ANALYSIS OF ORGANIC AND INORGANIC ELEMENTS IN COAL USED IN CEMENT INDUSTRY, BRICK KILNS, THAR MINES AND COMMON MARKET (USED IN HOUSEHOLD) IN PAKISTAN

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A thesis submitted to Bahria University, Islamabad in partial fulfillment of the requirement for the degree of MS in Environmental Sciences

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ABSTRACT

This present study is conducted to analyze the organic and inorganic elements in coal that are being utilized in different sectors in Pakistan. Nine coal samples were collected from four selected locations (industry, local market, mines, and brick kilns) and analysis was carried out using Inductively Coupled Plasma–Atomic Emission Spectrometry (ICP-AES) and Gas Chromatography (GC). The result showed that trace elements Fe, Pb, Hg, Zn, Ni, Cr, soluble sulfates, Cu, Al, Ca, Mg and Na are present in all coal samples, whereas As, Cd and inorganic sulfide concentration is not detected in any sample. Pb and Hg concentration is found high in the coal samples that are being utilized in brick kilns and local markets. The coal used in brick kilns is mainly brought from the Mianwali, Peshawar and Chakwal. The Fecto-cement coal samples (imported coal) showed heavy metal concentration below the detection limits. Further results were compared and interpreted in light of previous studies which also showed that Hg concentration is very high in indigenous coal. Hydrocarbons i.e. benzene, toluene, and m-xylene (BTX) were analyzed and high toluene concentration is found in all coal samples with a minor concentration of m-xylene in the sample collected from the local market, brick kilns and Fecto-cement. The coal mined from Thar and used in brick kiln 3 brought from Dalwal city have the same quality and can be used as a substitute for imported coal.

ACKNOWLEDGEMENTS

ABBREVIATIONS

AAS	Atomic Absorption Spectrometry
Ag	Silver
Al	Aluminium
As	Arsenic
ATSDR	Agency for Toxic Substances and Disease Registry
B	Boron
Ba	Barium
BDL	Below Detection Limit
BEN	Balkan Endemic Nephropathy
Br	Bromine
BTEX	Benzene, Toluene, Ethylbenzene and Xylenes
C	Carbon
Ca	Calcium
CATM	Center for Air Toxic Metals
CCW	Coal Combustion Waste
Cd	Cadmium
Cl	Chlorine
Co	Cobalt
CO	Carbon monoxide
CO_2	Carbon-dioxide
Cr	Chromium
CSIRO	Commonwealth Scientific and Industrial Research Organization
CTB	Coal Trading Blog
Cu	Copper
DWG	Drinking Water Guideline
EERC	Energy and Environmental Research Center
EPA	Environmental Protection Agency
Fe	Iron
GC	Gas Chromatography
Ge	Germanium
H	Hydrogen
HAPs	Hazardous Air Pollutants
Hg	Mercury
IARC	International Agency for Research on Cancer
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
IEA	International Energy Agency
IEEE	Institute of Electrical and Electronics Engineers
K	Potassium
Li	Lithium
Mg	Magnesium
mg/kg	Milligram Per Kilogram
Mn	Manganese
N	Nitrogen

Na	Sodium
ND	Not Detected
NHMRC	National Health and Medical Research Council
Ni	Nickel
NO_x	Nitrogen Oxide
NRC	National Research Council
O	Oxygen
OM	Organic Matter
PAHs	Polycyclic Aromatic Hydrocarbons
Pb	Lead
PEQS	Punjab Environmental Quality Standards
PM	Particulate Matter
S	Sulphur
Sb	Antimony
Se	Selenium
Si	Silicon
SO_2	Sulfur Dioxide
Sr	Strontium
Te	Tellurium
TE	Trace Element
Ti	Titanium
TI	Thallium
TLUD	Top-Lit Up-Draft
US EPA	United States Environmental Protection Agency
US NPDWS	United States National Primary Drinking Water Standards Australian Drinking Water Guideline
V	Vanadium
VOCs	Volatile Organic Compounds
WHO	World Health Organization
XRF	X-ray Fluorescence
Zn	Zinc

