribution of height (for males from Peshawar)

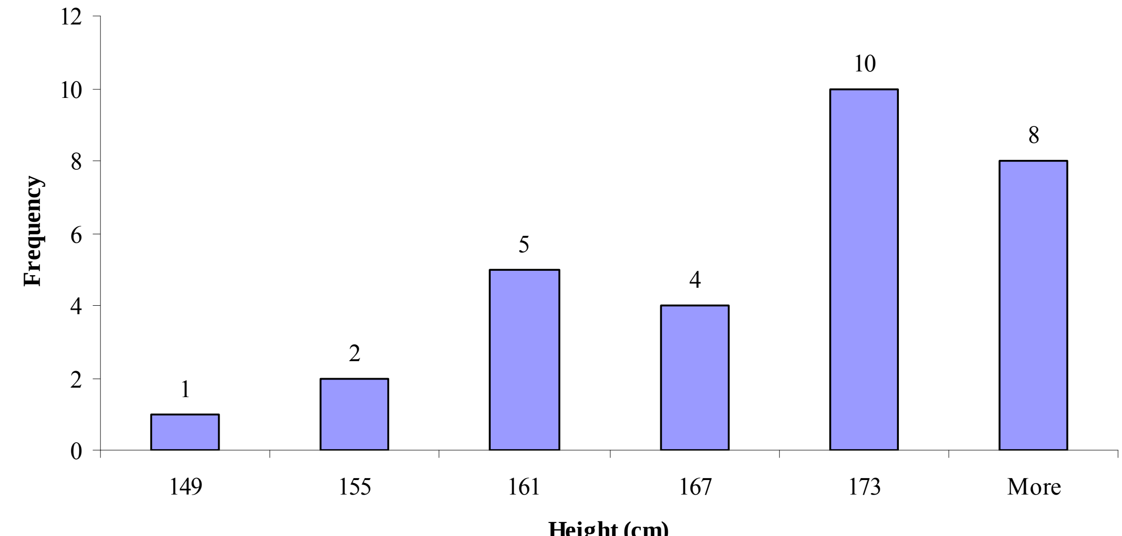

Fig.27 Frequency distribution of height (for males from Dir)

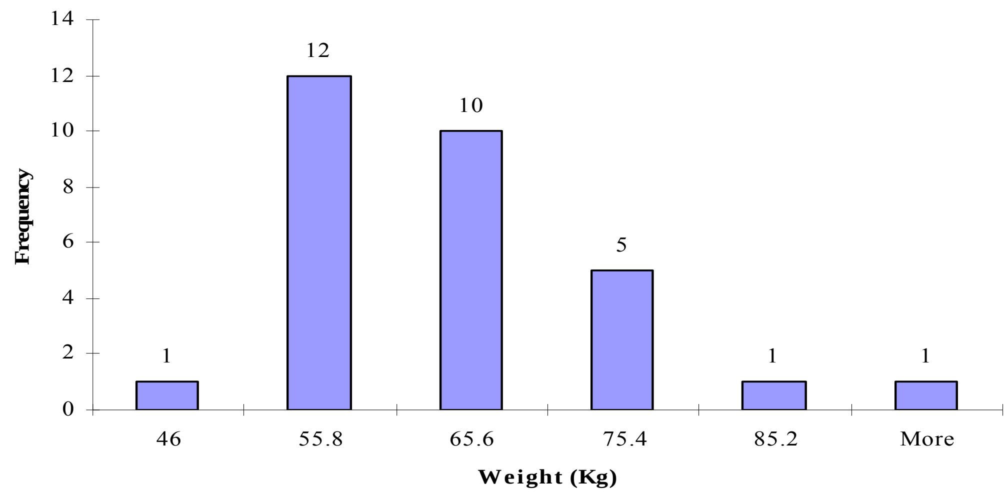

Fig.28 Frequency distribution of weight (for males from Peshawar)

