HEAVY METAL CONTENT IN PHOSPHATE FERTILIZED SOIL AND ITS UPTAKE IN WHEAT AND RICE GRAINS

BY

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ISLAMABAD

2012

Heavy equipment; household equipment

بسم الله الرحمن الرحيم

HEAVY METAL CONTENT IN PHOSPHATE FERTILIZED SOIL AND ITS UPTAKE IN WHEAT AND RICE GRAINS

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80/FBAS/MSES-04

Submitted in partial fulfillment of the requirements for the
Master of Philosophy in discipline Environmental Science
At the faculty of Basic and Applied Sciences
International Islamic University,
Islamabad

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Prof. Dr. M. Tufail, T.I.

September, 2012

Dedicated to:

ALMIGHTY ALLAH

HAZRAT MUHAMMAD (S.A.W)

My loving family and my parents for their love, protection, prays, faith and much more

DECLARATION

I hereby declare that the work present in the following thesis is my own effort, except where otherwise acknowledged and that the thesis is my own composition. No part of the thesis has been previously presented for any other degree.

Date: September, 2012

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FORWARDING SHEET

The thesis entitled Heavy metal content in phosphate fertilized soil and its uptake in wheat and rice grains submitted by Sara Elahi in partial fulfillment of MS in Environmental Science has been completed under my guidance and supervision. I am satisfied with the quality of student's research work and allow her to submit this thesis, for further processes per IIU rules and regulations.

Dr. Tahira Sultana

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ABSTRACT

In order to get better yield of crops various types of fertilizers are applied to soil for nutrition of the crop plants. Heavy Metals (HMs) in the fertilizers are present as the contaminants that may be transferred to the crops through soil along with the nutrients of interest. The present study was therefore conducted to investigate the presence of Heavy Metal ions including cadmium ions (Cd^{2+}), chromium ions (Cr^{3+}), copper ions (Cu^{2+}), lead ions (Pb^{2+}), nickel ions (Ni^{2+}) and zinc ions (Zn^{2+}) in the fertilized soils; and wheat and rice grains. To achieve the goal, three types of Phosphate Fertilizers (PFs) were applied separately to the wheat and rice plants grown in the pots at Nuclear Institute for Agriculture and Biology (NIAB), Faisalabad, Pakistan. Grains were separated from the plants at the time of harvesting. The samples were digested for analysis of Heavy Metal ions by Flame Atomic Absorption Spectroscopy (FAAS). The standard addition calibrations were applied to quantify the concentration levels of the Heavy Metal ions of concern in the study samples. The results indicated that the concentration levels for Cr^{3+}, Cu^{2+}, and Zn^{2+} in the grains were within the recommended limits (20, 30, and 50ppm) but Pb^{2+} and Ni^{2+} were found to be the contaminants of great concern in terms of their cumulative values above the tolerable limits (2.5, and 1.5ppm) in the grains. Cd^{2+} content of all grains was below the detection limit (0.05ppm) of the instrument for it. The overall Transfer Efficiency (TE) of the applied fertilizers for the concentration of Heavy Metal ions in experimental wheat and rice was 194.4, 263.2, 168, and 235.0 for wheat and 87.2, 184.2, 111.5, and 78.8 % for rice. Proper actions should be taken to remove Heavy Metal content from the Phosphate Fertilizers at the stage of manufacturing so that it can help to control soil pollution associated with Heavy Metals.

ACKNOWLEDGEMENTS

All acclamation and appreciation are for ***Almighty Allah,*** *the merciful and* ***His Prophet (PBUH),*** *who is source of guidance and knowledge for mankind.*

First of all I am deeply grateful to ***Dr. Muhammad Sher,*** *Dean, Faculty of Basic and Applied Sciences (FBAS), IIUI and* ***Dr. Asma Gul,*** *Acting Chairperson of Deptt. of Environmental Sciences (DES), IIUI, for their cooperation extended during my study.*

I express my heartfelt appreciation towards my supervisor ***Dr. Tahira Sultana,*** *Assistant Professor, DES for all the support she has lent me. Her supervision and opinions over the year have made my research successful.*

I would also like to express my deep and sincere gratitude to my co-supervisor, ***Dr. Muhammad Tufail (Tamgh-i-Imtiaz, Izaz-i-Fazeelat, Tamgh-e-Baq)****, Dean, Deptt. of Nuclear Engineering (DNE), Pakistan* Institute of Engineering and Applied Sciences *(PIEAS) who did a meticulous supervision of my MS research despite his tight schedule. My special thanks to* ***Dr. Mansha Chaudhry,*** Deputy Chief Scientist *(DCS; PIEAS) who guide my experimental work in PIEAS. I am very thankful to* ***Ms. Sabiha Javied,*** *Ph.D scholar (PIEAS) and to the* **laboratory technicians,** *PIEAS who have assisted me during my project.*

I feel happy to express my gratitude to entire **DES,** *IIUI, my* ***friends and colleagues*** *for their kindness during my entire duration of MS.*

I am very grateful to ***my family*** *for their encouragement and understanding during my whole project.*

Last but not least, I will pay special thanks to all the researchers whose material I have used in this research.

September, 2012 Sara Elahi

ACRONYMS

AAS	Atomic Absorption Spectroscopy
ASTM	American Society for Testing and Materials
AT	Averaging time
B_m	Background value
BW	Body weight
°C	Degree Celcius
Ccs	Concentration in control soil
Ccg	Concentration in control grain
Cd	Cadmium
C_d	Degree of Contamination
Cf	Contamination Factor
Cfg	Concentration in fertilized grains
Cfs	Concentration in fertilized soil
CFs	Chemical Fertilizers
C_i	Actual concentration
C_m	Metal concentration
DAP	Di-Amonium Phosphate
DI	Daily Intake
dS/m	Deci-. Siemens/metre
EC	Electrical Conductivity
ED	Exposure duration
EF	Exposure frequency
EHS	Environment Health Safety
E_r^i	Potential ecological risk
E.U	European Union
EVS	European Voluntary Service
°F	Degree Fahrenheit
FAAS	Flam Atomic Absorption Spectrometer
FAO	Food and Agriculture Organization
FFC	Fauji Fertilizer Company Limited
FI	Fertilizer Impact
FIFA	Fertilizer Industry Federation of Australia
g	Gram
GFAA	Graphite Furnace Atomic Absorption
HMs	Heavy Metals
HQ	Hazard quotient
HSL	Hue, Saturation, Luminous
ICP-AES	Inductively-Coupled Plasma Atomic Emission

IFC	International Finance Corporation
IFPRI	International Food Policy Research Institute
INAA	Instrumental Neutron Activation Analysis
IPI	Integrated Pollution Index
IR	Ingestion Rate
IRIS	Integrated Risk Information System
IUPAC	International Union of Pure Applied Chemistry
Km	Kilo metre
LOI	Loss-On-Ignition
LPA	Leeds Public Analyst
μl	micro Liter
mA	milli Ampere
MDH	Minnesota Department of Health
MGD	Millennium Development Goals
Mg	Magnesium
mm	Millimeter
mmol	milli-mole
μS/cm	micro Siemens per cm
mS/cm	milli Siemens per cm
μl	micro Litre
Ml	milli Litre
NFWG	National Fertilizer Working Group
Ni	Nickel
NIAB	Nuclear Institute for Agriculture and Biology
Nm	Nano meter
NP	Nitro Phosphate
OFs	Organic Fertilizers
OMC	Organic Matter Content
PAEC	Pakistan Atomic Energy Commission
PFs	Phosphate Fertilizers
PI	Pollution Index
PIEAS	Institute of Engineering and Applied Sciences
ppm	Parts per million
PRs	Phosphate Rocks
S_i	Environmental value of metal
SSP	Single Super Phosphate
TOA	Touch of Asia
TF	Transfer Factor
T_r^i	Toxic response factor
USEPA	United States Environment Protection Agency
WHO	World Health Organization
XRF	X-ray Floursence

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CHAPTER 1

INTRODUCTION

Pollution is the introduction of harmful substances into natural environment that has detrimental affects on living organisms in their environment. The population growth and intensive agriculture are major causes of discharge of wastes into environment. This initiates serious environmental issues and can cause different risks to human health also.

Pollution started from the prehistoric times when man created first fires. However at that time, it was comparatively less and could be handled by nature itself. With the passage of time, rapid industrialization gave birth to environmental pollution as we know it today. The potential problems in environment are caused by wastewater, sewage sludge, solid wastes, agricultural residues and chemical products. Pollution can be divided into air pollution, water pollution, noise pollution, land pollution, radioactive pollution and thermal pollution depending upon their effects.

Soil pollution is one of important type of pollution that is the devastation of land by human activities. One of the major human activities is application of chemical products on agricultural land to get high productivity of crops. These products make land uninhabitable for living things. Although soil system has more buffering power against the external factors compare to other mediums that are water and air. However, several problems have been arisen when some pollutants added in the system become complex and difficult to be corrected.

Recently, issues associated with Heavy Metals (HMs) pollution of soil are increasingly common. HMs in general are pure element or an alloy of metallic elements which rarely have biological significance (Duffus, 2002). They include Arsenic (Ar), Iron (Fe), Copper (Cu), Cadmium (Cd), Cromium (Cr), Zinc (Zn), Nickel (Ni), Lead (Pb) and Manganese (Mn) etc. (Hochmuth, Maynard, Vavrina, Hanlon, & Simonne, 1991). These elements should be present within recommended limits. However sufficiently high concentration of these elements can alter the physical properties of soil and can ultimately affect the ecosystem.

Different studies have been done to trace out the sources of HMs contamination in agricultural land. It was also recognized that naturally, the actual HMs content of soil of certain region, primarily derived from parental rock material (Yap, Adezrian, Khairiah, Ismail, & Ahmad-Mahir, 2009). The other sources of HMs pollution in soil include natural (marine aerosols, volcanic eruptions and forest fires), and anthropogenic (energy and fuel production, mining and smelting, automobiles, urban/industrial complexes and recycling operations) that enhance the HMs fraction of soil (Reichman, 2002). Another significant contributor of HMs in soil is Phosphate Rocks (PRs). PRs by their composition have different ores that contain HMs as minor constituents (Allaway, 1971). HMs are leached from PRs in the course of production of phosphoric acid (H_3PO_4) when PRs are processed with acids (H_2SO_4, HNO_3 or HCl). These are present in various proportions into the PRs of different areas depending upon their environmental factors. Moreover they may vary within same source also (Stocia, Georgescu, Filip, & Bunus, 1997). Different researchers worked on the same lines and gave comprehensive account on the concentration of some HMs in PR deposits. In Pakistan, the concentration of HMs in PRs was found to be within the worldwide range (Sabiha-Javied, Mehmood, Chaudhry, Tufail & Irfan, 2009).

PRs in variable proportion are mixed with different synthetic compound to form different types of fertility enhancers that are fertilizers. Fertilizer is any agriculturally beneficial ingredients, added in soil to enhance the natural fertility of soil or even acts as a substitute to provide chemical elements that have been vanished as a result of cropping, grazing, leaching or even erosion (Tekin, & Bayramoglu, 2001). There are three types of the fertilizers including Nitrogen Fertilizers (NFs), Potasium Fertilzer (KPs) and Phophorus Fertilizers (PFs).

HMs are transferred to all of these types of fertilizers from PRs but PFs have maximum level than rest of the two types of fertilizers. Further it was also recognized that even two different types of PFs can also have variable concentrations of HMs (Charter, Tabatabai & Schafe, 1993). The end products of processing of PRs (mainly the PFs to larger extent) however have same proportions of HMs as that in PRs along with essential nutrients (Righi, Luciallib, & Bruzzia, 2005). These HMs especially Cd within the fertilizers has been found to be related with the corresponding PRs (Williams, & David, 1973; Wakefield, 1980). However in the course of production of PFs, a small fraction of these metals can be lost from PRs (Sabiha-Javied et al., 2009). HM analysis of PFs has been focused specially in India, Australia, Italy, England, New Zealand and USA to comply with the environmental regulations (Williams, &

David, 1973; Pezzarossa, Malorgio, Lubrano, Tognoni, & Petruzzeli, 1990).

The application of PFs transfers HMs (As, Cd, Cr and Zn) in soil which may have potential risks of its accumulation in soil (Sauerbeck, 1992). However long-term application of PFs causes slight variation in the level of HMs in soil (Modaihsh, Abdallah, & Mahjoub, 2001). It is reported that once HMs enter in the soil, they persist there for years (Alloway, 1995). The presence of metals in soil may also affect the overall physiochemical properties of soil. It is stated that addition of Single Super Phosphate (SSP) may drop the pH of soil (Oyedele, Asonugho, & Awotoye, 2006). Soil on the other hand, itself has some HMs that are combined with fertilizer-derived HMs constituting the overall metals fraction of soil. These metals in soil are present in ionic form and can be divided into soluble fraction within soil solution or ions that are associated with clay and organic matter, metal precipitates and mineral deposits (Norvell, 1991). HM ions which contributed the soluble fraction of metal pool in soil are thought to be readily available for the uptake of plants. Other ionic fractions in soil are less available (Davis, & Leckie, 1978; Castilho, Chardon, & Salomons, 1993). The available fraction of soil is designated as bio-available fraction. It is investigated that bioavailability of metal ions in soil is subjected to a number of physiochemical factors such as light, temperature, soil properties; and characteristics of plants itself (Parasad, Simmons, & Maher, 2004).

The adsorption criterion of HM ions within plants is apo-plastic adsorption (direct transport to vascular stele, xylem and phloem through free spaces, cell walls of the epidermis and cortex). In this process, the metals transporters are served to transport the metal ions within plants, from epidermis to xylem tissues and then to phloem from where metal ions are transported to the maturing grains. The amount of metal ions being transported to the grains actually depends upon magnitude of elemental mobility from soil to plant root, percentage of elements pass across the epidermis of root, transport of adsorbed elements from epidermal cells to xylem and its final transport to storage parts through phloem transport system (David, & Joel, 1995). The intercellular transport of metal ions in monocotyledons is shown in Fig. 1.

The accumulation of HM ions within plants depends upon its transfer quotient from soil-to-aerial portions. Leafy vegetables are at more risk to accumulate metal ions because of higher translocation and transpiration rate as compared to other vegetables (Itanna, 2002). Root intake and uptake of HM ions forms basis of transfer coefficient for soils and plants as well (Kloke, Sauerbeck, & Vetter, 1984). Different portions of plants show variable transfer ratio due to mobility difference of different ions (Liu et al., 2009). The transfer quotient is also suggested as a suitable way for assessment of health risks by quantifying the differences in bioavailability of metal ions to plants (Cui et al., 2004). In Pakistan, radionuclide intake of wheat crop has been studied to asses the associated risks of radionuclide on human health due to application of PFs (Nasim-Akhtar, 2006; M. Tufail, Sabiha-Javied, Akhtar N., & Akhter J., 2010).