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CHAPTER 1
INTRODUCTION

Energy has become an important prerequisite for the economic growth of all countries throughout the world. It is a basic requirement for the industrial, agricultural, and domestic use of the citizens (Chaudhry et al., 2008). Oil is very costly and prices are rising erratically to exceptional height, whereas, natural gas reserves are limited. About half of the thermal power generation is based on imported oil or on natural gas. On the other hand, coal is a major substitute naturally occurring energy source and is abundantly available as fossil fuel throughout the world. The International Energy Agency (IEA) report indicates that the global usage of coal for the power generation is about 42 % (Bada and Potgieter, 2008). Practically 30% share of coal and 3.2 % yearly increase in world energy utilization represents coal importance. Expanding patterns in the world population particularly in developing countries generate various difficulties for governments and policymakers. To deliver various facilities for the bulk of the additional population is putting pressure on natural resources with the passage of time (Ali et al., 2019).

Pakistan has vast coal reserves and ranked 6th in coal-rich countries but the country is currently facing a critical power shortage due to fast emergent population and economy, and severely dependent on thermal power generation. Total out of 17664 MW total power generation capacity, coal-fired power generation is currently only 50 MW. Pakistan has entire coal reserves of 185 billion tons and currently facing a demand and supply gap of electricity about 5000 MW and energy demand may increase in the future. A coal reserve available in Pakistan are mostly Lignite (low-grade coal) and therefore no safe for combustion from an environmental point of view. Beside local coal reserves, Currently, Pakistan is importing coal from other developed countries like South Africa, China, Indonesia and, Australia. A total of 3.5 million tons of coal has been produced in Pakistan and only four to five million tons of coal per year have been imported to meet a need for different sectors like steel, cement, and power generation. In this scenario, the primary solution to resolve the country's energy crises relies on the utilization of coal reserves (Fessett and Durrani, 1994).

At present about 96% of the country's yearly coal production is being utilized in brick kilns, with 185 billion tons of coal reserves, has just 7.89% share in terms of

coal in overall energy consumption, 2% in electric power generation and the rest by small industries, Since most of the brick kilns are situated around the major city settlements, their activity is probably going to enhance the environmental pollution of the cities (Ali et al., 2019). Recently, during coal combustion the topic of trace elements has drawn increasingly more interest from researchers in light of their toxicological and natural impacts. The elements which are occurring in a very low amount (< 100 ppm) is called trace element (TE). Heavy metal is another more common term for these elements with an atomic density greater than 4 g/cm³ which applies to the group of metals and Metalloids. This term was received attention first since at the beginning when the concerned elements were all heavy metals. At this point, some light elements have also been found to have great impacts on nature, for example, B, Be, As (Younas, 1998).

Hydrocarbons like cyclic and polycyclic aromatic hydrocarbons (PAHs) (Naphthalene, biphenyl, acenaphthylene, fluorene, phenanthrene, anthracene, carbazole, fluoranthene, pyrene, and benzo-pyrene) are harmful organic pollutants commonly present in the environment. Many of them have the cancer-causing, teratogenic, and mutagenic impacts which are mostly originated from incomplete combustion of fossil fuels and from the pyrolysis (Furuhata et al., 2012). Aromatic hydrocarbons (ring structure) and PAHs are not certainly degraded via photo-degradation and oxidation/reduction processes or biodegraded by living organisms. On release into air or through seepage, these organic pollutants tend to bio-accumulate or accumulate in the organic matter (OM) of surface soils because of their extremely low solubility in aqueous media (Song et al., 2006; Wang et al., 2013). Levels of PAHs in soils can be considerably correlated with those in the atmosphere due to their potential soil–air exchange (Ruzi ckova, 2007). Therefore, soil levels can be a good indicator of air pollution and of the nearby sources (Motelay, 2004; Simeonov, 2009). BTX is the term used to define a group of chemicals related to benzene and alone found about fourteen percent of the aromatic portion of petroleum hydrocarbons, whereas, about 5% of this (35% of the BTX mixture) is meta-xylene. BTX compounds are part of the group of compounds known as volatile organic compounds (VOCs). This comprises a variety of compounds like toluene (methylbenzene), ethylbenzene, xylenes, and benzene itself. These compounds are specifically noteworthy since they are viewed as destructive to human health (Mackay and Leinonen, 1975).