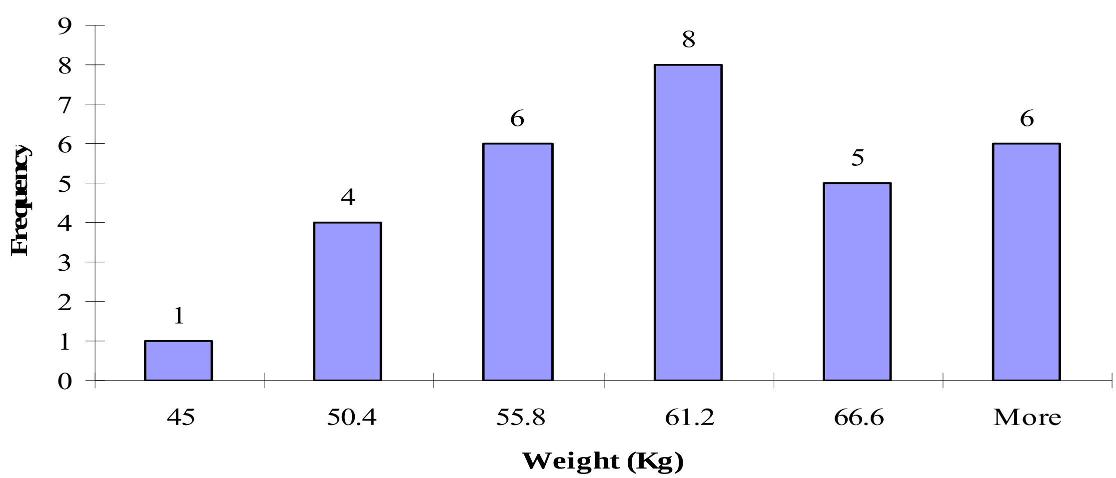

Fig.29 Frequency distribution of weight (for males from Dir)

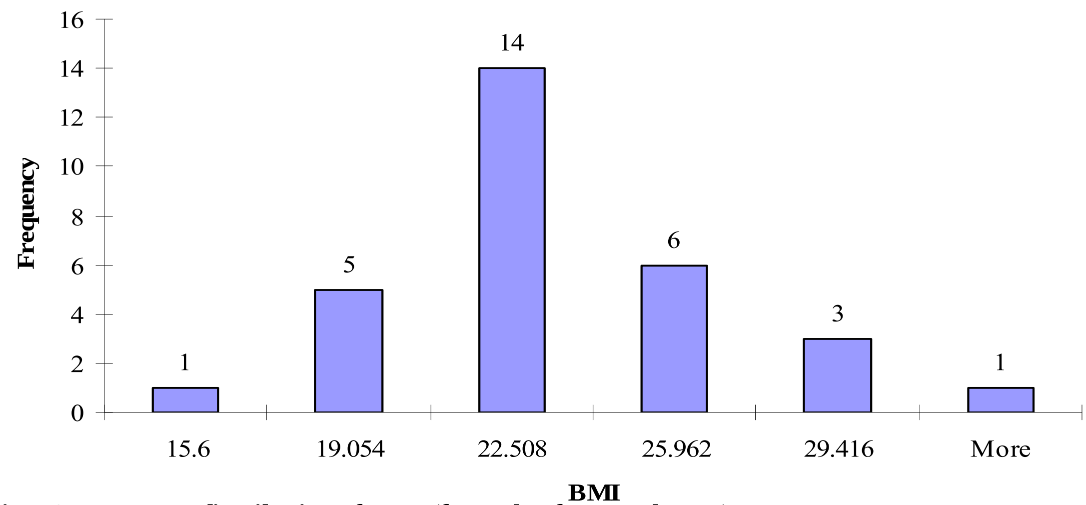

Fig. 30 Frequency distribution of BMI (for males from peshawar)