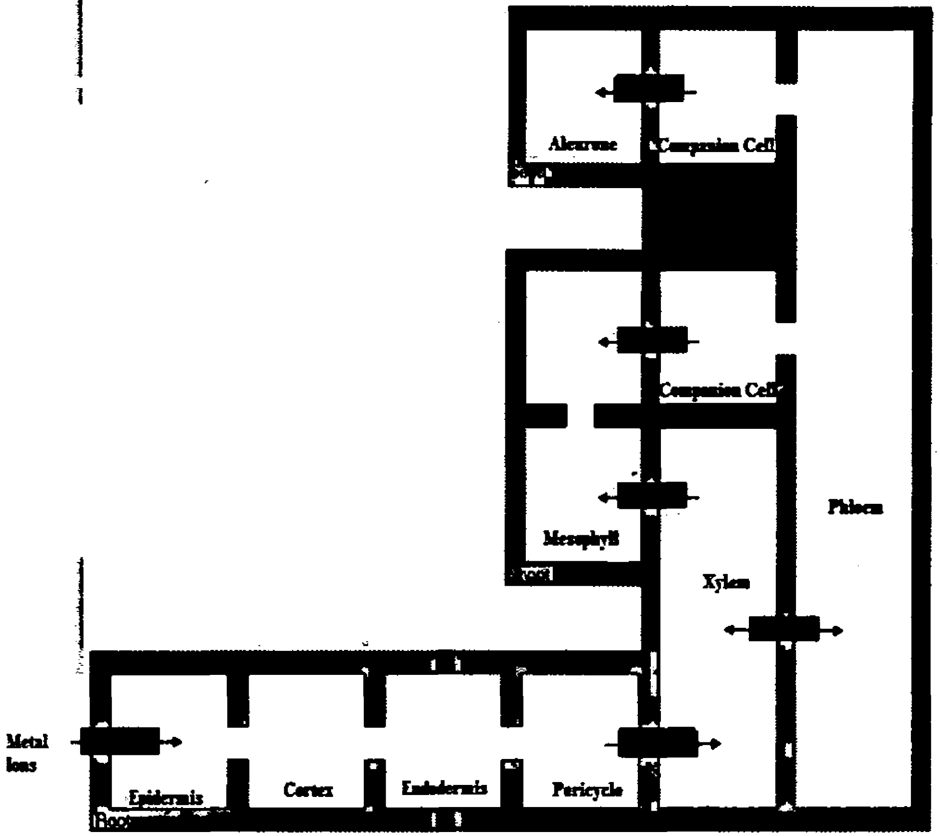

Fig. 1 Modified form of model of intercellular transport of metal ions in monocots. Black boxes represent transporters that are responsible for the transport of metal ions from roots to shoot then to seeds (Palmer, & Guerinot, 2009).

The high level entrance of HM ions within plants may hinder its growth and other metabolic activities. It may cause the inhibition of root development, shoot enlargement and numerous metabolic processes in plants (Pahlsson-Balsberg, 1989). Moreover HM ions can cause the overall inhibitory effects of seed germination (Mahmood, Islam, & Muhammad, 2007). Once HM ions are transported to grains, they then start accumulating there and finally are transferred to humans via food chain (Mc-Laughlin, Tiller, Naidu, & Stevens, 1996). The entry of HM ions in food chain by the application of fertilizers on crops is shown in Fig. 2.

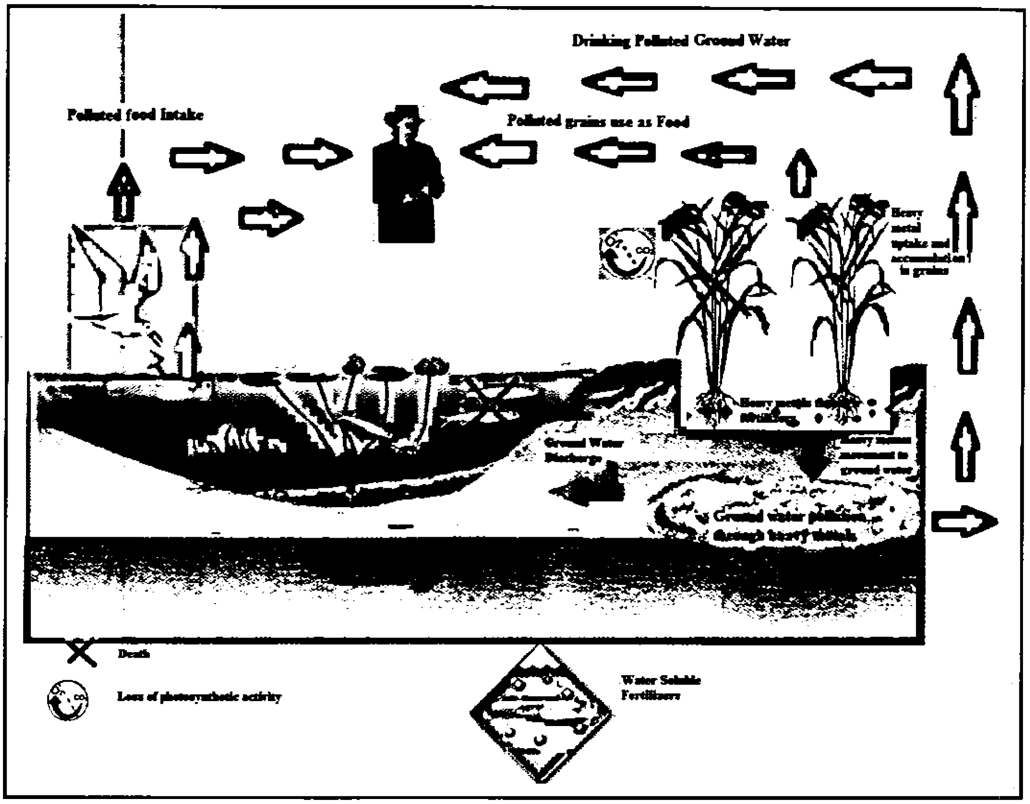

Fig. 2 Transfer of HM ions from grains to human in a food chain. Yellow arrows represent flow of HM ions within food chain while blue represents HM ions flow through water.

The biotoxic cause of HM ions signifies its destructive effect to body when used beyond the recommended limits. High levels of Copper ions (Cu^{2+}) causes symptoms of acute toxicity, including nausea, jaundice, diarrhea, haemoglobinuria and haematuria, hypotension, anuria, coma and ultimately may lead to human death. The excessive doses of Zinc ions (Zn^{2+}) can cause weakness, loss of hair, anaemia, anorexia, diminished growth and changes in kidneys. In humans, Lead ions (Pb^{2+}) can result in wide range of biological effects including neurological, behavioural, haematological, renal, cardiovascular effects and effects on the reproductive system. Cadmium ions (Cd^{2+}) accumulate in the kidneys leading renal dysfunctioning (FAO/WHO, 2010). Exposure to higher levels of Nickel ions (Ni^{2+}) is toxic to humans. The inhalation of Ni ions can cause cancer of lungs, nose, throat sinuses and stomach (Duda-Chodak, & Baszczyk, 2008). The stomach, kidneys and liver are damaged by Chromium ions (Cr^{3+}). It can also cause allergy on skin. Hexavalent Chromium (Cr^{6+}) is classified to be carcinogenic by U.S. Environmental Protection Agency (EPA) after chronic inhalation. However, it is not cancerous via oral route

(EVS, 2005).

Different international agencies are currently advocating the compliance to permission criteria of pollutants in agricultural products. For analysis of the concentration of metal ions, the process of screening evaluation of HM in fertilizers was introduced (Minnesota Department of Health, 1999). Moreover different agencies proposed the permissible limits for HM in soil and plants as well to control the amount of ingestion of metal ions in humans (Awashthi, 2000; EU, 2002; WHO/FAO, 2007). In Pakistan, till now no standards for safe limits of metals within vegetables have been established therefore Indian standards are used as reference. Some researchers argued that there are several chemical procedures to get rid of HMs from H_3PO_4 prior to its conversion in PFs (Stenstrom, & Aly, 1985; Tjioea, Weija, Wesselingha, & Rosmalena, 1988). Further control on Cd was introduced in many countries by limiting the metal use. An extensive check of fertilizer legislation was provided though the establishment of a National Fertilizer Working Group (NFWG) which developed a national standard for the contaminants in fertilizers. At the same time, the Fertilizer Industry Federation of Australia (FIFA) developed a national code of practice for fertilizer standards (Mc-Laughlin, Hamon, McLaren, Speir, & Rogers, 2000).

There are different analytical techniques to carry out qualitative as well as quantitative measurements of HMs. Some involve the emission or absorption of electromagnetic energy; that include Atomic Absorption Spectroscopy (AAS), Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES), mass spectrometry, X-Ray Fluorescence spectroscopy (XRF) and Instrumental Neutron Activation Analyses (INAA). Some use chemical interactions; like ion chromatography and chemical testing kits; and still remaining practices are electrical interaction such as voltammetery and amperometric cell sensor techniques. The choice of analytical technique depends upon its application. For simple screening and biological assessment, chemical kits are thought to be appropriate. The most precise analytical methods include AAS, ICP-AES, XRF and ion-chromatography.

The AAS is considered to be one of important analytical techniques that may be preferred where low detection limits are required. There are two types of AAS, Flame Atomic Absorption spectrometry (FAAS) and Graphite Furnace Atomic Absorption Spectroscopy (GFAA). In present study FAAS technique was available to investigate the concentration level of environmental samples. Moreover it is one of important techniques for investigating larger volume of samples for restricted number of elements. The technique was preferred because it was easy-to-use, widely accepted and widespread application information. Moreover this technique was relatively cheaper as compared to the others.

1.1 Significance Of The Study

Wheat and rice contribute major portion of total calories and protein of our food. Therefore round the world, these crops are cultivated on major portion of the agricultural land. Moreover for profitable wheat and rice production, huge mass of Phosphate Fertilizers (PFs) are applied annually on agricultural land. So it is very important to check the status and trends of HMs contamination of these crops. In present study environmental pollution assessment due to the application of PFs will be managed through collection and cataloguing the samples of soil and the grains of wheat and rice, selection of measurement technique, preparation of the samples as per requirements of the measurement technique, determination of specific HM ions, determination of soil-to-grain transfer factor of HM ions, and assessment of hazards on human health. So environmental problems related to the contamination of metal ions will be resolved to some extent. This will lead a way to further researches on contamination of some other HM ions in crops that is not covered in current study.

1.2 Objectives

The aim of this study is to:

- To compare the concentrations of the HM ions in phosphate fertilized and unfertilized soil.
- To monitor the uptake of the HM ions by wheat and rice grains from the soil using FAAS analysis.
- To assess the degree of pollution, ecological as well as health risks associated with HM ions through application of the assessment models.

CHAPTER 2

EXPERIMENTAL

In this section, the materials and methods for FAAS analysis are being discussed. Moreover different ways of the interpretation of procured data are discussed through application of reported models. This in turns will help to predict the risks associated with application of PFs.

2.1 Chemicals and Reagents

The chemical used were of research grade. Nitric acid (65% m/v) was obtained from Merck (Germany) while Hydrogen Peroxide (30% m/v) was procured from Fluka (Switzerland). High purity standard solutions of Cd^{2+}, Cr^{3+}, and Cu^{2+} were purchased from Fluka (Switzerland) and the standard solutions of Ni^{2+}, Pb^{2+}, and Zn^{2+} were obtained from Fisher Scientific International Company (U.K).

2.2 Apparatus and Equipment

The samples were weighed with the help of digital balance (ranged 1 x 10-4 - 2 x 102 g) made by YMC-Co Ltd, Japan. Sample drying was done using D-6450 Hanau made by Heraeus Instrument, Germany. Organic matter was destroyed by mean of furnace manufactured by Carbolite, U.K of type HTF 15/88. For dissolution of HMs in acidic solution, hot plate (model PC-420D manufactured by Corning, USA) was used. The condensation assembly was used to enhance the process of dissolution of metals by simultaneous heating and cooling of the solvent acid, consisted of water cooled column condenser set at approximately 90° on the round bottom flask (500ml), placed over heating mantle. Electrical Conductivity was measured by conducto-meter of model CM-8ET made by Ogwa Seiki Co-Ltd, Tokyo, Japan. pH was determined using pH meter of model HM-1k made by Touch of Asia (TOA), China. For elemental analysis, Flame Atomic Absorption Spectrometer (FAAS; model Varian Spectr AA-300, Australia) was used, with air/acetylene burner, auto-sampler PSC-56 and 4-fold lamp changer. The optimum conditions that have to be maintained during FAAS analysis are given in Table 1. All the instruments were always calibrated by mean of appropriate standards. All glassware was of Pyrex, Germany and cleaned with Nitric acid (HNO_3), Hydrochloric acid (HCl) and Distilled deionized water (H_2O_2).

Table 1 Optimum conditions for FAAS analysis

Element	Wavelength (nm)	Lamp current (mA)	Flame stoichiometry	Slit width (nm)	Working range (µg/ml)
Cu^{2+}	324.7	4	Oxidizing	0.5	0.03-10
Cr^{3+}	357.9	7	Reducing	0.2	0.06-15
Ni^{2+}	232.0	4	Oxidizing	0.2	0.1-20
Pb^{2+}	217.0	5	Oxidizing	1.0	0.1-30
Cd^{2+}	228.8	4	Oxidizing	0.5	0.02-3
Zn^{2+}	213.9	5	Oxidizing	1.0	0.01-2

2.3 Preparation of Environmental Samples

Preparation of environmental samples involves different steps that are discussed below;

2.3.1 Study Area

A suitable site was selected for the crops to be grown. For this purpose, the city of Faisalabad (shown in Fig. 3 in map of Pakistan) was chosen which is considered as hub for agricultural researches. Moreover it was founded as an agricultural marketplace, since the time of its establishment in 1970. The city of Faisalabad is the 3rd biggest metropolitan of Pakistan with many agricultural research institutions. The location of the area of study is shown in Fig. 3. Faisalabad lies within latitude 31°-24′ N and longitude 73°-05′ E on Western side of Lahore, the Capital of the Punjab province. It is situated in middle of lower part of the Rachna Doab with Chenab River flowing at a distance of about 32.18 km (20 miles) to its West and Ravi River at a distance of about 138.4 km (86 miles) to its East. The topography is however marked by valleys local depression and relatively high ground. The weather is partially dry with remarkable seasonal variations of temperature. The annual rainfall of this area is about 310 mm. The maximum temperature in summer reaches up to 50°C (122°F). In winter, it may falls below freezing point (Pakistan Meteorological Department, 2004). Generally the soil of Faisalabad region is fertile however it is suffering from an extreme problem of salinity. Additionally the underground water is somewhat brackish. Due to these problems it has been estimated that total productivity of crops has reduced by 10% in most of the area and to 60% in some areas. Therefore, chemical and biological amendments are used extensively to restore the original growing potential of agriculture soil of this region (Ghafoor, Zia-Ur-Rehman, Ghafoor, Murtaza, & Sabir, 2008).