Toluene is one of the members of the BTX (ortho-, meta-, and para-xylenes) group of pollutants. Toluene is a natural organic solvent generally used in numerous industrial processes (Vander et al., 1988). The odor threshold in water is 0.024–0.17 mg/l whereas the reported taste threshold ranges from 0.04 to 0.12 mg/l (Alexander et al., 1982; US-EPA, 1988; Chang, 1989). It produces psychoactive impact when deliberately breathed in pure form or from various commercial products, for example, gasoline, paints, varnishes, paint thinner, adhesives, and inks (Balster et al., 2009).
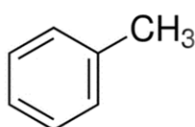
Figure 1.1. Structure of toluene

Benzene is an organic chemical compound with the chemical formula C_6H_6. It is a colorless and highly flammable liquid with a sweet smell and is responsible for the aroma around petrol (gas) stations. It is used primarily as a precursor to the manufacture of chemicals with more complex structures such as ethylbenzene and cumene (iso-propylbenzene) and annually billions of chemicals are produced. In gasoline, the benzene itself has been limited to less than 1% because it is a known human carcinogen. Therefore due to this reason, most non-industrial applications have been limited the usage of benzene (Campo et al.1997). The benzene has a high octane number, aromatic derivatives like toluene and xylene typically comprise up to 25% of gasoline (petrol).
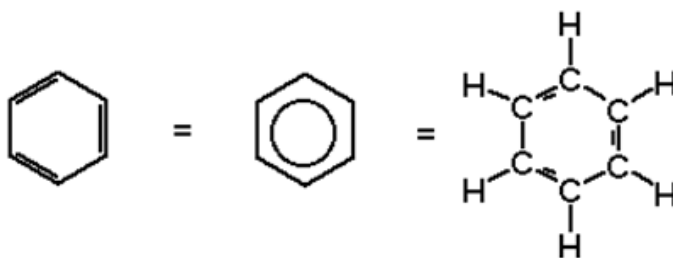
Figure 1.2. Structure of benzene

M-xylene is a colorless liquid and is used as a solvent, as a main essential of paints, enamels and rubber cement. It is additionally used in the making of dyes, insecticides, and pharmaceuticals. M-xylene is classified as a hazardous substance by US-EPA (Bennett, 1985).
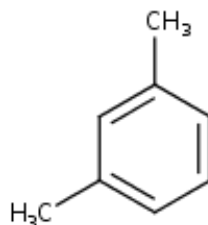
Figure 1.3. Structure of m-xylene

Researches showed those labors who were exposed to the mixtures of hydrocarbons and other compounds had more chances to prone skin, lung, bladder, and abdominal cancers. Reproductive and developmental changes are seen in animals from hydrocarbons exposure, these impact have usually not been seen in humans (Chang, 1989).

1.1 Coal

Coal is a major alternative naturally occurring energy source and is abundantly available as fossil fuel throughout the world. Coal is a black or brown solid combustible substance used as fuel from centuries which is formed under the earth's crust from the decay of plant material (Damste et al., 1992) due to the very high pressure and temperature and due to the absorption of moisture from the soil. It is a heterogeneous substance comprises of organic and inorganic mineral components (Ali et al., 2019). The organic components of coal determine its rank, and the appropriateness for its use as renewable energy (Saeed et al., 2010). The inorganic mineral elements present in coal acts as catalysts during the coal conversion process such as liquefaction, gasification and pyrolysis (Tian et al., 2002).

1.2 Geological information

Depositional environments, the interaction between the organic matter and basinal fluids, sediment diagenesis and sedimentary volcanic participations are geological factors that are the main determinant of the concentration, and modes of occurrence of trace elements in coal (Dai et al., 2011; Singh, 1991). In this manner, the study of trace elements in coals provides geologic information about depositional conditions, coal-bearing sequence formation, and regional tectonic just as distinguishing proof and connection of coal in various basined regions.

1.3   Coal harmful effect on environment and human health

Thermal power plants release many trace elements into the atmosphere and also contaminate soil and through leachate it also contaminate the groundwater quality. The waste which is generated after the burning of coal i.e. fly ash, bottom ash, waste of flue gas desulfurization, and molten coal ash at the bottom of the boiler (known as Boiler slag) is called Coal Combustion Waste (CCW). Due to leachate wastewater enters into freshwater resources therefore the management and disposal of coal combustion waste (CCW) is always very important. In a few countries, CCW is disposed of either by the landfill or into the artificial ponds known as surface impoundment where waste is mixed with water. During rainfall, toxic elements present in this waste start to dissolve into water and later contaminated water is known as leachate. Sometimes sludge can be formed in this way which can then easily be transported through a pipeline to the dumping site from the coal power plant. For landfill activity, almost a hundred acres may be required for a single mega coal power plant to dispose of its waste, which results in damage to green areas (Shen et al., 2010).