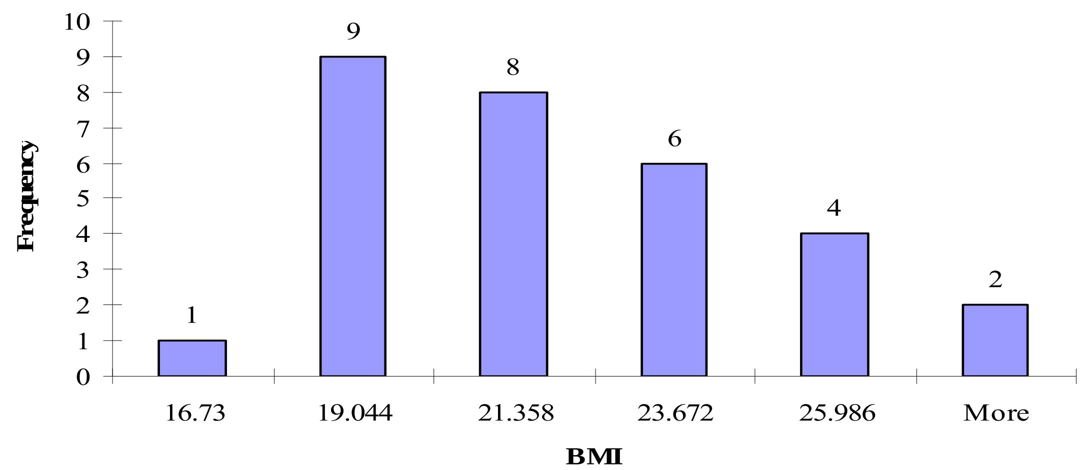

Fig. 31 Frequency distribution of BMI (for males from Dir)

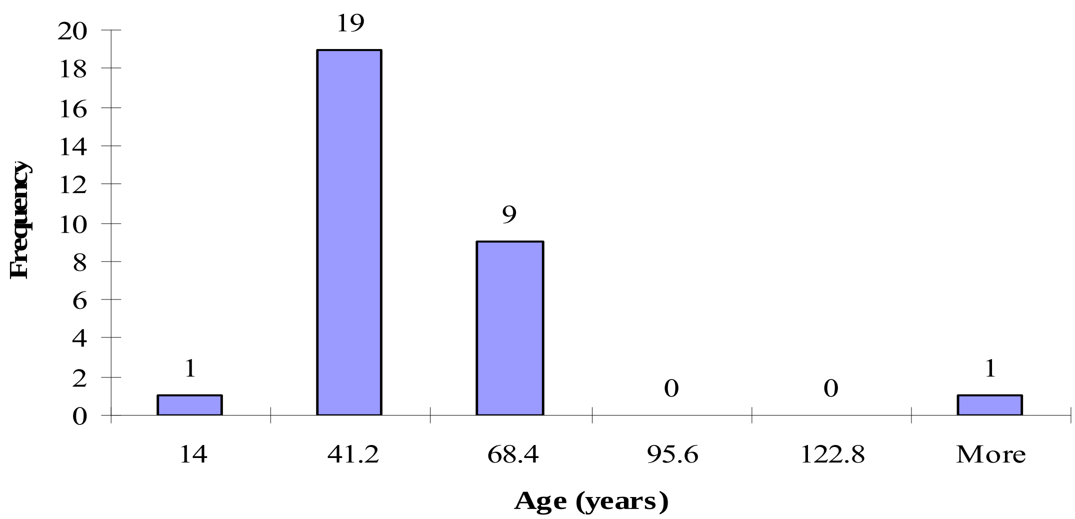

Fig. 32 Frequency distribution of age (for female from Peshawar)