The study location at Faisalabad was NIAB that was established by Pakistan Atomic Energy Commission (PAEC) in 1972. The extended portion in Fig. 3 shows the location of NIAB farm, is situated at a distance of 7 km from the centre of Faisalabad city. NIAB has invigorated laboratories within an enclosed area of 60 acres (24 hectares) attached with an experimental farm.

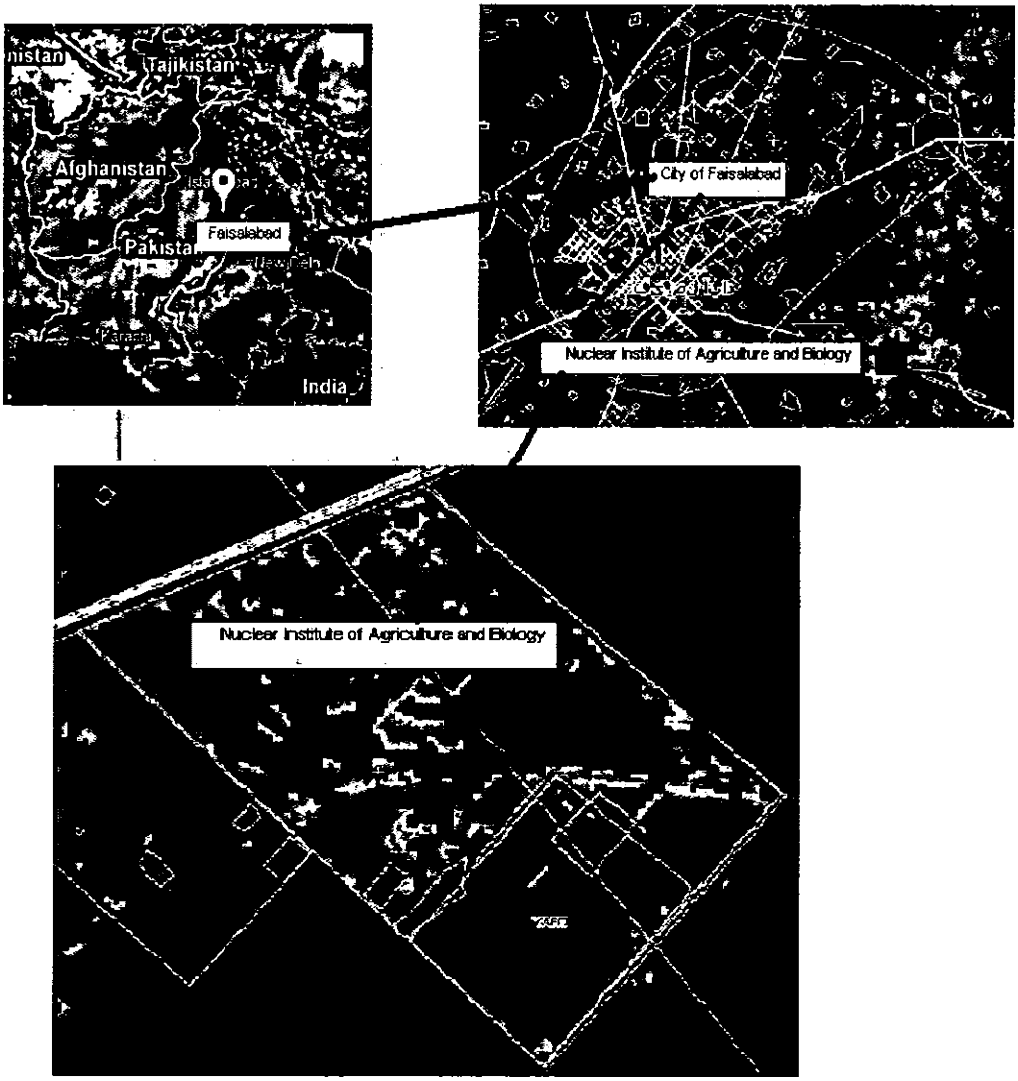

Fig. 3 Study area in map of Pakistan

2.3.2 Crop growing

In order to grow study crops, a patch of plain land was selected in agricultural research farm of NIAB. The surface soil layer was then removed from the selected site and enough amount of soil from the subsoil layer (at 0–20 cm in depth) was collected, homogenized and settled in eight groups of plastic pots of surface area 0.25m^2. The seeds of rice crops were sowed in August 2010, while wheat crops were planted in December 2010. Three types of PFs including Single Super Phosphate (SSP), Di-Ammonium Phosphate (DAP) and Nitro Phosphate (NP), were applied separately at optimum rate of 2.3, 0.9 and 1.85 g (at required rate of 17P) to all of the pots of both crops. One pot of both crops was left as control (without fertilizer). The plants were grown as per standardized procedure. After 136 and 210 days (for rice and wheat from the time of sowing of seeds), the crops were ready to be harvested. Each treatment involved three replicates to get the authenticated results (Nasim-Akhtar, 2006).

2.3.3 Sample collection and preparation

When the plants were mature for harvesting, the whole plants were up-rooted along with the soil around the root zone area. The samples of grains and the corresponding soils from root zone were removed from the plants. The samples of grains and that of soils were assigned code names for their identification as presented in Table 2. A representative soil sample was also collected from the farm (where from soil was taken into pots) to determine the physical properties: soil colour, particle size, soil texture, organic matter content, pH and electrical conductivity (EC). The samples were stored in air-tight polythene bags, properly catalogued and brought to Analytical Chemistry Laboratory at Pakistan Institute of Engineering and Applied Sciences (PIEAS), Islamabad, Pakistan. The samples of grains were rinsed with double distilled water to remove dust impurities. The grain and soil samples were dried at 100°C to constant weight, grinded with the help of a mortar and pestle and passed through a sieve of mesh size 0.5mm (Nasim-Akhtar, 2006).

Table 2 Codes of samples used collected after harvesting

Sr. No	Sample type	Sample code	Fertilizer applied	Sr. No	Sample type	Sample code	Fertilizer applied
1.	RICE SOIL SAMPLES	SRS	SSP	5.	RICE GRAIN SAMPLES	RSG	SSP
2.		NRS	NP	6.		RNG	NP
3.		DRS	DAP	7.		RDG	DAP
4.		CRS	Control	8.		RCG	Control
9.	WHEAT SOIL SAMPLES	WSS	SSP	13.	WHEAT GRAIN SAMPLES	WSG	SSP
10		WSN	NP	14.		WNG	NP
11.		WSD	DAP	15.		WDG	DAP
12		WSC	Control	16.		WCG	Control

2.4 Experimental design

Principle experimental design of present study involved determination of pollution level of collected samples and assessment of risks associated with HMs contamination of PFs on the selected crops. Different steps of the experimental design are shown in Fig. 4.

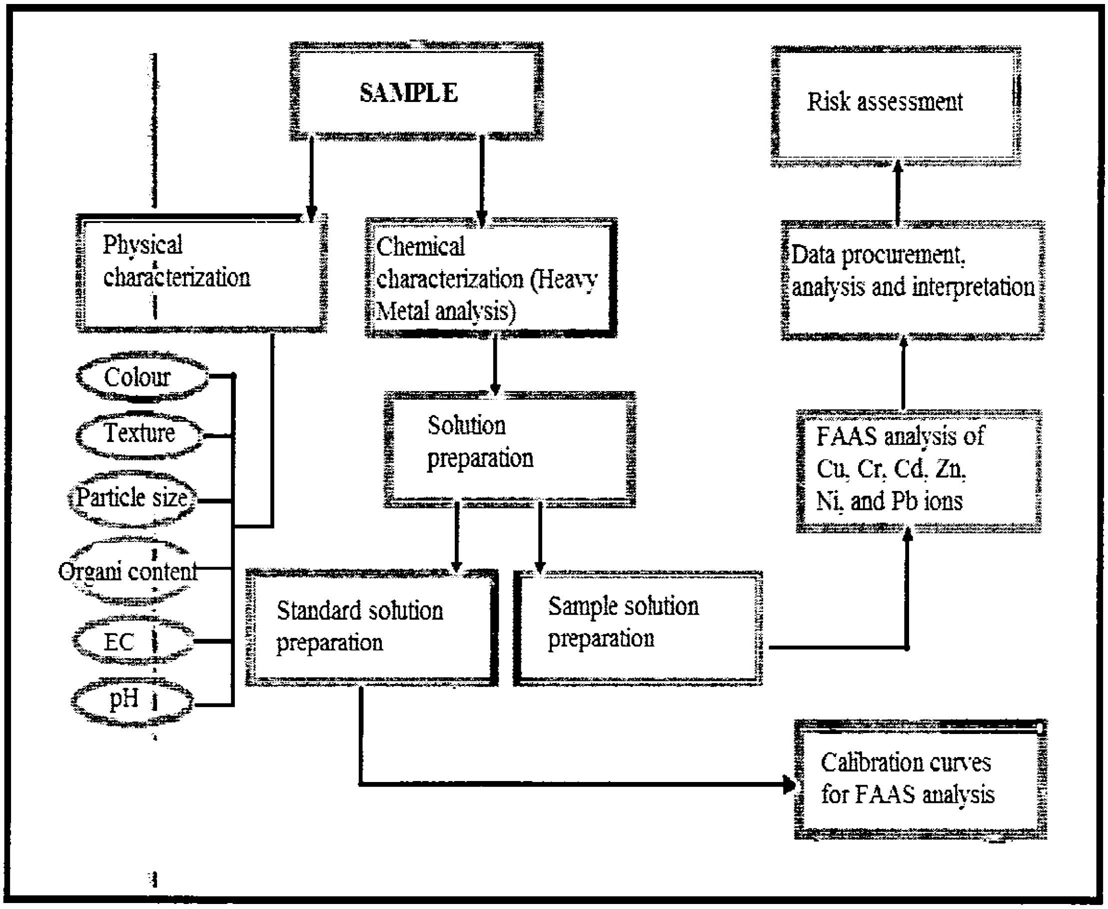

Fig. 4 Experimental design for the present study

2.4.1 Physical Characterization

The physical characteristics are those that can be seen or felt. These are of utmost importance for the production of crops and are difficult to change, compared to the chemical properties of soil. The deterioration in physical properties of soil as a result of continuous cropping can affect crop growth adversely. In present study, a representative soil sample was taken to determine the following selected physical properties:

2.4.1.1 Soil Colour

Colour is an obvious characteristic of soil. It can provide a valuable insight into the soil environment. Thus it can be very important in the assessment and classification of soil. In present study, a snapshot of enough amount of soil sample was taken and it's RGB (Red, Green and Blue on the scale of 0 to 255) and HSL (Hue, Saturation and Luminous on the scale from 0 to 240) values were determined by treating these attributes on Adobe Photoshop CS5. Both HSL and RGB are natural way of dealing with colours. Hue links to the actual colour, saturation is related to the intensity or purity of colours, and luminous corresponds to brightness. RGB reveals the mode in which different colours actually display on computer screen.

2.4.1.2 Particle Size

Particle size is a very important characteristic of soil. It determines surface area that influences chemical and physical characteristics of soil (Pendias, & Kabata-Pendias, 2001). Smaller particles, like clay, let not water pass through as easily as larger particles, like sand. Particle size determines retention of water and nutrients in soil (Sandor, 2008). In present study, the particle size of soil was determined by simple sieving. For this a definite amount of oven dried representative soil sample was taken and mixed properly. Later the huge particles of gravels and sand were separated and the samples were passed though different sieve size to determine the particle size of soil.

2.4.1.3 Soil Texture

Soil texture is one of the most important physical properties of soil. It refers to basic composition of soil, which consists of sand, silt and clay contents. The soil texture affects all properties of soil either directly or indirectly (Sandor, 2008). In order to determine soil texture, one litre beaker was filled with 200ml of soil sample and rest with water. The beaker was then shaken for five minutes and kept for 24hours. After that the depth of soil was gauged with ruler. The beaker was then shaken for 5minutes and the settled soil was again evaluated. The beaker was then kept for 25minutes and the settled soil was measured again (Sandor, 2008).

2.4.1.4 Organic Content

Organic matter plays very important role in sustaining soil fertility; ability to hold nutrients and water; and structural stability of soil. In soil, it may form huge sized complexes with metals. The method named Loss-On-Ignition (LOI) was used for the determination of organic matter in soil. 5g of soil sample was placed on a ceramic crucible and heated at 350°C overnight (American Society for Testing and Materials, 2000). The sample was then cooled and weighed again. Organic matter content was determined as a difference between the initial and final weights of sample divided by the initial weight of sample times 100%.

2.4.1.5 Electrical Conductivity (EC)

Electrical Conductivity (EC) is ability of any material to transfer an electrical charge. It depends on the amount of dissolved solids. The major purpose of calculating EC is to identify the amount and quality of salts in soil. EC will be greater if salt content of soil is higher and vice versa. It is expressed in milli Siemens per cm (mS/cm) or micro Siemens per cm (µS/cm). In present study, a saturated soil paste was made by continuous stirring of distilled water during addition of soil, unless characteristic endpoint was attained. In order to get sufficient amount of the extract, a suction filter was then used (US Salinity Laboratory Staff, 1954). Later EC value was determined with the help of calibrated EC meter.

2.4.1.6 pH

pH is logarithm of reciprocal of hydrogen ion concentration [H^+], which is represented as follows:

$$pH = -\log\left[H^+\right]$$

The pH value measures the ratio of H^+ ions to OH^- ions in soil. In neutral soil, the amount of H^+ and OH^- remains same (pH=7). However if OH^- dominates, the soil is alkaline (pH>7). If the soil solution has more H^+ (pH<7), the soil is acidic. In present study, a saturated soil sample was prepared as mentioned in EC determination test (US Salinity Laboratory Staff, 1954). Later pH value was determined with the help of calibrated pH meter.