The waste which is generated by power plants is 100 percent toxic as compared to other industries that waste may not be completely toxic (Macknick et al., 2012). Therefore our ecosystems existing in rivers, seas, ponds are damaged and the fish we eat could also get poisoned. Further, water supplies are under the risk of contamination which could be a threatening factor for the people whose living is dependent on these water systems. Furthermore, coal ashes analysis will provide a scientific foundation for their widespread utilization and for reducing environmental pollution (Macknick et al., 2012).

Due to the release of heavy metals like arsenic and selenium during the burning of coal is causing severe health problems in Asia. Especially in developing countries, where health problems are severe due to the extensive use of coal in homes for heating and cooking purposes. Arsenism and fluorosis are diseases that are found in the people living in nearby areas (Finkelman, 1999). The brick furnaces owners and brick makers that burn the coals without knowing their qualities, as a result of putting the public in great trouble. Residences in nearby of that furnaces, for being effected from coal dust as well as from the harmful health hazard. Further, by natural and Anthropogenic sources these trace elements are being incorporated in the surrounding medium (Andriono, 2013).

The fly ash mineralogy refers to both amorphous and crystalline phases and other mineral parts in the fly ash debris. During ignition, the minerals in coal can change into fluid form (totally melted) or unstable and may oxidize or undergo other gas-phase reactions (Kim et al., 2004). Despite the fact that coal is considered to have more environmental impacts than any other energy source, the overall shortage of some profitable components has incited numerous organizations to search for new mineral sources. A few organizations are now investigating strategies to extract rare metals from coal ash and investigating whether coal ash processing can serve as an economical and environmentally friendly substitute to conventional mining (Mayfield and Lewis, 2013). Fly ash and bottom ash can be utilized in various industrial applications to limit ecological effects i.e. ion-exchange (in industrial wastewater and soil contamination), separation, removal of gases and solvents (Depoi et al., 2008).

Harmful gases are emitted from the brick kiln during the burning of coal. When inhaled by humans, these causes heart disease, brain damage and various lung diseases such as lung cancer, chronic bronchitis, asthma, cough etc. Other health issues which are caused by the emission of harmful gases are irritation of eyes, nose, and throat (Skinder et al., 2014a, 2014b).

Ozbayoglu in 2012 conducted a study and concluded that the amount of trace elements emission from coal combustion is dependent on the modes of occurrence in the coal. Elements attached typically with the coal organic and sulfide fractions and to tend to vaporize or adsorb on the fine particles when the flue gas temperature drops. On the other hand, elements combined mainly with the other minerals remain in the ash. The researcher suggested that one possibility for controlling the release and dissemination of these trace elements is to remove them earlier to combustion. Coal cleaning is an economical and effective technique in reducing the damaging effect of trace elements on the environment. Similarly, as per research conducted by Zevenhoven and Kilpinen (2001) washing the coal is an extensively used method to reduce trace element emission.

The role of the trace metals is dependent upon the coal types (Sekine et al., 2008; Iwashita et al., 2004) and its burning parameters. Elevated combustion temperature and reducing atmosphere increases the release of more trace elements (Guo et al., 2004). A lot of researches is carried out on the elemental composition of Thar

coal, as people are not motivated to use Pakistani coal for power production because it has a high concentration of ash and on burning the release of lethal chemicals and hazardous gases. Various toxic chemicals like Al, Ca, B, As, Mn, Cr and Pb are present in Coal Combustion Waste and are damaging to the brain, kidneys, also causes cancer and listening problems in children. Pakistan has severe climatic conditions, and also suffering global warming like other countries of the world. Due to air pollution or contaminated water, many people are suffering from various kinds of incurable diseases (Haneef and Akintug, 2016).

Lately, according to World Bank report (Cleaning Pakistan's Air, 2014), Pakistan was ranked third in the world with 110,000 deaths per year mainly due to air pollution alone and different studies in this regard showed that source of air pollution in the country is mainly due to utilization of coal in power sector (Van der Wall, 2015; Yousuf et al., 2014).