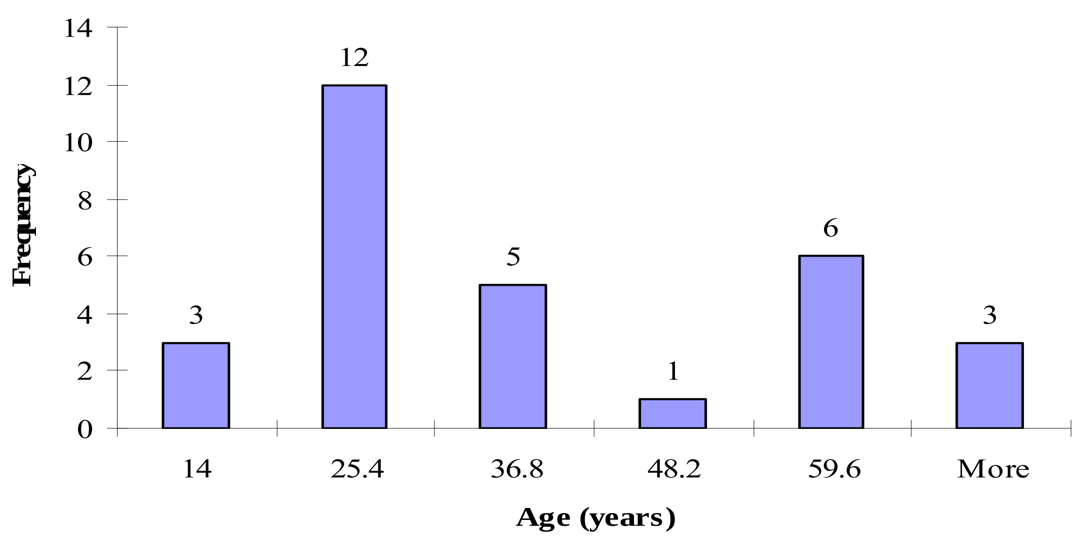

Fig. 33 Frequency distribution of age (for female from Dir)

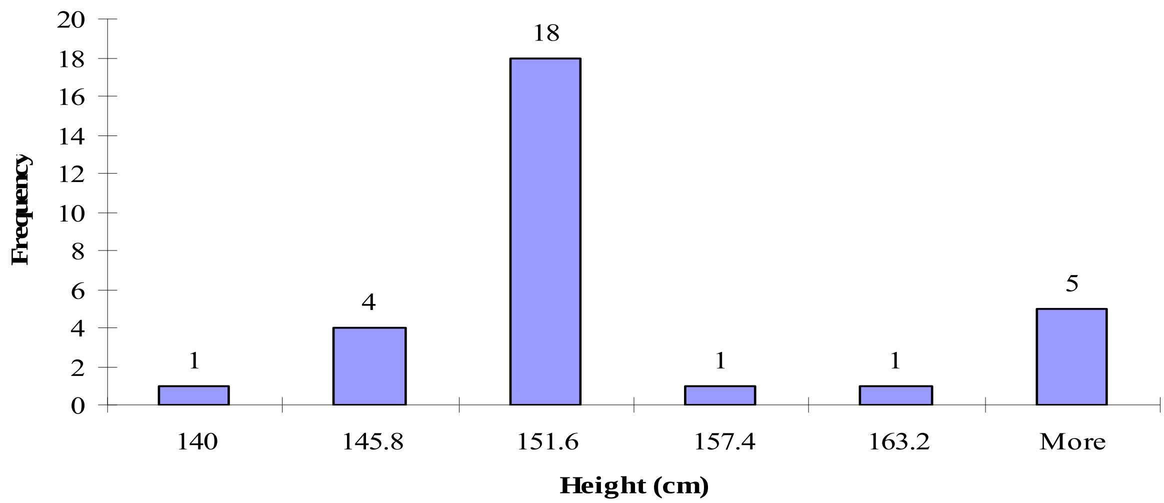

Fig. 34 Frequency distribution of height (for female from Peshawar)