2.4.2 Chemical Characterization

Soil has different metals in various proportions that are characteristic to the soil of particular area. These metals determine the overall chemistry of soil and also monitor the uptake of metal ions within plants. In present study, the application of different types of PFs may change the inorganic constituents of soil and also affect its intake as well as the uptake in selected crops. The chemical analysis (FAAS analysis) of all soils and grain samples was therefore performed to observe the overall translocation pattern of metal ions in both types of crops under application of different PFs.

2.4.2.1 Solution Preparation

Solution preparation is the important step in FAAS analysis because it requires liquid samples to be aspirated, aerosolized, and mixed with combustible gases (acetylene and air or acetylene and nitrous oxide). It involves preparation of standard solution for the calibration of instrument and preparation of sample solution for analysis.

2.4.2.1a Standard Solution Preparation

Multiple sets of standard solutions of the selected metal ions were prepared using high purity standards (1000ppm). This was done by taking different volumes of standards in 25ml volumetric flasks using the baseline information available in Varian Analytical Methods (1989). Details are given in Table 3. The standards were then made up to the mark with distilled water and were then used to set analytical working range of the instrument for each metal ion. The calibration curves for all of the selected metal ions established good linearity over concentration range with correlation coefficients (R^2) in the range of 0.998 to 0.999. Instrument Detection Limit (IDL) was detected by mean of the Standard Deviation (SD) and absorbance for the standard concentration values measured by FAAS.

Table 3 Sets of standard solutions prepared for calibration curve

Sr. No	Element	Volume of standard used (µl)	Concentration range (ppm)	No of sets of standard solutions
1.	Cd^{2+}	50-250	2-10	5
2.	Cr^{3+}	50-250	2-10	5
3.	Cu^{2+}	50-250	2-10	5
4.	Pb^{2+}	50-250	2-10	5
5.	Ni^{2+}	100-400	4-16	4
6.	Zn^{2+}	5-35	0.2-1.4	4

2.4.2.1b Sample solution preparation

A portion of approximately 1.0g of each oven dried soil sample was taken and furnaced for 30min at 350°C to get ashes. 25ml of conc. HNO_3 was added to the ashes and refluxed for 15minutes till digestion completed. The digestate was filtered through a 125mm acid-resistant filter paper. Afterwards, the filtrate was diluted with distilled water up to the mark (Sezgin, Ozcan, Demir, Nemlioglu, & Bayat, 2003).

Approximately 1.0g dried grain sample was taken in 100ml beakers. 5ml of concentrated HNO_3 was added to the sample and the beaker was covered with watch glass till frothing subsides. The covered beaker was placed on a hot plate at 125°C for 1hour then removed and allowed to cool. 2ml of 30% H_2O_2 was added and digested at same temperature. The heating and H_2O_2 addition were repeated till digestate become clear. Watch glass was then removed as digestate became clear and temperature lower down to 80°C. The heating was continued until dryness. Dilute HNO_3 and distilled water were then added to dissolve sample residue and bring sample to final volume (Plank et al., 1988).

2.4.2.2 FASS Analysis

Each sample solution was diluted up to 100ml so that the analyte absorbance lies on calibration curve. Suitable hollow lamp was installed and warmed for 15-20minutes. Lamp alignment was done in such a way to get maximum signals at minimum photomultiplier voltage. Flame was ignited and flame conditions were optimized to get maximum signals for analyte and minimum for blank and background. Calibration curves for each element were drawn using the sets of standard solutions. All samples were then analyzed using respective lamps for each element. Spike recovery was examined to check the validity of results (Rothery, 1986).

2.4.2.3 Quality Assurance

In order to minimize the chances of errors, soil and plant samples were digested along with blanks following same procedures and subtract the blank readings from samples readings. FAAS was also calibrated through a series of standard solutions supplied by the manufacturer (Varian). All determinations were replicated three times to get reliable results.

2.4.3 Data procurement and analysis

Data was procured using FAAS analysis of all samples. The data was then analysed by the use of different statistical tools and formulas which are actually the assessment models that describe concentration trends of HM ions under specific conditions. Statistical tools involve the calculation of minimum, maximum and mean values of concentrations; Standard Deviation (SD); Correlation Coefficient (R), Probability (P) and Confidence Interval (CI). Among the available pollution indicators, Pollution Index (PI), Integrated Pollution Index (IPI), Contamination Factor (Cf), Degree of Contamination (Cd) and Transfer Factor (TF) have been addressed.

2.4.3.1 Statistical Analysis

A statistical analysis of the results was accomplished to determine different statistical parameters. The SD was calculated based on the Percentage Relative Standard Deviation (%RSD) of results obtained from FAAS analysis. Pearson correlation coefficient (R) of concentrations was determined to suggest the extent of association between two selected metals within a specific group (soil or grain), or that of the corresponding metals determined in soils and grains. Two tailed probability test was performed by the mean of r to P Calculator to predict the statistical significant relationship between two concentration values. Confidence Interval (CI) of significant relationships was determined by the mean of Confidence Intervals of rho Calculator to generalize the range of relationship between metals of studied crops to whole population at confidence level of 95%.

2.4.3.2 Pollution Assessment Models

The measured concentrations of HM ions in soils and grains were used for the assessment of their contamination level. The overall impact of HM ions in soils and grains was determined through indices. These indices were not only used to describe the concentration trends but also allow an easy comparison between the determined parameters. The following parameters were taken into account for the assessment of contamination level in present study:

2.4.3.2a Contamination Factor

The Contamination Factor (C_f) is used to assess degree of contamination of soil for ecological risk assessment. In present study, it actually represented a comparison of concentration of metal ions in fertilized soil to the measured background value from geologically similar control soil samples. The C_f is calculated by following formula (Hakanson, 1980):

$$C_f = \frac{C_m}{B_m}$$

C_m is the concentration of metal ion in individual samples and B_m is the background value of control samples. The C_f has been as follows (Hakanson, 1980).

$C_f < 1$: low contamination factor

$1 \leq C_f < 3$: moderate contamination factor

$3 \leq C_f < 6$: considerable contamination factor

$C_f \geq 6$: very high contamination factor

The degree of contamination (C_d) was determined as sum of contamination factors of all elements for a single sample to trace out the most contaminated fertilized sample. The following terminology is adopted to describe C_d values (Hakanson, 1980).

$C_d < 6$: low degree of contamination

$6 \leq C_d < 12$: moderate degree of contamination

$12 \leq C_d < 24$: considerable degree of contamination

$Cd \geq 24$: very high degree of contamination indicating serious metal pollution

2.4.3.2b Pollution Index

Pollution Index (PI) was used for the determination of pollution level of a material in which HM ions have already been measured. In present study PI was calculated using following equation (Chen et al., 2005; Wei, & Yang, 2010):

$$PI = \frac{C_i}{S_i}$$

where PI is the Pollution Index of the selected metal i; C_i the actual concentration (μg/g) of HM ions comes as an outcome of this study; S_i is the minimum tolerable value (μg/g) of the selected metal in soil and plants based on assessment criteria of Indian (Awashthi, 2000) and European Union (EU, 2002) standards (for Cr in soil only). The values are given in Table 5.

The PI has been classified as follows:

$PI \leq 1$: low level of pollution

$1 < PI \leq 3$: middle level of pollution

$PI > 3$: high level of pollution

The Integrated Pollution Index (IPI) or an average of Pollution Index (PIavg) can be defined as (Chen et al., 2005; Wei, & Yang, 2010):

$$PIavg = \frac{1}{m}\sum Pi$$

where Pi is the single Pollution Index of selected metal ion i; and m is the count of the HM species. In present study, IPI was calculated to determine the average PIs of all the selected elements in a sample. IPI has been classified as follows:

$IPI \leq 1$: low level of pollution

$1 < IPI \leq 2$: middle level of pollution

$IPI > 2$: high level of pollution.

2.4.3.2c Transfer Factor

The Transfer Factor (TF) was designed to determine the overall soil-to-grain transfer of HMs within the selected crop by following equation (Cui et al., 2004):

$$TF = \frac{concentration\ of\ metal\ in\ edible\ part}{concentration\ of\ metal\ in\ soil}$$

2.4.4 Risks Assessment

The application of PFs on selected crops can cause different risks to environment as well as human health. These risks can be estimated by assessing the magnitude of exposures. For this purpose, different models reported in literature concerning ecological and health risks assessment were applied to outcomes of FAAS analysis.

2.4.4.1 Ecological Risk Assessment

The core quality management is based upon the impacts of HMs in soil on environment (Hernande, Probst, Probst, & Ulrich, 2003). Potential ecological risk index method was put forward in relevance to the features of HMs in nature and environment (Hakanson, 1980). It gives quantitative methods to carve up potential ecological risk levels. HM impacts on environment can be determined successfully because of differences in toxicity and environmental sensitivity towards HMs. In present study the impact assessment of HM ions on environment was estimated using potential ecological risk index (Phase, Hongxiao, & Zijian, 1994; Chen, Tan, & Tay, 1996).

2.4.4.1a Potential Ecological Risk

The potential ecological risk of toxic HM ions can be calculated by following relation (Hakanson, 1980):

$$E_r^i = T_r^i \times C_f^i$$

where E_r^i is Potential Ecological Risk, C_f^i is Contamination Factor, T_r^i is Toxic Response Factor for a given substance (T_r^i for Cu, Cr, Cd, Zn and Pb is 5, 2, 30, 1 or 5 respectively). No T_r^i value was available for Ni. Five categories of E_r^i were identified.

< 40: Low potential ecological risk
40-80: Moderate potential ecological risk
80-160: Considerable potential ecological risk
160-320: High potential ecological risk
≥ 320: Significantly high potential ecological risk

2.4.4.1b Potential Ecological Risk Index

The sum of individual potential risks of each element in any soil sample was determined as potential Risks Index (RI) as a result of application of specific fertilizer. The following terminology was used for RI values (Hakanson, 1980).

< 150: Low potential ecological risk
150-300: Moderate potential ecological risk
300-600 High potential ecological risk
≥ 600: Significantly high potential ecological risk.

2.4.4.2 Health Risk Assessment

Health risk assessment is a scientific process by which quantification of potential environmental hazards to human health. This principal method of risk assessment utilizes the tools of science, and statistics to measure hazard, suggest possible exposure routes, and ultimately utilizes that information to sort out numerical value which represent overall potential risk to human health. Risk assessment plays an important role to protect adverse environmental effects on public health (Cohrssen and Covello, 1989).

2.4.4.2a Exposure assessment

Some HMs are carcinogenic while some are non carcinogenic. Identification of exposure pathways is an important step by which exposure route followed by any toxicant in human body is mark out. Among the HMs, arsenic is an exception that is carcinogenic via oral route. So the selected metals are either non-carcinogenic or are non-carcinogenic via oral routes over its life time exposure to human beings (Dibiasio, & Klein, 2003). The term Daily Intake (DI) was used for dose assessment of non-carcinogens. It is well said that an estimation of daily intakes of HM ions is advantageous to judge its toxicity meant for human health. The DI was determined by the following equation (RAGS I Part A, 1989):

$$DI = \frac{CM \times IR \times EF \times ED}{BW \times AT}$$

where:

C = Metal concentration in grains in µg/g or mg/kg

IR = Mean ingestion rate of wheat grain products considered in present study = 0.3835kg/day (United Nations Scientific Committee on Effects of Atomic Radiations, 2000)

IR = Mean ingestion rate of rice grain taken in present study= 0.165 kg/day (Nogawa, & Ishizaki, 1979; Rivai, Koyama, & Suzuki, 1990)

EF = Exposure frequency = 365 days/year

ED = Exposure duration (years) over a lifetime = 70 years

BW = Body weight = 70 kg

AT = Averaging time = ED x 365 days/year = 70 years x 365 days/year

Values of BW, ED, AT and EF are default referred in Exposure Factors Handbook (USEPA. 1997).

2.4.4.2b Hazard Quotient

The Hazard Quotient (HQ) is ratio of daily dose to reference dose for safe health (IUPAC Glossary). The HQ is used to estimate the risk of elements due to ingestion of average daily dose of wheat and rice grains contaminated by selected PFs. The HQ is defined by the following relation (RAGS I Part A, 1989):

$$HQ = \frac{DI}{R_f D}$$

Where R_fD is Reference Dose for daily intake of metals. The Tolerable Daily Intake (TDI) values can be considered as R_fD (Health Canada, 2004c; 2006). The TDI values for Cu, Cr, Zn, Ni, Pb and Cd are 0.125, 1.5, 0.7, 0.025, 0.00357, and 0.001 respectively. If the value of HQ is less than 1 (HQ<1), then the population are considered to be safe from the health risks (IRIS, 2003).

CHAPTER 3

RESULTS AND DISCUSSION

Plants pay key function in biotransformation of chemical elements from soil, air and water; thus PFs may act as a significant source for entry of HM ions into food chain. The translocation of HM ions from soil solution to plants is mainly dependent upon bioavailability pattern of them that varies with physiochemical properties of soil, elemental mobility and characteristics of plants. Different portions of plants have different tendency to accumulate HM ions which do not follow any particular pattern. So the impacts of HM ions through ingestion can be well established by determining the overall translocation pattern of HM ions from Soil-to-Plant especially in the edible portion.

3.1 Physicochemical Properties Of Soil

Soil itself constitutes a complex system with different physical, chemical and biological properties. Presence of microorganisms within soil makes up the biological properties of soil system. Physiochemical properties are characterized physically or chemically by analysis of soil. All of these factors affect the overall availability of HM ions to plants.

3.1.1 Physical Characterization Of Soil

Physical properties of soil are given in Table 4. The physical analysis of soil shows that the study soil has 122, 107, 83 RGB and 22, 58, 105 HSL values and thus has light olive brown colour (Munsell colour chart, 1994). Soil colour is subjective to soil mineralogy. The study soil appeared to have 10YR 5/3 Munsell notation. It is more luminous with less organic content and leaching of carbonates and clay minerals while presence of iron minerals gives it reddish yellow colour. These minerals actually provide supportive surfaces to the metal ions, so presence of iron enhances; while absence of carbonates and clay minerals; and less organic content decrease the availability of metal ions in soil. Different minerals give different shades to the soil as given in literature. Iron minerals give yellowish or reddish colour; organic matter form blackish compounds; and sulfur, manganese and nitrogen form black minerals.

These pigments can yield different colours in soil (United States Department of Agriculture, 2008).