1.4   Literature review

Finkelman et al. (2002) conducted a study on coal where analysts found that coal was just a prevailing energy source in developed and developing country and still it was a requirement for countries till mid of the 21st century. In this exploration, principle issues related to coal was addressed to how waste items were created during activities like before mining, during mining, away, during ignition, and post burning. Further, three research programs were developed to explain this collaboration of trace elements with human health problems that were potentially caused by coal. In China, people's health was affected by domestic use of coal because it contains arsenic, fluorine, selenium, and possibly, mercury, etc. and was causing a kidney disease called Balkan endemic nephropathy (BEN), due to proximity of Pliocene lignite deposits but the origin was unknown. The hypothesis in this research was the percolation of organic leachate into groundwater where they were passed through the lignite, and that these organics were then ingested by the local population contributing to this health problem. During the mining process, there was release of particulate matter and then inhaled by people who were exposed to them. The disease was called coal worker's black lung disease that was mostly because of coal residue and lungs were affected in this ailment.

Bergh et al. (2011) reported that South Africa is the fifth predominant producer and 4th biggest exporter of coal within the world. It is also a primary provider of coal to

the European Union. It has the most important coal reserves in Africa at approximately 75% of Africa's total coal reserves, mining between 245 Mt to 250 Mt of coal consistent with year and exporting around 71.4 Mt which was about a 3rd of the whole annual manufacturing (Wagner et al., 2005) and 6th globally in economically recoverable coal reserves (34,224 Mt) and 5th inside the international in annual manufacturing. South Africa has ample coal reserves that are consumed in producing electricity, chemical production and during the combustion process about 40 Mt of coal fly ash is generated annually (Bada and Potgieter, 2008). Almost 70% of coal reserves the South Africa are found in the Waterberg, Witbank, and Highveld coalfields, as well as minor reserves, are found in the Ermelo, Free State and Springbok Flats coalfields (Jeffrey, 2005). These coals are generally contained a low concentration of S, N and P, and on account of the initial two, the substance is subject to maceral synthesis and rank (Snyman et al., 1993).

A study conducted by Xu and others (2003) on elements present in coal were prescribed into three groups: Major components: C, H, O, N, S. These components were occurred at greater than 1000 ppm; Minor elements were included coal mineral matter i.e. Si, Al, Ca, Mg, K, Na, Fe, Mn, Ti and F, Cl, Br and I. These were present in concentrations between 100 to 1000 ppm; and Trace elements which were the constituents with concentrations below 100 ppm (US-EPA, 1998).

Xavier and others (1994) were conducted a study to investigate the trace elements such as Cd, As, Co, Cr, Cu, Hg, Mn, Ni, Pb and Zn in a subbituminous coal and behavior of elements during combustion (organic and/or inorganic affinities) and in the combustion wastes (partition and volatility). All collected samples were fractionated by density and magnetic separations and cascade impactors. The techniques were used in this research were X-ray diffraction, ICP-MS, ICP-AES, AAS and ICP-AES with hydride generation. Anhydrite ($CaSO_4$,) was used as a high sorption capacity and important in the sorption of trace elements like As, B, Ge, Se, Pb, Mo, Zn and Ti from flue gas. This sorption phenomenon and the condensation, mainly as fine fly ash particles, of important fractions of the trace elements during the cooling of flue gas, significantly reduced the gaseous emissions of potentially toxic trace elements from coal combustion in the power station studied.

Research on the different aspects of coal quality, such as proximate, ultimate, calorific value and trace element concentration and its effects on human health was conducted in 2015 by Cheepurupalli and others. The study showed that trace elements are presented in coal in a very low percentage and through the production and consumption process these are released from coal. The release of TE is dependent on the mode of occurrence in coal and to investigate this hypothesis. Many samples were collected from different locations of Thar coalfield by applying the channel sample method. To find out the result statistical analysis of trace elements was computed such as moderate moisture content (2.9% to 7.6%, average 5.04%), volatile matter (19% to 24%, average 21.57%), fixed carbon content (16.6% to 27.5%, average 21.3%) and ash content (42.7% to 61.5%, average 51.86%). Further result values were compared with World and USA values for trace elements that showed concentrations of trace elements were very high in all samples. Further, the matrix association coefficient of ash indicated the inorganic association of iron and sodium. Therefore, the occurrence of trace elements can give a better awareness of coal quality which further might help to lessen some health issues caused by the trace elements.