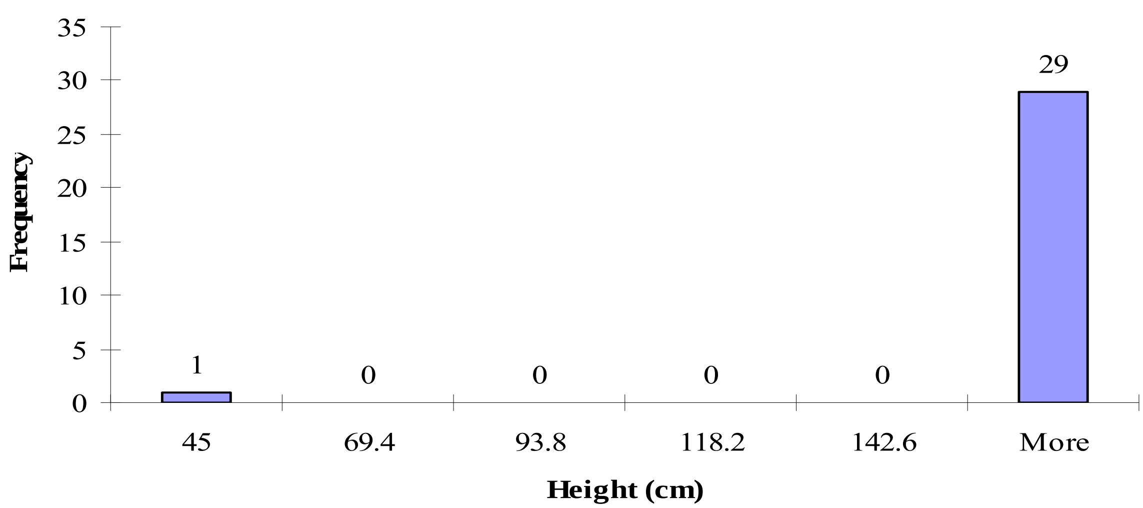

Fig.35 Frequency distribution of height (for female from Dir)

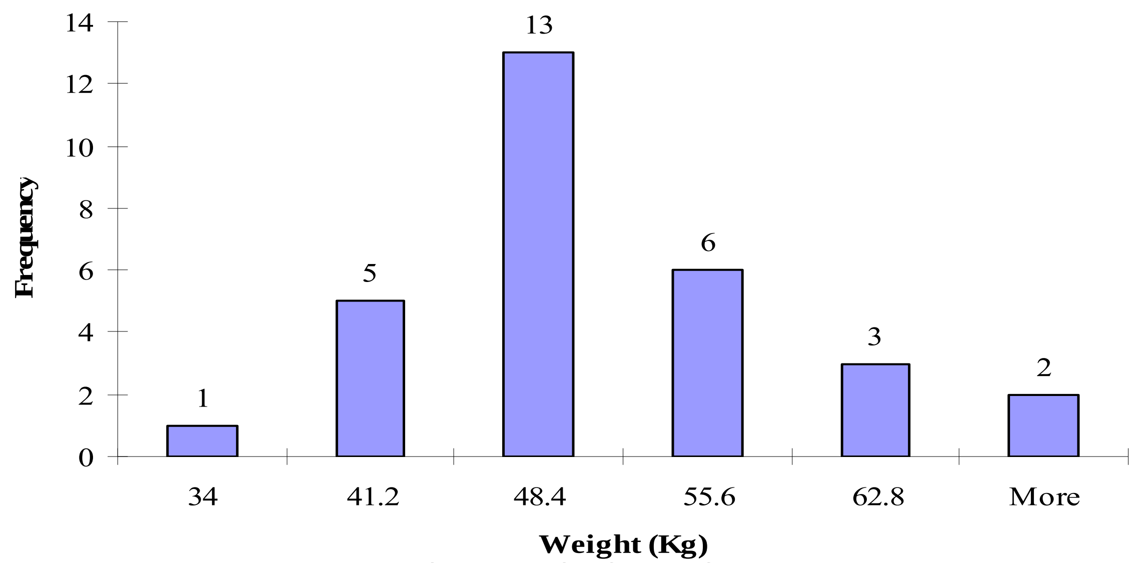

Fig. 36 Frequency distribution of weight (for female from Peshawar)