The grain size of study soil is 0.025mm that enhances the concentration of HM ions within soil. The soil with small particle size enable sufficient binding to HM ions within soil thus affecting the chemical features of soil (Pendias, & Kabata-Pendias, 2001). Soil classification based on grain size is shown in Table 4. On the basis of diametric measurements of soil particles, the study soil is categorized as fine textured soil (Kopec, 1995). There is an increase in concentration values of metal ions with decrease in particle size of soil reported in literature (Loredo, 2006).

The availability of HM ions in study soil is more than normal sandy soil. The particle size distribution on soil textural division test shows that study soil belong to loamy texture (with 48, 30, and 22% of sand, silt, and clay) based on the textural classification of soil given in Table 4. The clay soil retains high amount of metal ions as compared to the sandy soil. Different researchers related the concentration of HM to soil texture. It is reported that the fine textured soils hold more Pb^{2+} than coarse textured soil (Jean-Claude, & Roy, 1991). Similarly majority of the metal ions in light; medium loam and clay are much more mobile than those in sandy and sandy loam soils (Lubyte, & Antanaitis, 2003; Mazvila, & Adomaitis, 2007).

The Organic Matter Content (OMC) of study soil is 0.63%. Actually Organic Matter (OM) in soil combines to metal fraction of soil forming huge organometallic complexes. Plants cannot absorb huge complexes, so the bioavailability of metal ions to plants may decrease (Reichman, 2002). The division of soil based on the OMC is presented in Table 4. Cataloguing study soil on the basis of OMC represents it as class of low OMC, so the formation of organometallic complexes is not favoured. Ultimately the metal ions are more likely to be available for plant uptake within study soil.

In present study, acidity test of sample soil revealed that the study soil has the pH of 7.7. The study soil is alkaline according to the classification given in Table 4. The alkaline pH is not favourable for the availability of metal ions. A number of studies have established that soil pH undertake a large effect on metal bioavailability to roots (Turner, 1994; McBride, Sauve, & Hendershot, 1997). The adsorption of metal ions decreases with increase in the pH of soil. This is due to the availability of metals in colloids from which metal ions are released at acidic pH (Marschner, 1995).

The EC of study soil (given in Table 4) may minutely influence the availability metal ions to rice while has no affect on the accessibility of metal ions to wheat crop. Actually the availability of metal ions in soil solution to plants is decreased with increasing soil salinity. In this case metals form complexes in water which is hard to be taken up by plants (Greger, Kautsky, & Sandberg, 1995). Wheat is considered to be salt tolerant (Watling, 2007) while rice is sensitive to salinity (Grattan, Zeng, Shannon, & Roberts, 2002). The general limit for irrigation of salt sensitive crops is 0.65dS/m and that of salt tolerant crops is 5.2dS/m (Akbar, Yabuno, & Nakao, 1972; Mori, & Kinoshita, 1987). As the study soil has EC values that were little more than the suggested limits for rice, so metal availability to rice might decrease under present study conditions while have no affect on wheat. The current guidelines however, points out that salinity affects rice yield at or above 3.0 dS/m (Grattan et al, 2002).

Table 4 Physical parameters of study soil

Physiochemical parameters of study soil

Soil properties	Values
RGB	122, 107, 83
HSL	22, 58, 105
Particle size	0.25mm
Sand	48%
Silt	30%
Clay	22%
Organic matter	0.63%
EC	1.1dS/m
pH	7.7

Classification on the basis of particle size (David, 1995)

Soil Particle	Very Coarse sand	Coarse sand	Medium sand	Fine sand	Very fine sand	Silt	Clay below
Diameter (mm)	2.00-1.00	1.00-0.50	0.50-0.25	0.25-0.10	0.10-0.05	0.05-0.002	0.002

Textural classification (Carlile, 2001)

Texture class	Sands	Sandy loams	Loams	Clay loams	Light clays	Clays	-
%Sands	86.8	68.3	51.5	27.5	44.6	21.4	-
%silt	6.1	13.2	28.1	34.1	13.1	15.7	-
%clay	7.2	18.5	20.3	38.4	42.3	62.9	-

Classification on the basis of OMC (Rusco, 2001)

Classes	High	Medium	Low	Very Low	-	-	-
% OM content	> 6.0%	2.1-6.0%	1.1-2.0%	< 1.0%	-	-	-

Classification on the basis of pH (Sandor, 2008)

Categories	Extremely acidic	Strongly acidic	Acidic	Slightly acidic to neutral	Alkaline	Strongly alkaline	Extremely alkaline
pH value	<4.0	4.5 – 5.5	5.5 - 6.5	6.5 – 7.2	7.3 – 7.8	7.8 – 8.5	>8.5

3.1.2 Chemical Characterization Of Samples

The study soil has different proportion of HMs that are being combined with PF-derived HMs constituting the overall metal fraction of soils. The magnitude of these metals actually determines the availability of metal ions to plant roots. Different soils show different concentration trends for the selected metal ions. These concentration values are helpful in determining the risks through the application of different models.

3.1.2.1 Concentration Level In Wheat Soil

The concentration level of HM ions measured by the FAAS in the samples of soil is given in Table 5. Amongst the soil samples, the sum of the concentration values for the selected HM ions within a sample shows following order: WSS > WSD > WSC > WSN.

Cadmium Ion: The concentration of Cd^{2+} in all soils including the control soil samples is almost same; suggesting that the study soil having enough amount of Cd^{2+} and is not affected by the applied fertilizers. The concentration values of all samples are more than the range of reported values (0.1-1.00μg/g) and the recommended values (3-6μg/g) for Cd^{2+} in soils.

Chromium Ion: The average concentration of Cr^{3+} is more than all of the individual sample concentration for Cr^{3+} except of WSS. This means that SSP is the major source of input of Cr^{3+} in soil. The concentration values for study soils are found to be within the range (9-64.75μg/g) of the values. The content of Cr^{3+} is less than the concentration values suggested by INAA analysis of soil (Sabiha-Javied, 2012), while are comparable to that proposed for Haroonabad, Faisalabad. All samples are safe from Cr^{3+} toxicity on the basis of its tolerable value (150μg/g) suggested for soil.

Copper Ion: The concentration of Cu^{2+} in all soil samples is close to each other (except WSD). The study soils are found to be more polluted for Cu^{2+} from the soils of India, Yemen and Eastern Europe. However the concentration values are close to the Cu content of soils in China, USA and Haroonabad, Faisalabad. All samples are far below the upper tolerable limits (135-270μg/g) suggested for Cu in soil thus are safe from any hazards.

Lead Ion: A variable amount of Pb^{2+} is present in soil samples. The concentration values for all samples are more than the compiled values for soils. This seems that the study samples are heavily polluted with Pb^{2+} compared to the worldwide reported values for Pb^{2+} in soils but are still within safe limits (250-500μg/g) suggested for soil.

Nickel Ion: The concentration of Ni^{2+} in the samples of soil is very close to each other, this means that PFs do not have any effect on the Ni^{2+} fraction of soil in comparison to the control soil. The concentration values are less than the soil polluted with waste water (Jeroen et al., 2010). Rest of the compiled values in soils around the world are less than study soils. The concentration of Ni^{2+} in all soil samples is within the recommended limits (75-150μg/g) for Ni in soil.

Zinc Ion: Zn^{2+} is an essential element for plant growth. The amount of Zn^{2+} for all soil samples is considered to be adequate for the growth of crops (Pantelica, Salagean, Georgescu, & Pincovshi, 1997). The Zn^{2+} content of the samples is found to be within the worldwide range (0.1-74μg/g). The concentrations of Zn^{2+} in all soil samples are within the safe limits (300-600μg/g).

3.1.2.2 Concentration Level In Wheat Grain

The concentration of Heavy Metal ions measured in the samples of wheat grain is presented in Table 5. Amongst the samples of wheat grain, the sum of concentration values for the selected HM ions within all sample shows following order: WGD > WGC > WGS > WGN.

Cadmium Ion: As observed, the concentration of Cd^{2+} in all the samples under study is below the detection limit (0.05μg/g). It means that all samples are safe from the toxicity of Cd^{2+}.

Copper Ion: The concentration of Cu^{2+} is comparable in all samples of grain except in WGN. The average concentration of the grains is more than the reported values. All samples are far below the tolerable limits suggested for Cu^{2+} in crops (30μg/g). This means that the grains are not polluted with Cu^{2+} and safe to grow in terms of the tolerable limits for the wheat plants.

Chromium Ion: All wheat grains have comparable values for Cr^{3+}. It is found to be many times less than the concentration reported in India and Haroonabad, Faisalabad. Rest of the reported values are less than the concentration of Cr^{3+} in study grains. All samples are safe from Cr^{3+} toxicity on the basis of its tolerable value (20μg/g) suggested for grains.

Lead Ion: The samples of wheat show close concentration values for Pb^{2+}. It seems that control grain also show sufficient level of Pb^{2+} in comparison to the fertilized grains. Grain samples have concentration values beyond the tolerable concentration (2.5µg/g) for Pb^{2+} and are many times greater than the values reported in literature. So Pb toxicity is seen in the study wheat samples.

Nickel Ion: The concentration of Ni^{2+} in grains is close to each other. Average concentration of study grains is many times less than the values reported in Haroonabad, Faisalabad and is more than the compiled values from India (Barman et al., 2000). All samples have Ni^{2+} far above the tolerable limits (1.5µg/g) suggested for Ni in crops. So it seems that the wheat crops are heavily polluted with Ni^{2+}.

Zinc Ion: Wheat grains show a vast range in the concentration values for Zn^{2+}. The average concentration of Zn^{2+} is close to that suggested by INAA analysis of wheat in NIAB, Faisalabad (Sabiha-Javied, 2012) while is many times more than rest of the values reported. The grains of wheat have more Zn^{2+} than the tolerable limit (50µg/g) in plants except WGN (Awashthi, 2000).

3.1.2.3 Concentration Level In Rice Soil

The concentration level of HM ions measured by the FAAS in the samples of soil is given in Table 5. Amongst the soil samples, the sum of the concentration values for the selected HM ions within a sample shows following order: CRS > DRS > SRS > NRS.

Cadmium Ion: The concentration of Cd^{2+} in all soils including the control soil samples is almost same; suggesting that the study soil having enough amount of Cd^{2+} and is not affected by the applied fertilizers. The concentration values are more than the range of reported values (0.12-6.4µg/g) and the recommended values (3-6µg/g) for Cd^{2+} in soils.

Chromium Ion: The average concentration of Cr^{3+} is more than all of the individual sample concentration for Cr^{3+} except NRS. This means that NRS contribute more Pb than rest of the fertilizers in soil. The concentration values for study soils are found to be within the range (2.08-67.96µg/g) of the values reported in literature. The content of Cr is less than the concentration values suggested by INAA analysis of soil (Sabiha-Javied et al., 2012) and other compiled values while are close to that proposed for Malaysia. All samples are safe from Cr^{3+} toxicity on the basis of its tolerable value (150µg/g) suggested for soil.

Copper Ion: The concentration of Cu^{2+} in all soil samples, given in Table 5, possessed variation. The study soils are found to be less polluted for Cu^{2+} from the soils of Iran and Eastern Macedonia while was more polluted than that of Taiwan. All samples are far below the upper tolerable limits (135-270μg/g) suggested for Cu in soil thus are safe from any hazards.

Lead Ion: All the samples show variable amount of Pb. The concentration values for all samples are more than the compiled values for soils. Only the soil of Eastern Macedonia is more polluted than all of the study soils. All the samples were actually safe from the toxicity of Pb^{2+} in terms of the tolerable values (250-500μg/g) suggested for Pb in soils.

Nickel Ion: The concentration of Ni^{2+} in the samples of soil is very close to each other, this means that PFs do not have any effect on the Ni^{2+} fraction of soil in comparison to the control soil. The concentration values are very close to the concentration values proposed for Irani soil while was slightly less than that recorded for Taiwani soil. The concentration of Ni^{2+} in all soil samples is within the recommended limits (75-150μg/g) for Ni^{2+} in soil.

Zinc Ion: The concentration values for Zn^{2+} in all samples are very close to each other. Moreover the Zn^{2+} content of all of the samples is found to be within the worldwide range (21.09-1245μg/g). The concentration value for Zn^{2+} in all soil samples are within the safe limits (300-600μg/g).

3.1.2.4 Concentration level in rice grain

The concentration of Heavy Metal ions measured in the samples of rice grain is presented in Table 5. Amongst the samples of rice, the sum of concentration values for the selected HM ions within all sample shows following order: RDG > RNG > RCG > RSG.

Cadmium Ion: The concentration of Cd^{2+} in all the samples is below the detection limit (0.05μg/g). It means that all samples are safe from the toxicity of Cd^{2+}.

Copper: The concentration of Cu^{2+} is comparable in all samples of grain. All samples are far below the tolerable limits suggested for Cu^{2+} in crops (30μg/g). This means that the grains are not polluted with Cu^{2+} and safe to grow in terms of the tolerable limits for the rice plants.

Chromium Ion: All rice grains have comparable values for Cr^{3+}. It is found to be many times less than the concentration reported in literature and is close to the concentration values proposed for Malaysia. All samples are safe from Cr^{3+} toxicity on the basis of its tolerable value (20μg/g) suggested for grains.

Lead Ion: Pb^{2+} concentration of all samples show small variation. It seems that control grain also show sufficient level of Pb^{2+} in comparison to the fertilized grains. Grain samples have concentration values beyond the tolerable concentration (2.5μg/g) for Pb^{2+} and are many times greater than the values reported in literature. So Pb^{2+} toxicity is seen in the study rice samples.

Nickel Ion: The concentration of Ni^{2+} for all samples is close to each other except RDG. The average concentration of Ni^{2+} is more than all of the individual sample and reported concentrations for Ni^{2+} except of RDG. This means that DAP is the great source of Ni^{2+} contamination in rice grains. All samples have Ni^{2+} beyond the tolerable limits (1.5μg/g) suggested for Ni^{2+} in crops. So it seems that the wheat crops are heavily polluted with Ni^{2+}.

Zinc Ion: Rice grains show variable concentration values for Zn^{2+}. The average concentration of Zn^{2+} is more than all of the reported values. The concentration values for Zn^{2+} in the rice grains are less that the tolerable limit (50μg/g) in plants (Awashthi, 2000).