A study was conducted by Khan and Bibi in 2016 to analyze trace elements present in coal samples collected from the Thar coalfield. For this study, four lignite coal samples were collected and analyzed by using technique X-ray Fluorescence (XRF) Spectrometer. It was concluded that trace elements like Al, As, Ba, Br, Ca, Ce, Co, Cr, Cs, Cu, Fe, Ga, La, Mn, Mo, Nb, Nd, Ni, Pb, Rb, Sb, Sc, Se, Si, Sn, Sr and Sm elements were present in all coal samples and had an adverse effect on the health of the living organisms intact with coal utilization. Some of these elements such as Ba, As, Br, Cr, Co, Cu, Pb, Mo, Ni, Se, U, V, and Z were exceptionally harmful to human health. Further, coal samples were washed with a standard solution of 2N HCl to demineralize. Then samples were run through the XRF spectrometer for elemental analysis. Then the comparison of elements present in raw samples was compared with the elements present in the respective demineralized samples. It was concluded from the result that demineralization caused a better effect, in terms of metals removal from coal.

Medunic et al. (2018) conducted a study on fossil fuels, particularly on coal because it was a cheap energy source throughout the world and released environmental contaminants, like CO_2, SO_2, and a range of organic and inorganic compounds during

combustion. However, and despite the fact that these emissions had caused air pollution and regional acid rain problems, there had been no evidence that their use was completely low CO_2 Energy source. The purpose of this research was to focus on the latest advances in coal research by leading international scientists from India, China, and the United States. This article briefly presents selected articles from several research groups in India and Croatia that address environmental issues and emerging wastewater treatment technologies.

The research was conducted on trace elements presence in coals of the Republic of Macedonia, Balkan Peninsula in Southeast Europe by Panov et al. (2012) in which the ICP-AES technique was used to determine the trace element concentrations. Proximate analysis was applied to interpret the final results. A total of five samples were collected in this research from different locations and were analyzed for trace elements like Ba, Cr, Pb, Zn, Cu, Ni, Mo, V, Se, Ag and Co. The outcome was drawn for trace elements showed that the content was in a range about Ba (83-298), Cr (12-29), Zn (8-89), Cu (4.4-27), Pb (1.8-8.7), Ni (7.8-17.5), Co (1.9-9.7), Mo (0.42.8), V (14-57), As (6.5-26), Se (1.7-7.0). Further, the range was contrasted with the scope of world-class coals which demonstrated that the range of all elements in these coals was inside the scope of the world-class coals. In this manner, the results had not shown any potential for environmental or human health as well as concern with financial considerations.

Chattopadhyay and others (1997) conducted a study on Benzene, toluene, and xylene in the air of Calcutta, India. The study was conducted in winter to monitor the air quality through the year 1992-1994. Sampling was done through activated carbon traps and packed column chromatography technique was used to analyze the samples which were collected from five locations within the same city. The element concentration was found to be very high in years when it was compared with the results of other studies conducted for the same area in previous years whereas average benzene concentrations during the winter in 1992, 1993 and 1994 were 1004 μgm^3, 7082 μgm^3 and 491 μgm^3 respectively. The average compositional ratios of benzene: toluene: xylene (B: T: X) in winter were 1:0.39:0.05, 1:0.16:0.04 and 1:0.26:0.13 for 1992, 1993 and 1994 respectively. The toluene/benzene concentration ratio in the samples varied from 1.033 at the end of summer to 0.092 at the end of winter. This variation had been attributed to changes in the environmental stability of the released compounds due to

thermal inversion. It is estimated that in Calcutta, 5280 coal-burning stoves are used for cooking per square kilometer. The median number of benzene, toluene, and xylene in the smoke plume found on the coal-burning stove used for cooking was 5497 μgm^3, 4080 μgm^3, and 962 μgm^3, respectively. The composition ratio of B: T: X for coal-fired cooking stoves was therefore 1: 0.74: 0.18. Different types of vehicle-driven automobile routes were also analyzed for BTX. This study showed that the main sources of this high concentration of benzene were the automobile exhaust and a large number of coal burning stoves. The Thermal Reversal was responsible for the extremely high ambient concentration incidents of BTX in Calcutta. The climate change in the toluene/benzene ratio in Calcutta resulted in a permanent change of caste environment due to thermal inversion.