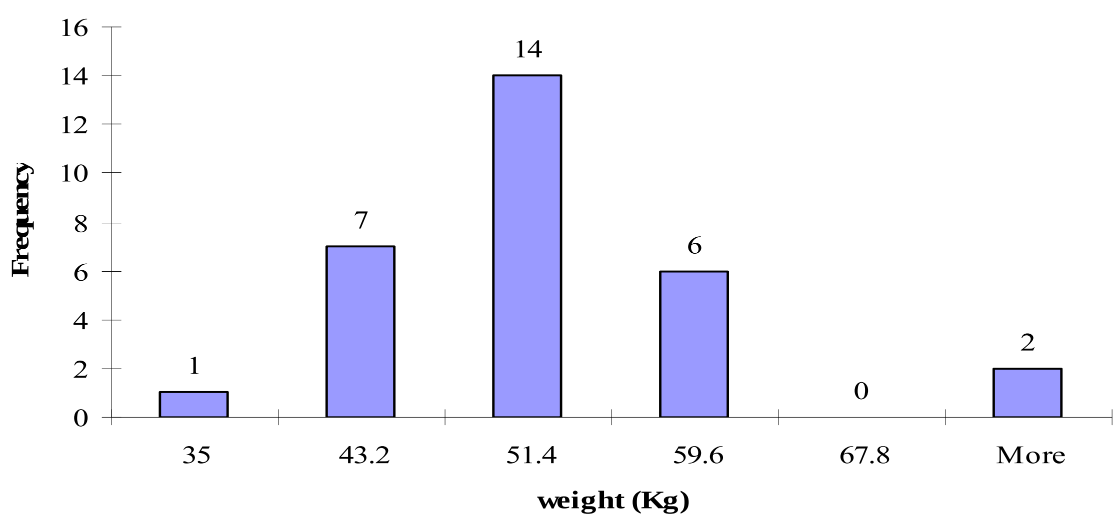

Fig. 37 Frequency distribution of weight (for female from Dir)

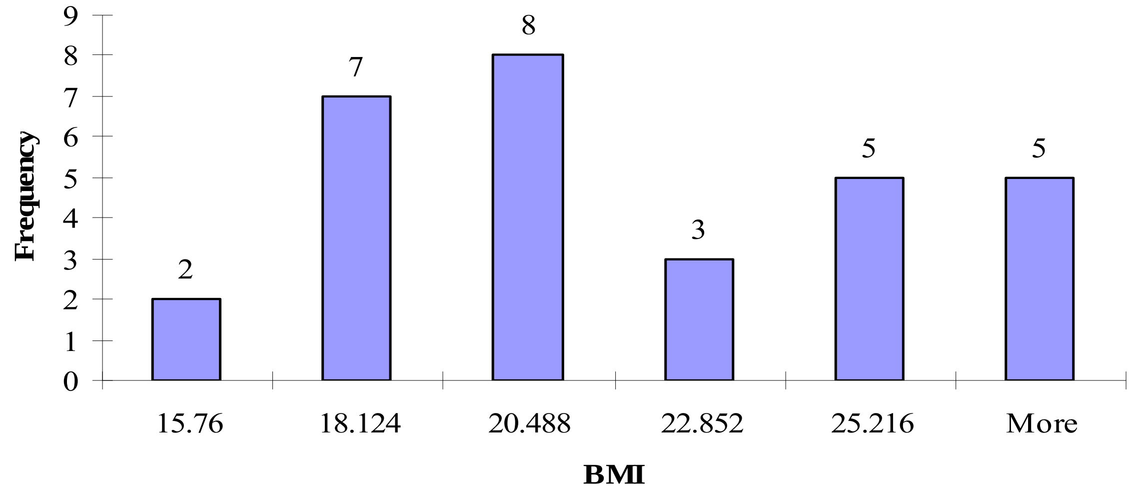

Fig. 38 Frequency distribution of BMI (for female from Peshawar)