Table 5 Concentration of Heavy Metal (HM) ions in the samples of present study and available literature (μg/g)

Sample	Cu^{2+}	Cr^{3+}	Cd^{2+}	Ni^{2+}	Pb^{2+}	Zn^{2+}	Reference
Instrument Detection Limit (ppm)	0.11	0.07	0.05	0.29	0.54	0.02	
WHEAT SOIL							
WSS	26.60±1.72	45.49±2.21	6.97±0.50	30.10±2.42	85.15±9.04	67.75±0.26	Present study
WSD	63.57±1.39	18.64±1.22	6.97±0.76	29.19±2.24	40.10±6.93	71.40±0.19	Present study
WSN	25.90±0.22	26.48±1.48	6.96±0.38	32.86±2.45	44.05±17.3	56.72±0.56	Present study
WSC	29.02±2.59	24.89±2.86	6.97±0.54	30.85±2.48	68.81±6.87	49.48±0.33	Present study
Range	25.90-63.6	18.64-45.5	6.96-6.97	29.19-32.9	40.10-85.15	49.48-71.40	Present study
Average	36.30±1.50	28.90±1.94	6.97±0.54	30.75±2.40	59.53±10.03	61.33±0.335	Present study
India	4.00	10.50	1.00	4.80	11.60	19.40	Barman (2000)
Yemen	1.54	n.L	0.25	n.L	0.97	1.76	Matloob (2004)
Eastern Europe	0.10	9.00	0.10	1.10	0.31	0.10	Luksiene (2008)
USA	25	54	n.D	19	19	60	Shacklette (1984)
China	23	61	0.10	27	27	74	Chen (1991)
Haroonabad, Faisalabad	22.8	24.1	0.21	36.2	11.6	44.5	Jeroen (2010)
NIAB, Faisalabad	n.L	64.75	n.L	n.L	n.L	62.37	Sabiha-Javied (2012)
RICE SOIL							
SRS	23.99±3.56	27.64±1.72	6.97±0.81	30.64±3.2	50.39±6.86	60.43±0.49	Present study
DRS	9.74±1.55	29.36±0.44	6.97±0.46	33.26±2.8	91.04±13.64	42.16±0.34	Present study
NRS	14.27±1.20	36.25±3.13	6.96±0.49	29.15±3.3	44.14±12.60	53.14±0.47	Present study
CRS	17.00±4.56	31.07±1.6	6.97±0.49	36.83±3.5	108.21±13.7	49.45±0.63	Present study
Range	9.74-23.99	27.64-36.25	6.96-6.97	29.15-36.8	44.14-108.21	42.16-60.4	Present study

Continued

Average	16.25±2.72	31.08±1.72	6.97±0.56	32.47±3.2	73.44±11.7	51.3±0.48	Present study
Iran	36.09	67.96	0.77	36.92	16.46	217.99	Hani (2011)
Malaysia	n.D	2.08	0.78	n.L	n.D	21.09	Yap (2009)
Taiwan	21.6	42.7	1.87	42.4	39.5	190	Chen (1995)
China	n.L	61.23	0.12	n.L	17.35	n.L	Liu (2007)
Eastern Macedonia	99	n.L	6.4	n.L	983	1245	Rogan (2009)
NIAB. Faisalabad	n.L	67.47	n.L	n.L	n.L	62.36	Sabiha-Javied (2012)
Standards for soil	**135-270**	**150**	**3-6**	**75-150**	**250-500**	**300-600**	**Awashthi (2000), EU (2002)**
WHEAT GRAIN							
WGS	10.75±0.66	1.65±0.07	n.D	12.26±0.72	27.88±3.48	51.87±0.26	Present study
WGD	9.70±2.76	0.99±0.03	n.D	8.34±1.30	25.14±4.40	107.76±0.2	Present study
WGN	3.24±3.23	1.44±0.03	n.D	8.35±1.89	18.18±4.24	47.02±0.56	Present study
WGC	10.74±1.55	1.32±0.07	n.D	9.63±0.67	16.71±4.91	67.54±0.33	Present study
Average	8.61±2.05	1.35±0.05	n.D	9.65±1.14	21.98±4.26	68.55±0.33	Present study
Range	3.24-10.75	0.99-1.65	n.D	8.34-12.26	16.71-27.9	47.0-107.8	Present study
India	5.60	8.00	1.00	4.20	9.20	28.00	Barman (2000)
Yemen	7.70	n.L	0.27	n.L	0.31	14.50	Al-Gahri (2008)
Austria, Eastern Europe	4.70	n.L	n.D	n.L	n.D	11.55	Al-Gahri (2008)
USA	5.24	n.L	0.12	n.L	0.35	17.13	Al-Gahri (2008)
Zhengzhou, China	n.L	0.15	0.02	n.L	1.00	n.L	Liu et (2009)
Haroonabad, Faisalabad	6.5	26.3	0.16	33.8	10.5	28.0	Jeroen (2010)
NIAB, Faisalabad	n.L	0.74	n.L	n.L	n.L	72.69	Sabiha-Javied (2012)

Continued

			RICE GRAINS				
RSG	5.37±3.01	2.09±0.07	n.D	1.75±0.22	16.72±4.92	10.87±0.14	Present study
RDG	3.23±1.10	1.98±0.06	n.D	20.18±2.08	20.94±6.16	25.40±0.38	Present study
RNG	3.23±2.46	0.99±0.11	n.D	1.75±0.84	20.93±6.15	17.20±0.10	Present study
RCG	2.15±1.11	2.09±0.06	n.D	4.38±1.48	15.33±4.51	16.30±0.07	Present study
Average	3.5±1.92	1.8±0.075	n.D	7.01±1.15	18.48±5.43	17.44±0.17	Present study
Range	2.15-5.37	0.99-2.09	n.D	1.75-20.18	15.33-20.94	10.87-25.40	Present study
Iran	n.L	0.31	n.L	n.L	n.L	n.L	Zazouli (2006)
Malaysia	0.31	1.34	0.18	n.L	n.D	0.69	Yap (2009)
Taiwan	2.22	0.1	0.01	0.29	0.01	13.1	Haw-Tarn (2003)
China	n.L	0.25	0.02	n.L	0.34	n.L	Liu (2007)
Eastern Macedonia	5.8	n.L	0.31	n.L	0.5	67	Rogan (2009)
NIAB Faisalabad	n.L	1.87	n.L	n.L	n.L	15.52	Sabiha-Javied (2012)
Standards for plants	**30**	**20**	**1.5**	**1.5**	**2.5**	**50**	**Awashthi (2000)**

R stands for Rice
G stands for Grains
D stands for Di-Ammonium Phosphate
W stands for Wheat
S stands for Single Super Phosphate
C stands for Control
S stands for Soil
N stands for Nitro-Phosphate

3.1.3 Statistical Interpretation Of Data

The relationship between HM ions of soils and grains was checked by different statistical parameters. The mean, minimum and maximum values (range) and Standard Deviations (SDs) are shown in Table 5, along with the concentration values for all elements. Pb^{2+} in the study soils (with average less than Zn) while Zn^{2+} in the grains (with maximum average) show wide range of concentration in both crops. In terms of SDs, Pb^{2+} in all the samples of soils and grains shows maximum values while Zn^{2+} possessed least variation in their concentrations. The intra-metal correlation in Table 6 shows that with the exception of Ni^{2+} in wheat and Cr^{3+} in rice, there are all positive correlations between soil and grains for all of the selected metal ions. These relations are positively significant for Cr^{3+} ($r=0.90$ with probability of 0.0025 in wheat) and Zn^{2+} ($r=0.99$ with $p<0.0001$ in rice) while are negatively significant for Cr^{3+} ($r=-0.92$ with probability of 0.0012 in rice only). The remaining relations are not significant for the rest of the metal ions ($p>0.05$). The positive correlation between soil and grains has been supported previously (Fatoki, & Awofolu, 2003). However, the negative correlation results indicated by Ni^{2+} (in wheat) and Cr^{3+} (in rice), supported the fact that it might be taken directly from atmospheric deposition. The confidence interval (CI) for statistically significant relations of Cr^{3+} is -0.703-0.705 in wheat and -0.985--0.613 in rice while 0.944-0.998 for Zn^{2+} in rice so the results can be generalized to rest of the whole population of wheat crop which was not studied.

The correlation matrix (inter-metal correlation) in Table 7 shows that in wheat crop, both significant negative (Ni^{2+}, Cd^{2+} with $r=-0.97$, $p<0.01$ for soils; and Cr^{3+}, Zn^{2+} with $r=-0.92$, $p<0.01$ for grains) and positive (Cr^{3+}, Pb^{2+} with $r=0.84$, $p<0.01$ for soils and Cr^{3+}, Ni^{2+} with $r=0.75$, $p<0.05$ for grains) correlations are present in the group of soils and grains as well. The Cr^{3+}, Pb^{2+} correlation in soil is found to be in agreement to that proposed by Fernandez (1999). Thus presence of Cr^{3+} greatly reduces the amount of Pb^{2+} sorbed, thereby drastically increasing their mobility and potential for transport to plants. Similarly Cu^{2+}, Ni^{2+} and Cu^{2+}, Pb^{2+} are also positively related as reported in literature which is in contrast to the present correlation factors (Fernandez, 1999). The CI for Ni^{2+}, Cd^{2+}; and Pb^{2+}, Cr^{3+} correlations are 0.84-0.99 and 0.33-0.97 in the soils while for Cr^{3+}, Zn^{2+}; and Cr^{3+}, Ni^{2+} are 0.57-0.98 and 0.097-0.95 in the grains. While in case of rice crop, most of the metal ions have significant positive relationships including Zn^{2+}, Cu^{2+} ($r= 0.92$,

$p<0.05$); Cd^{2+}, Cu^{2+} ($r=0.73$, $p<0.05$); Zn^{2+}, Cd^{2+} ($r=0.80$, $p<0.05$); and Ni^{2+}, Pb^{2+} ($r=0.97$, $p<0.01$) for soils and Ni^{2+}, Zn^{2+} ($r=0.90$, $p<0.01$) for grains. The CI for Zn^{2+}, Cu^{2+}; Cd^{2+}, Cu^{2+}; Zn^{2+}, Cd^{2+}; and Ni^{2+}, Pb^{2+} correlations are 0.613 - 0.985, 0.053 - 0.947, 0.219 - 0.962 and 0.839 - 0.994 in the soils while for Ni^{2+}, Zn^{2+} is 0.534 - 0.981 in grains.

Table 6 Pearson Correlation Coefficient (intra-metal correlation) for the level of Heavy Metal ions in soil and grain samples

Correlation between soils and grains	Correlation Coefficient (r)	
	For Wheat	For Rice
Cu^{2+}	$0.25^{n.s}$	$0.65^{n.s}$
Cr^{3+}	0.90^{a}	-0.92^{b}
Zn^{2+}	$0.48^{n.s}$	0.99^{a*}
Ni^{2+}	$-0.28^{n.s}$	$0.29^{n.s}$
Pb^{2+}	$0.29^{n.s}$	$0.56^{n.s}$

a=significant at 0.01 probability with confidence interval of -0.703-0.705
a*=significant at 0.01 probability with confidence interval of 0.944-0.998
b=significant at 0.01 probability with confidence interval of -0.985--0.613
n.s=not significant relation ($p>0.05$)

Table 7 Pearson Correlation Coefficient Matrix (inter-metal correlation) in soil and grains

	Cu^{2+}	Cr^{3+}	Zn^{2+}	Ni^{2+}	Pb^{2+}	Cd^{2+}
			Wheat Soil			
Cu^{2+}	1					
Cr^{3+}	$-0.61^{n.s}$	1				
Zn^{2+}	$0.63^{n.s}$	$0.18^{n.s}$	1			
Ni^{2+}	$-0.69^{n.s}$	$0.00^{n.s}$	$-0.65^{n.s}$	1		
Pb^{2+}	$-0.59^{n.s}$	0.84^{a}	$-0.11^{n.s}$	$-0.18^{n.s}$	1	
Cd^{2+}	$0.52^{n.s}$	$0.10^{n.s}$	$0.48^{n.s}$	-0.97^{b}	$0.37^{n.s}$	1
			Wheat Grain			
Cu^{2+}	1					
Cr^{3+}	$0.09^{n.s}$	1				
Zn^{2+}	$0.40^{n.s}$	-0.92^{d}	1			
Ni^{2+}	$0.55^{n.s}$	0.75^{c}	$0.44^{n.s}$	1		
Pb^{2+}	$0.43^{n.s}$	$0.11^{n.s}$	$0.25^{n.s}$	$0.55^{n.s}$	1	n.D
			Rice Soil			
Cu^{2+}	1					
Cr^{3+}	$-0.38^{n.s}$	1				
Zn^{2+}	0.92^{e}	$-0.07^{n.s}$	1			
Ni^{2+}	$-0.16^{n.s}$	$-0.33^{n.s}$	$-0.50^{n.s}$	1		
Pb^{2+}	$-0.37^{n.s}$	$-0.30^{n.s}$	$-0.69^{n.s}$	0.97^{e***}	1	
Cd^{2+}	0.73^{e*}	$0.31^{n.s}$	0.80^{e**}	$-0.16^{n.s}$	$-0.38^{n.s}$	1
			Rice Grain			
Cu^{2+}	1					
Cr^{3+}	$0.15^{n.s}$	1				
Zn^{2+}	$-0.53^{n.s}$	$-0.06^{n.s}$	1			
Ni^{2+}	$-0.23^{n.s}$	$0.31^{n.s}$	0.90^{f}	1		
Pb^{2+}	$-0.03^{n.s}$	$-0.64^{n.s}$	$0.65^{n.s}$	$0.48^{n.s}$	1	n.D

a= significant at 0.01 probability with confidence interval of 0.332 - 0.97
b= significant at 0.01 probability with confidence interval of -0.994 - -0.839
c= significant at 0.05 probability with confidence interval of 0.097 - 0.951
d=significant at 0.01 probability with confidence interval of -0.985 - -0.613
e= significant at 0.05 probability with confidence interval of 0.613 - 0.985
e*= significant at 0.05 probability with confidence interval of 0.053 -0.947
e**= significant at 0.05 probability with confidence interval of 0.219 - 0.962
e***= significant at 0.01 probability with confidence interval of 0.839 - 0.994
f= significant at 0.01 probability with confidence interval of 0.534 - 0.981
n.s=not significant relation (p>0.05)

3.2 Pollution Assessment

Application of assessment models show that the study samples are more polluted for some of the selected HM ions while are less polluted for the remaining elements. The discussion is given below;

3.2.1 Contamination Level Of Heavy Metal Ions In Soil

The contamination factor (C_f) for the selected HM ions in wheat soil samples was determined using Eq. (1) and results of the metal ions of concern are given in Table 8. The overall Cf values for all of the selected metal ions in the understudy soil samples shows following order: $Cu^{2+} > Zn^{2+} > Cr^{3+} > Cd^{2+} = Ni^{2+} > Pb^{2+}$. Cu^{2+}, Zn^{2+} and Cr^{3+} are the elements that caused maximum contamination of soil. Ni^{2+} and Cd^{2+} are present at the middle of Cf value chart with same values while Pb^{2+} possesses least Cf values. The analysis of the Cf of the corresponding metal ions separately in all samples shows that Cd^{2+} and Zn^{2+} (with Cf=1-3) fall in the category of moderate contamination. Cr^{3+} (with Cf>1) for WSS and WSN belong to the category of moderate contamination. Cu^{2+} (except in WSD), Pb^{2+} (except in WSS) and Ni^{2+} (except in WSN) for all samples are found in the category of low contamination (with Cf<1) while in moderate group for the remaining soils. In order to determine the Cf for reported concentrations in soils, the typical background concentrations for HM ions of control samples in present study was taken as background value of the controlled samples of soil. The Cf for Pb^{2+}, Cd^{2+} and Cu^{2+} in study samples are more than the soils of most of the countries (Shacklette, 1984; Chen, 1991; Barman, 2000; Matloob, 2004; Luksiene, 2008; Jeroen, 2010), while the Cf values for Cr^{3+}, Zn^{2+} and Ni^{2+} come within the range of Cf values of reported concentrations of corresponding metal ions (Chen, 1991; Jeroen, 2010).

The contamination factor (Cf) for the selected HM ions was determined for rice using Eq. (1) and the results of the metal ions of concern are given in Table 8. The overall Cf values for all of the selected metal ions in the understudy soil samples shows following order: $Zn^{2+} > Cd^{2+} = Cr^{3+} > Cu^{2+} > Ni^{2+} > Pb^{2+}$. Zn^{2+}, Cd^{2+}, and Cr^{3+} are the elements that caused maximum contamination of soil. Cu^{2+} and Ni^{2+} are present at the middle of Cf value chart with same values while Pb^{2+} possesses least Cf values. The analysis of the Cf of the corresponding metal ions separately in all samples shows that Cd^{2+} and Zn^{2+} for all samples (except DRS) fall in the category of moderate contamination with Cf range between1 to 3. Cr^{3+} for NRS and Cu^{2+} for SRS belong to the category of moderate contamination (with Cf>1) while Ni^{2+} and Pb^{2+} cause least contamination with Cf<1. The Cf for almost all of the selected elements (except of Cd^{2+}) in study samples of rice falls within the Cf derived from available literature (Chen, 1995; Rogan, 2009; Hani, 2011).

The degree of Heavy Metal contamination (C_d) as sum of contamination factors (Cf) of all elements for a single place was determined and given in Table 8. Among wheat soils, WSS and WSD are the sample of moderate contamination while WSN and all of the rice soils posses moderate degree of contamination (Table 8).

Table 8 Contamination Factor of Heavy Metal ions for present study and literature

Location	Material	Cu^{2+}	Cr^{3+}	Cd^{2+}	Ni^{2+}	Pb^{2+}	Zn^{2+}	Cd	Reference
WHEAT CROP									
NIAB, Faisalabad	WSS	0.92	1.83	1.00	0.98	1.24	1.37	7.34	Present
NIAB, Faisalabad	WSD	2.19	0.75	1.00	0.95	0.58	1.44	6.91	Present
NIAB, Faisalabad	WSN	0.89	1.06	1.00	1.07	0.64	1.15	5.81	Present
NIAB, Faisalabad	WSC	1	1	1	1	1	1	6	Present
NIAB, Faisalabad	Soil	n.L	2.60	n.L	n.L	n.L	1.26	-	Sabiha-Javied (2012)
Haroonabad, Faisalabad	Soil	0.79	0.97	0.03	1.17	0.17	0.90	-	Jeroen (2010)
India	Soil	0.14	0.42	0.14	0.16	0.17	0.39	-	Barman (2000)
Yemen	Soil	0.05	n.L	0.04	n.L	0.01	0.04	-	Matloob (2004)
Eastern Europe	Soil	0.003	0.36	0.01	0.04	0.005	0.002	-	Luksiene (2008)
USA	Soil	0.86	2.17	n.D	0.62	0.28	1.21	-	Shacklette (1984)
China	Soil	0.79	2.45	0.01	0.88	0.39	1.50	-	Chen (1991)
RICE CROP									
NIAB, Faisalabad	SRS	1.41	0.89	1	0.83	0.47	1.22	5.82	Present
NIAB, Faisalabad	DRS	0.57	0.94	1	0.90	0.84	0.85	5.1	Present
NIAB, Faisalabad	NRS	0.84	1.17	1	0.79	0.41	1.07	5.28	Present
NIAB, Faisalabad	CRS	1	1	1	1	1	1	6	Present
Iran	Soil	2.12	2.19	0.11	1.00	0.15	4.41	-	Hani (2011)
Malaysia	Soil	n.D	0.07	0.11	n.L	n.D	0.43	-	Yap (2009)
Taiwan	Soil	1.27	1.37	0.27	1.15	0.37	3.84	-	Chen (1995)
China	Soil	n.L	1.97	0.02	n.L	0.16	n.L	-	Liu (2007)
Eastern Macedonia	Soil	5.82	n.L	0.92	n.L	9.08	25.18	-	Rogan (2009)
NIAB. Faisalabad	Soil	n.L	2.17	n.L	n.L	n.L	1.26	-	Sabiha-Javied (2012)

R stands for Rice
S stands for Soil
D stands for Di-Ammonium Phosphate
W stands for Wheat
C stands for Control
N stands for Nitro-Phosphate
S stands for Single Super Phosphate

3.2.2 Pollution Index Of Heavy Metal Ions In Soil

The values of Pollution Index (PI) for wheat soils, calculated using Eq. (2), are also given in Table 9. The overall PI values for all of the selected metal ions in the wheat soil samples shows following order: $Cd^{2+} > Ni^{2+} > Cu^{2+} > Pb^{2+} > Zn^{2+} > Cr^{3+}$. Cd^{2+} in the wheat soil samples possesses maximum PI values in comparison to rest of the selected HMs. Cu^{2+} and Ni^{2+} are present at the middle of PI value chart causing medium level of pollution, while Cr^{3+}, Pb^{2+} and Zn^{2+} possess least PI values. The analysis of the PI of the corresponding metal ions separately in all samples showed that almost all of the selected HM ions are less than 1 thus included in the class low level of pollution except Cd^{2+}. The Pollution Index (PI) for Cd^{2+} ranged between 1 and 3, therefore falls in the category of moderate contamination. The PI values for studied samples falls with the range of the PI derived from reported concentration values for almost all elements (Matloob, 2004). The PI for Cd^{2+} and Pb^{2+} in study sample is more that PI for the soil of China and Yemen (Chen, 1991; Matloob; 2004).

The values of Pollution Index (PI) for rice soils, calculated using Eq. (2), are also given in Table 9. The overall PI values for all of the selected metal ions in the rice soil samples shows following order: $Cd^{2+} > Ni^{2+} > Pb^{2+} > Cr^{3+} > Zn^{2+} > Cu^{2+}$. Cd^{2+} in the rice soil samples had maximum PI values. Pb^{2+} and Ni^{2+} are present at the middle of PI value chart causing medium level of pollution, while Cr^{2+}, Cu^{2+} and Zn^{2+} possessed least PI values. The analysis of the PI of the corresponding metal ions separately in all samples showed that almost all of the selected HM ions are less than 1 thus included in the class low level of pollution except Cd^{2+}. The Pollution Index (PI) for Cd^{2+} ranged between 1 and 3, therefore fall in the category of moderate contamination. The PI values of studied samples falls with the range of the PI derived from reported concentration values for almost all elements (Chen, 1995; Rogan, 2009; Hani, 2011; Sabiha-Javied, 2012). The PI for Cd^{2+} in study samples is slightly more than that calculated from the concentration value reported by Rogan (2009).

The Integrated Pollution Index (IPI) as mean of Pollution Indices (PI) of all elements for a single sample of study crops was determined. All of the samples thus categorized to have as low level of pollution as given in Table 9.

Table 9 Pollution Index of Heavy Metal ions for present study and literature

Location	Material	Cu^{2+}	Cr^{3+}	Cd^{2+}	Ni^{2+}	Pb^{2+}	Zn^{2+}	IPI	Reference
				WHEAT CROP					
NIAB, Faisalabad	WSS	0.20	0.30	2.32	0.40	0.34	0.23	0.63	Present
NIAB, Faisalabad	WSD	0.47	0.12	2.32	0.39	0.16	0.24	0.62	Present
NIAB, Faisalabad	WSN	0.19	0.18	2.32	0.44	0.18	0.19	0.58	Present
NIAB, Faisalabad	WSC	0.21	0.17	2.32	0.41	0.28	0.16	0.59	Present
NIAB, Faisalabad	Soil	n.L	0.43	n.L	n.L	n.L	0.21	-	Sabiha-Javied (2012)
Haroonabad, Faisalabad	Soil	0.17	0.16	0.07	0.06	0.05	0.15	-	Jeroen(2010)
India	Soil	0.03	0.07	0.33	n.L	0.05	0.06	-	Barman (2000)
Yemen	Soil	0.47	n.L	0.11	0.015	0.11	0.37	-	Matloob (2004)
Eastern Europe	Soil	0.001	0.06	0.03	0.25	0.001	0.00	-	Luksiene (2008)
USA	Soil	0.19	0.36	n.D	0.36	0.08	0.20	-	Shacklette (1984)
China	Soil	0.17	0.41	0.03	0.48	0.11	0.25	-	Chen (1991)
				RICE CROP					
NIAB, Faisalabad	SRS	0.18	0.18	2.32	0.41	0.20	0.20	0.58	Present
NIAB, Faisalabad	DRS	0.07	0.20	2.32	0.44	0.36	0.14	0.59	Present
NIAB, Faisalabad	NRS	0.11	0.24	2.32	0.39	0.18	0.18	0.57	Present
NIAB, Faisalabad	CRS	0.13	0.21	2.32	0.49	0.43	0.16	0.62	Present
Iran	Soil	0.27	0.45	0.26	0.49	0.07	0.73	-	Hani (2011)
Malaysia	Soil	n.D	0.01	0.26	n.L	n.D	0.07	-	Yap (2009)
Taiwan	Soil	0.160	0.28	0.62	0.56	0.16	0.63	-	Chen (1995)
China	Soil	n.L	0.41	0.04	n.L	0.07	n.L	-	Liu (2007)
Eastern Macedonia	Soil	0.73	n.L	2.13	n.L	3.93	4.15	-	Rogan (2009)
NIAB. Faisalabad	Soil	n.L	0.45	n.L	n.L	n.L	0.21	-	Sabiha-Javied (2012)

R stands for Rice
C stands for Control
D stands for Di-Ammonium Phosphate
W stands for Wheat
S stands for Single Super Phosphate
S stands for Soil
N stands for Nitro-Phosphate

3.2.3 Soil-to-Grain Transfer Of Heavy Metal Ions

The Transfer Factor (TFs) of Heavy Metal ions from soil-to-grain was determined using Eq. (3). The values of TFs in study samples and those reported in literature are given in Table 10. Zn^{2+} and Pb^{2+} show more mobility based on the TFs in study crops in comparison to rest of the selected metal ions. The concentration of Cd^{2+} in the grains is below the detection limit therefore its TFs could not be determined. The uptake of Cd^{2+} by the grain is suppressed in the presence of Zn^{2+} in soil (Hart, Welch, Norvell, & Kochian, 2002; Hassan, Zhang, Wu, Wei, & Chonghua, 2005b). Cu^{2+} and Ni^{2+} are present at the middle of Transfer Factor (TF) values chart. Cr^{3+} rests at the bottom of TF value chart. In present study, Soil-to-Grain Transfer of almost all of the selected metal ions are less for wheat crop as compared to that derived from the reported concentration values. On the other hand TF values for all of the selected metal ions (except of Cr^{3+}) in rice crops are more than that comes from the reported values (Table 10).

Table 10 Soil-to-Grain transfer factor of Heavy Metal ions in the study crops for present study and literature

Location	Material	Cu^{2+}	Cr^{3+}	Cd^{2+}	Ni^{2+}	Pb^{2+}	Zn^{2+}	References (Grains/Soils)
WHEAT CROP								
NIAB, Faisalabad	S-to-G(SSP)	0.40	0.04	n.D	0.41	0.33	0.77	Present
NIAB, Faisalabad	S-to-G(DAP)	0.15	0.05	n.D	0.29	0.63	1.51	Present
NIAB, Faisalabad	S-to-G(NP)	0.13	0.05	n.D	0.25	0.41	0.83	Present
NIAB, Faisalabad	S-to-G(Control)	0.37	0.05	n.D	0.31	0.24	1.36	Present
NIAB, Faisalabad	S-to-G	n.L	0.01	n.L	n.L	n.L	1.17	Sabiha-Javied (2012)
Haroonabad, Faisalabad	S-to-G	0.29	1.09	0.76	0.93	0.91	0.63	Jeroen(2010)
India	S-to-G	1.40	0.76	1.00	0.88	0.79	1.44	Barman (2000)
Yemen	S-to-G	0.12	n.L	0.83	n.L	0.01	0.13	Al-Gahri (2008)/Matloob (2004)
Eastern Europe	S-to-G	47.00	n.L	n.D	n.L	n.D	115.5	Al-Gahri (2008)/Luksiene (2008)
USA	S-to-G	0.21	n.L	n.D	n.L	0.02	0.29	Al-Gahri (2008)/Shacklette (1984)
China	S-to-G	n.L	0.002	0.20	n.L	0.04	n.L	Liu (2009)/Chen, 1991
RICE CROP								
NIAB, Faisalabad	S-to-G(SSP)	0.22	0.08	n.D	0.06	0.33	0.18	Present
NIAB, Faisalabad	S-to-G(DAP)	0.33	0.07	n.D	0.61	0.23	0.60	Present
NIAB, Faisalabad	S-to-G(NP)	0.23	0.03	n.D	0.06	0.47	0.32	Present
NIAB, Faisalabad	S-to-G(Control)	0.13	0.07	n.D	0.12	0.14	0.33	Present
NIAB. Faisalabad	S-to-G	n.L	0.028	n.L	n.L	n.L	0.249	Sabiha-Javied (2012)
Iran	S-to-G	n.L	0.005	n.L	n.L	n.L	n.L	Zazouli (2006/)Hani (2011)
Malaysia	S-to-G	n.L	0.644	0.231	n.L	n.L	0.033	Yap (2009)
Taiwan	S-to-G	0.103	0.002	0.005	0.007	n.L	0.07	Haw-Tarn (2003)/ Chen (1995)
China	S-to-G	n.L	0.004	0.189	n.L	0.020	n.L	Liu (2007)
Eastern Macedonia	S-to-G	0.059	n.L	0.048	n.L	0.001	0.054	Rogan (2009)

R stands for Rice
G stands for Grains
D stands for Di-Ammonium Phosphate
W stands for Wheat
S stands for Single Super Phosphate
C stands for Control
S stands for Soil
N stands for Nitro-Phosphate

3.3 Risks Assessment

The application of risk assessment models show that the study samples have some associated risks that are discussed below;

3.3.1 Ecological Risks

All samples of both crops belong to the class of low Ecological risks (E_r) and Risk Index (RI) given in Table 11. Moreover RI values for all samples are very close to each other. This means that the selected PFs contributed selected HM ions in a proportion that does not pollute soil and unable to cause any ecological risks. The statement is in excellent agreement to the arguments supported by previous researchers (Modaihsh et al., 2001; Lehoczky et al., 2004). The Potential Ecological Risk (E_r^i) for Pb^{2+}, Cd^{2+} and Cu^{2+} in wheat soils are more than the compiled values while the E_r^i values for Cr^{3+} and Zn^{2+} come within the range of the reported E_r^i values of corresponding metal ions. The E_r^i values for almost all of the selected elements (except of Cd^{2+}) in rice soils falls within the range of E_r^i derived from available literature (Table 11).