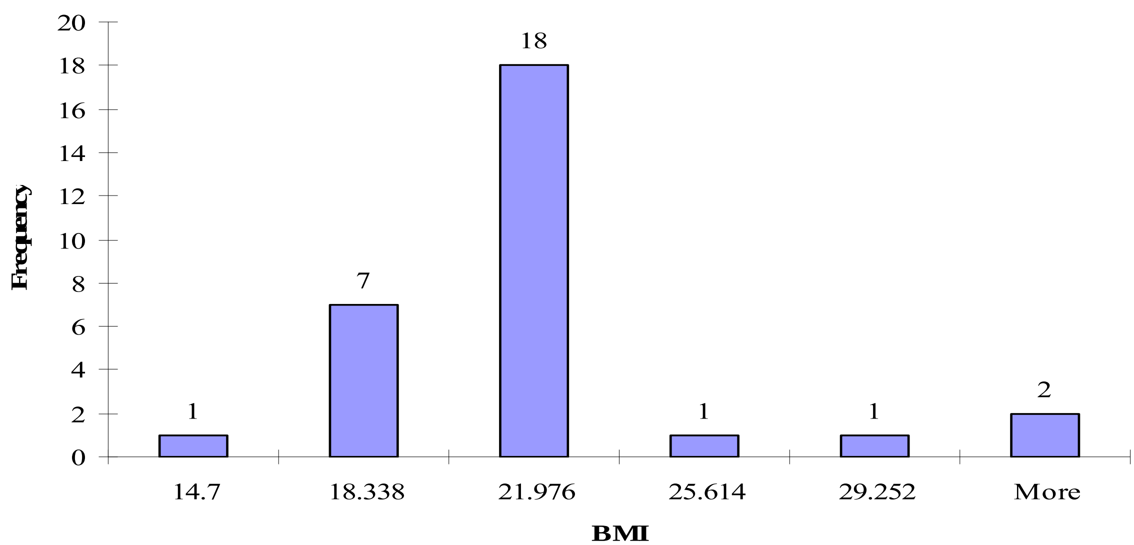

Fig. 39 Frequency distribution of BMI (for female from Dir)

shows that 1 person was 46 Kg weight, 12 of 56, 10 of 66,5 of 76 1 of 85 and 1 was of more than 85. Incase of males from Dir figure 29 that data shows that 1person was of 45 Kg weight

4 were of 51 ,6 were of 56,8 were of 62,5 of 67,and 6 were of more than 67. Figure 36 shows that 1 female from Peshawar was of 34 kg weight, 5 of 42, 13 of 49 ,6 of 56, 3 of 63, and 2 were of more than 63.Figure 37 shows that incase of Dir 1 female was of 35kg weight, 7 of 44, 14 of 52,6 of 60and 2 were more that 68.Figure 30,31,38 and 39 shows the BMI distribution of individuals from both the areas. Figure 30 shows that 1 person had a BMI of 16, 5 of 20, 14 of 23, 6 of 26 , 3 of 30 and 1 of more than 30. From figure 31 it is also clear that 1 male from Dir had a BMI of 17, 9 of 19, 8 of 22,6 of 24,4 of 26 and 2 were of more than 26.Figure 38 shows that 2 females from Peshawar had a BMI of 16, 7 of 18, 8 of 21, 3 of 23, 5 of 25 and of more than 25.Figure 39 indicate that 1 female from Dir had a BMI of 15, 7 of 19,18 of 22, 1 of 26 ,1 of 29 and 2 were of more than 29.Weight and height are the most common measurement made but because of significance and importance are not appreciated , they are frequently measured slpoely, incorrectly or inconsistently. Height is measure of chronic nutrition, or under nutrition, and should me measured as accurate as possible. Weight reflects more recent nutrition status of the child or adults that does length or height. In adults regular weights measurements are particularly important when there is chronic illness. Weight is measured in incase of all the subject except pregnant woman , wheelchair bound individuals, or person who have difficulty in standing steady.

CONCLUSIONS

1. Mercury and arsenic contamination of soil and ground water by industrial wastewater

From the results it is clear that As and Hg is detected in all samples. Drinking water samples in the polluted area have high Hg concentration compared to international permissible limits which apparently shows the effect of effluents on the drinking water quality. As concentration was found higher in nearly all effluents and drinking water samples than the Japanese, Pakistan, Canada and WHO limits but in some cases lower than US Environmental Protection Agency (USEPA) and European Economic Community (EEC) limits. Higher As concentration is found in case of effluent from textile industries, woolen mill and glass factory. Down stream dilution of both the toxic metals As and Hg is quite evident. Comparing the Hg and As contents of drinking and irrigation water of the polluted area with the control area and the drinking water sample which has Hg concentration of 0.011µg/L and As of 3.334µg/L of the background area away from industrial zone and effluent stream, it can be concluded that the industrial effluents have a clear deleterious effect on the water quality.

2. Heavy metals (Zn, Cr, Cu, Ni, Co, Mn, Pb, Cd) contamination of soil and ground water due to industrial wastewater

It can be concluded from the present study that multivariate and univariate statistical analyses holds good in point source identification, classification of various sources, the correlation between different metal pairs in effluents, soil and ground water. Principal components analysis reduced a large number of variables to a new set of variables based on mutual dependence. In short multivariate statistical analysis aid a lot in the interpretation of the complex data. In order to compare the contribution of various industries towards metal pollution in the main effluent stream one way ANOVA was applied which resulted in a p=0.658 showing that there is no significant difference between different industries in terms of contribution to the metals pollution. Cluster analysis using complete linkage method classified different industries into two broad groups and a minor group. From the data it is clear that Mn,Pb,Cd, Ni and Cu were found to be the most abundant elements in the three media The principal component analysis revealed that these effluents causing the contamination of the adjacent soil and corresponding water. By comparison between the metal levels with the background area and the control area it is evident that the effluents cause a potential health risk to the inhabitants in the surrounding area. This study provide a substantial information to the government agencies to implement strict regulatory procedures for the safer discharge of effluents from these industries and devise procedure for the safe recycling of effluent to ensure reclamation and the lost quality of ground water The environmental contamination of the adjoining areas by the effluents stream must be constantly monitored according to the WHO guidelines

3. Heavy metals contamination of agricultural soil and food crops due to wastewater irrigation and human health risks

Long-term wastewater irrigation of the soil has caused a substantial build up of heavy metals in the soil as compared to background and control soils, where stream water is used for irrigation. The sequential extraction study suggested that these soils were strongly enriched with Cu, Zn, Mn and Ni. As a result, the vegetables grown in the contaminated soil also showed elevated levels of individual metal. The soil metal concentrations were found within world health Organization (WHO) and Food and Agriculture Organization (FAO) limits in all study areas. HRI values indicated that vegetables grown on background and control areas were free of any risk for the consumers but in case of wastewater irrigated soil *B.rapa, Spinacia oleracae L, Lycopersicum esculantum*, *Mentha virids*, C*orriandum sativum*, *Lactuca sativa* can pose risks, particularly with high concentration of Mn.

4. Bioaccumulation of metals in human‘s blood due to consumption of contaminated foods

From the present study it can be concluded that the consumption of contaminated food crops, meat and milk have significantly increased the concentrations of trace metals in human blood as compared to the control area, indicating that these food chains may be one of the major pathways of exposure and sources of contamination of human blood with metals. This was further strengthened by correlation and regression study between metal concentrations in the food crops, meat, milk and the blood, where some positive correlation between Cu-Zn, Mn-Zn, Cr-Ni, Ni-Pb, and Cr-Pb metal pairs, while some negative correlations between Cr-Pb with Mn, Cu and Zn were observed in the form regression equations. Overall metal concentrations in males were higher as compared to females which may be due to diet habits and body mass along with other factors. Old age people were accumulated higher concentrations of trace metals as compared to younger ones due to slow accumulation of the metals in their bodies.

5. Anthropometry for the nutritional status of individuals from the study areas

The anthropometric data was taken for the measurement of BMI to asses the nutritional status of the people from Peshawar and Dir. The BMI values indicated that majority of males and females were normal, only few percent of the people were underweight, overweight or obese. Comparing the nutritional status of the people of the both areas the individual males from Dir were found healthier than the people from Peshawar with respect to underweight, overweight, and obese, which can be attributed to the strong muscular activities, including, farming, labor etc in the area. Female's underweight cases were also less in Dir as compared to Peshawar which may be due to socio-economic conditions of the people. Only 2 % females in Dir were found obese which can be explained in terms of luxurious life due to large families, where work is done by the younger ones allowing the elders just for praying and supervision of the household. The data indicated that the people were of different age, height and weight. Only few dwarf cases were noticed in the individuals from both the areas.

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