Table 11 Ecological risks of Heavy Metal ions in soils of wheat and rice for present study and literature

Location	Material	Cu^{2+}	Cr^{3+}	Cd^{2+}	Ni^{2+}	Pb^{2+}	Zn^{2+}	RI	Reference
WHEAT CROP									
NIAB, Faisalabad	WSS	4.6	3.66	30	n.A	6.2	1.37	45.83	Present
NIAB, Faisalabad	WSD	10.95	1.5	30	n.A	2.9	1.44	46.79	Present
NIAB, Faisalabad	WSN	4.45	2.12	30	n.A	3.2	1.15	40.92	Present
NIAB, Faisalabad	WSC	5	2	30	n.A	5	1	43	Present
NIAB, Faisalabad	Soil	n.L	5.20	n.L	n.A	n.L	1.26	-	Sabiha-Javied (2012)
Haroonabad, Faisalabad	Soil	3.93	1.94	0.90	n.A	0.84	0.90	-	Jeroen(2010)
India	Soil	0.69	0.84	4.30	n.A	0.84	0.39	-	Barman (2000)
Yemen	Soil	0.27	n.L	1.08	n.A	0.07	0.04	-	Matloob (2004)
Eastern Europe	Soil	0.02	0.72	0.43	n.A	0.02	0.00	-	Luksiene (2008)
USA	Soil	4.31	4.34	n.D	n.A	1.38	1.21	-	Shacklette (1984)
China	Soil	3.96	4.90	0.43	n.A	1.96	1.50	-	Chen (1991)
RICE CROP									
NIAB, Faisalabad	SRS	7.05	1.78	30	n.A	2.35	1.22	42.4	Present
NIAB, Faisalabad	DRS	2.85	1.88	30	n.A	4.2	0.85	39.78	Present
NIAB, Faisalabad	NRS	4.2	2.34	30	n.A	2.05	1.07	39.66	Present
NIAB, Faisalabad	CRS	5	2	30	n.A	5	1	43	Present
Iran	Soil	10.61	4.37	3.31	n.A	0.76	4.41	-	Hani (2011)
Malaysia	Soil	n.D	0.13	3.36	n.A	n.D	0.43	-	Yap (2009)
Taiwan	Soil	6.35	2.75	8.05	n.A	1.83	3.84	-	Chen (1995)
China	Soil	n.L	3.94	0.52	n.A	0.80	n.L	-	Liu (2007)
Eastern Macedonia	Soil	29.12	n.L	27.55	n.A	45.42	25.18	-	Rogan (2009)
NIAB. Faisalabad	Soil	n.L	4.34	n.L	n.A	n.L	1.26	-	Sabiha-Javied (2012)

R stands for Rice
W stands for Wheat
S stands for Soil
C stands for Control
S stands for Single Super Phosphate
N stands for Nitro-Phosphate
D stands for Di-Ammonium Phosphate

3.3.2 Health Risks

The Health Risks values are shown in Table 12. The WDG are the samples that can cause ingestion of greater amount of HM ions in daily basis via ingestion while the least contaminated among the grains of wheat is WNG. Elemental intake show following order via wheat grains: $Zn^{2+} > Pb^{2+} > Ni^{2+} > Cu^{2+} > Cr^{3+} > Cd^{2+}$. DI for Pb^{2+}, Cu^{2+} and Zn^{2+} is greater for all wheat grains from the values come from literature (Barman, 2000; Al-Gahri, 2008; Liu et al., 2009; Jeroen, 2010; Sabiha-Javied, 2012). The DI for Ni^{2+} and Cr^{3+} are many times less than the DI values come from the reported values for the wheat grains by Jeroen (2010). In case of rice crops, the DI value for some elements (Cu^{2+}, Cr^{3+}, and Pb^{2+}) is found to be comparable among all rice grains while some difference is present for Zn^{2+} and Ni^{2+}. RDG are the samples that can cause ingestion of greater amount of HM ions in daily basis via intake of rice while the least contaminated among the grains of rice is RSG. Elemental intake show following order via rice grains: $Pb^{2+} > Zn^{2+} > Ni^{2+} > Cu^{2+} > Cr^{3+} > Cd^{2+}$. The DI for Cu^{2+} and Zn^{2+} is less than the values given by Rogan (2009) for rice grains while the rest of the elements have more DI values than the previous DI values. This seems that the ingestion of rice grains cause entry of more amounts of Cr^{3+}, Ni^{2+} and Pb^{2+} than the previous values (Table 12).

For assessment of the risks associated with HM ions, the DI values were compared to the references doses for daily intakes (called Hazard Quotients; HQ). The values of HQ show that all samples for the selected elements do not pose any significant risks to the health of consumers except for Pb^{2+} (in both crops) and Ni (in wheat only). The HQ for Cu^{2+} and Pb^{2+} (via wheat grains), and Ni^{2+} and Pb^{2+} (via rice grains) causes greater risks compared to the reported values (Table 13).

No Cd^{2+} was detected in the grains. All the grains thus cause no accumulation of Cd^{2+} in the renal cortex (even less than 50 mg/kg) which otherwise supposed to protect normal function of kidney (Health Canada, 2006). The DI for Cr^{3+} via all grains show that the consumers of both grains will never suffer from reductions in liver and spleen weights (US EPA, 1998). The DI for Cu^{2+} of present study is less than the tolerable intake values. Health Canada however does not give any justification for the derivation of TDI for Cu^{2+}. In case of Pb^{2+}, all the consumers will suffer from the toxicity of Pb^{2+} (as have higher DI values than the recommended TDIs for Pb^{2+}) mainly have considerable effects on the neurobehavioral development of infants and children (Joint FAO/WHO Expert Committee on Food Additives, 2000). The DI values for Zn^{2+} are also less showing that the consumers do not have any effect on the reduction of copper absorption and activity of erythrocyte superoxide dismutase (EVM 2003). The DI of Ni^{2+} is less than No Observable Adverse Effect Level (NOAEL) of 5 mg/kg-bwday, thus the consumers of wheat and rice will never suffer from serious effects of Ni^{2+} toxicity including enlargement of heart and shrinkage of liver.

Table 12 Daily Intake of Heavy Metal ions via wheat and rice for present study and literature

Sample	Cu^{2+}	Cr^{3+}	Cd^{2+}	Ni^{2+}	Pb^{2+}	Zn^{2+}	Reference
WHEAT CROP							
WGS	0.59	0.09	n.D	0.67	1.53	2.84	Present study
WGD	0.53	0.05	n.D	0.46	1.38	5.90	Present study
WGN	0.18	0.08	n.D	0.46	0.99	2.58	Present study
WGC	0.59	0.07	n.D	0.53	0.91	3.70	Present study
India	0.31	0.44	0.05	0.23	0.50	1.53	Barman (2000)
Yemen	0.42	n.L	0.015	n.L	0.017	0.79	Al-Gahri (2008)
Austria, Eastern Europe	0.26	n.L	n.D	n.L	n.D	0.63	Al-Gahri (2008)
USA	0.29	n.L	0.006	n.L	0.02	0.94	Al-Gahri (2008)
Zhengzhou, China	n.L	0.008	0.001	n.L	0.055	n.L	Liu et (2009)
Haroonabad, Faisalabad	0.36	1.44	0.009	1.85	0.57	1.53	Jeroen (2010)
NIAB, Faisalabad	n.L	0.04	n.L	n.L	n.L	3.98	Sabiha-Javied (2012)
RICE CROP							
RSG	0.13	0.05	n.D	0.04	0.39	0.26	Present study
RDG	0.08	0.05	n.D	0.48	0.50	0.60	Present study
RNG	0.08	0.02	n.D	0.04	0.49	0.40	Present study
RCG	0.05	0.05	n.D	0.10	0.36	0.38	Present study
Iran	n.L	0.007	n.L	n.L	n.L	n.L	Zazouli (2006)
Malaysia	0.007	0.032	0.004	n.L	n.D	0.02	Yap (2009)
Taiwan	0.05	0.003	0.0002	0.007	0.0002	0.31	Haw-Tarn (2003)
China	n.L	0.006	0.0005	n.L	0.008	n.L	Liu (2007)
Eastern Macedonia	0.14	n.L	0.007	n.L	0.012	1.60	Rogan (2009)
NIAB. Faisalabad	n.L	0.04	n.L	n.L	n.L	0.37	Sabiha-Javied (2012)

R stands for Rice
W stands for Wheat
C stands for Control
G stands for Grains
S stands for Single Super Phosphate
N stands for Nitro-Phosphate
D stands for Di-Ammonium Phosphate

Table 13 Hazard Quotient of Heavy Metal ions in wheat and rice for present study and literature

Sample	Cu^{2+}	Cr^{3+}	Cd^{2+}	Ni^{2+}	Pb^{2+}	Zn^{2+}	Reference
WHEAT CROP							
WGS	0.47	0.006	n.D	2.69	42.8	0.41	Present study
WGD	0.42	0.004	n.D	1.83	38.6	0.84	Present study
WGN	0.14	0.005	n.D	1.83	27.9	0.37	Present study
WGC	0.47	0.005	n.D	2.11	25.6	0.53	Present study
India	0.24	0.029	5.479	0.92	14.12	0.22	Barman (2000)
Yemen	0.34	n.L	1.48	n.L	0.48	0.11	Al-Gahri (2008)
Austria, Eastern Europe	0.21	n.L	n.D	n.L	n.D	0.09	Al-Gahri (2008)
USA	0.23	n.L	0.66	n.L	0.54	0.13	Al-Gahri (2008)
Zhengzhou, China	n.L	0.001	0.110	n.L	1.53	n.L	Liu et (2009)
Haroonabad, Faisalabad	0.28	0.10	0.88	7.41	16.1	0.22	Jeroen (2010)
NIAB, Faisalabad	n.L	0.003	n.L	n.L	n.L	0.57	Sabiha-Javied (2012)
RICE CROP							
RSG	0.10	0.003	n.D	0.16	11.04	0.04	Present study
RDG	0.06	0.003	n.D	1.90	13.83	0.09	Present study
RNG	0.06	0.002	n.D	0.16	13.82	0.06	Present study
RCG	0.04	0.003	n.D	0.41	10.12	0.05	Present study
Iran	n.L	0.0007	n.L	n.L	n.L	n.L	Zazouli (2006)
Malaysia	0.006	0.003	0.42	n.L	n.D	0.002	Yap (2009)
Taiwan	0.04	0.0002	0.02	0.027	0.007	0.04	Haw-Tarn (2003)
China	n.L	0.0006	0.05	n.L	0.22	n.L	Liu (2007)
Eastern Macedonia	0.11	n.L	0.73	n.L	0.33	0.23	Rogan (2009)
NIAB. Faisalabad	n.L	0.003	n.L	n.L	n.L	0.05	Sabiha-Javied (2012)

R stands for Rice
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CONCLUSION

The present study indicates that application of PFs accumulate HMs in soil that are transferred to grains via plant channels. Physical properties of soil are very important to monitor the Soil-to-Root transfer of HM ions. Under current study conditions, presence of Iron, smaller particle size, loamy texture and less EC values of the study soil enhances availability of the metal ions in soil while absence of the clay minerals and carbonates, less OMC value and alkaline pH serves to decline its availability to the crops. All physical parameters of soil effect differentially in case of different crops under application of different PFs following non-uniform pattern. Different soils of the study crops have variable amount of HM ions. Zn^{2+} and Pb^{2+} have more concentration values than rest of selected elements in soils and grains. In soil, Cd^{2+} is above the recommended limit suggested for soil, so can effect the composition of soils. Zn^{2+} in rice soils while Cu^{2+} in wheat soils is entered via PFs in comparison to the control soils samples of respective crops. The soils of both types of crops show maximum contamination in case of application of SSP with respect to the control crops. Ecologically Cd^{2+} is found to be of greater concern but still unable to cause any environmental hazards. In crops, wheat show toxicity towards Ni^{2+}, Pb^{2+}, and Zn^{2+} while rice for Pb^{2+} and Ni^{2+} only in terms of their PI values. The Soil-to-Grains transfer of metal ions and the daily intakes model shows Pb^{2+} and Zn^{2+} translocation and accumulation in both crops. However Zn^{2+} is not as toxic as Pb^{2+} and thus has no toxicity for human beings. Pb^{2+} in both crops while both Pb^{2+} and Ni^{2+} in wheat only are proven to be hazardous in terms of their reference doses for daily intake.

RECOMMENDATIONS

Adhering to following actions, fertilizer technology can prove to be more effective option in agricultural fields.

- Application of different organic and inorganic amendments including Lime, Gypsum, and Potassium Di-hydrogen Phosphate should practice over agricultural land to reduce soil pH.
- The optimum rate of fertilizer application should be done on crops that do not transfer HMs above the safer limits.
- New options for fertilizer technology especially the application of organic amendments along with inorganic fertilizers should be investigated. This will cause the complexation of HMs, so that crop contamination can be easily avoided.
- The techniques to make fertilizers more eco-friendly should be investigated that involve discovering advance methods of fertilizers application, producing concentrated mixtures and manufacturing fertilizers that is less vulnerable to runoff.
- The manufacturing companies should adopt such methods to remove the HMs at the stage of fertilizer manufacturing.
- Government should emphasize on agro-based education of the farmers in order to make fertilizer technology more effective and to avoid the drawbacks of fertilizer.

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