1.5   Significance of study

In Pakistan, the expending environmental pollution and its possible control has consideration during the most recent decade (Ghaffar, 1995). In spite of the fact that at present, due depletion of the oil and gas reserves, coal reserves are in extensive use as a fuel in thermal power generation, cement industries, in brick kilns, and as a chemical feed stock for various industries such as fertilizers and metallurgical activities in this manner now-a-days coal is not considered as favorite source mostly due to its moderately high contamination and pollution potentialities (Ali et al., 2019). Moreover, practically 20% of the outside trade was spent on the import of non-renewable energy sources. Roughly 7 US$ billion on imports of regular conventional energy resources were spent equal to 40% of total imports by Pakistan. Careful estimates show that by 2050 Pakistan energy needs rely upon to expand multiple times while, the supplies are not very inspiring (Asif, 2009).

Combustion processes are viewed as the most significant sources of heavy metals mainly power generation, smelting, incineration, and the internal combustion engine. So the primary reason for this investigation is to examine the organic and inorganic elements mainly the presence of heavy metals in coal and release during coal combustion. Further, in this investigation, the term trace element is preferred to represent all considered low-content elements to avoid possible confusion (Younas, 1998).

In Pakistan, practically 8.0 million tons of coal is being imported by cement companies every year. Where 60% coal from South Africa, 33% coal from Indonesia,

and 7% coal from Australia, while 12 million tons were imported by power plants including Sahiwal Power Plant and Port Qasim power plants. Pakistan likes to purchase higher-quality coal from South Africa and Indonesia to boost the energy value of each tons imported as Pakistan's coal is considered as low-quality coal (Mirza, 2019). In different industries it is a normal practice that this implies lower-quality Pakistani coal is principally utilized as mixing with higher quality coal to get best outcomes (Mirza, 2019).The other reason for this investigation was likewise contrasting the indigenous coal and imported coal to control the economy of Pakistan and distinguish which coal type is appropriate as an option of imported coal.

Unfortunately, due to the lack of resources and other issues, continuous monitoring regarding coal utilization is not carried out properly. It is very important to monitor the track of pattern about our air, water, and soil quality nearby areas where coal is being utilized for energy purposes or abundance of coal reserves are present. Therefore, there is a need for quality monitoring, so that accordingly policies and strategies can be formulated. Keeping in view this need present study is planned with the below-mentioned objectives.

1.6   Objectives of the study

The main objectives of the present study are:

1. to analyze the concentration of inorganic elements contents in coal used in industries, brick kiln, Thar mines and common household
2. to measure hydrocarbons (benzene, toluene, and xylene) concentration in coal
3. to compare international coal quality with indigenous coal

CHAPTER 2
METHODOLOGY

2.1   Study area

The total of four (04) areas were chosen for this study and nine (09) coal samples were collected for analysis i.e. cement industries, Thar coal, brick kilns, and local market. Two coal samples were collected from the Fecto-cement industry, which is located at Sangjani, close to Islamabad. The Fecto-cement industry is ISO 9001:2000 guaranteed and it is Pakistan's first anti-pollution cement manufacturing plant and furthermore the first of its sort in South Asia. Currently, around 90 % of the Fecto-cement industry's coal need is met through imports from other countries, i.e. Indonesia and South Africa, with the present volume being more than 3,000,000 tons for every year. It is the only industry in Pakistan which is utilizing coal as an energy source (Khan and Bibi, 2016). Five coal samples collected from five (05) different Brick kilns which are situated in the same area at Choa Saidan Shah, union council of Chakwal District in the Punjab province. All brick kilns are using coal which is brought from different cities like Mianwali, Peshawar, Khushab, Dalwal, Quetta and Chakwal cities. One sample was collected from the coal mine of Thar, Sindh. The Thar coalfield is situated in the Thar Desert, Tharparkar District of Sindh province in Pakistan and having huge lignite coal resources (Saeed et al., 2010). One sample is collected from a local shop from the market situated at Khanna Pul, Islamabad where coal is mostly used for household purposes. Figure 2.2 below demonstrates the sampling points for the collection of coal samples that were selected for the study area. The study area includes Fecto-cement industries, Islamabad, Thar-Sindh, Brick Kilns at Choa Saidan Shah, Chakwal district and local market at Khana pul, Islamabad Capital Territory.
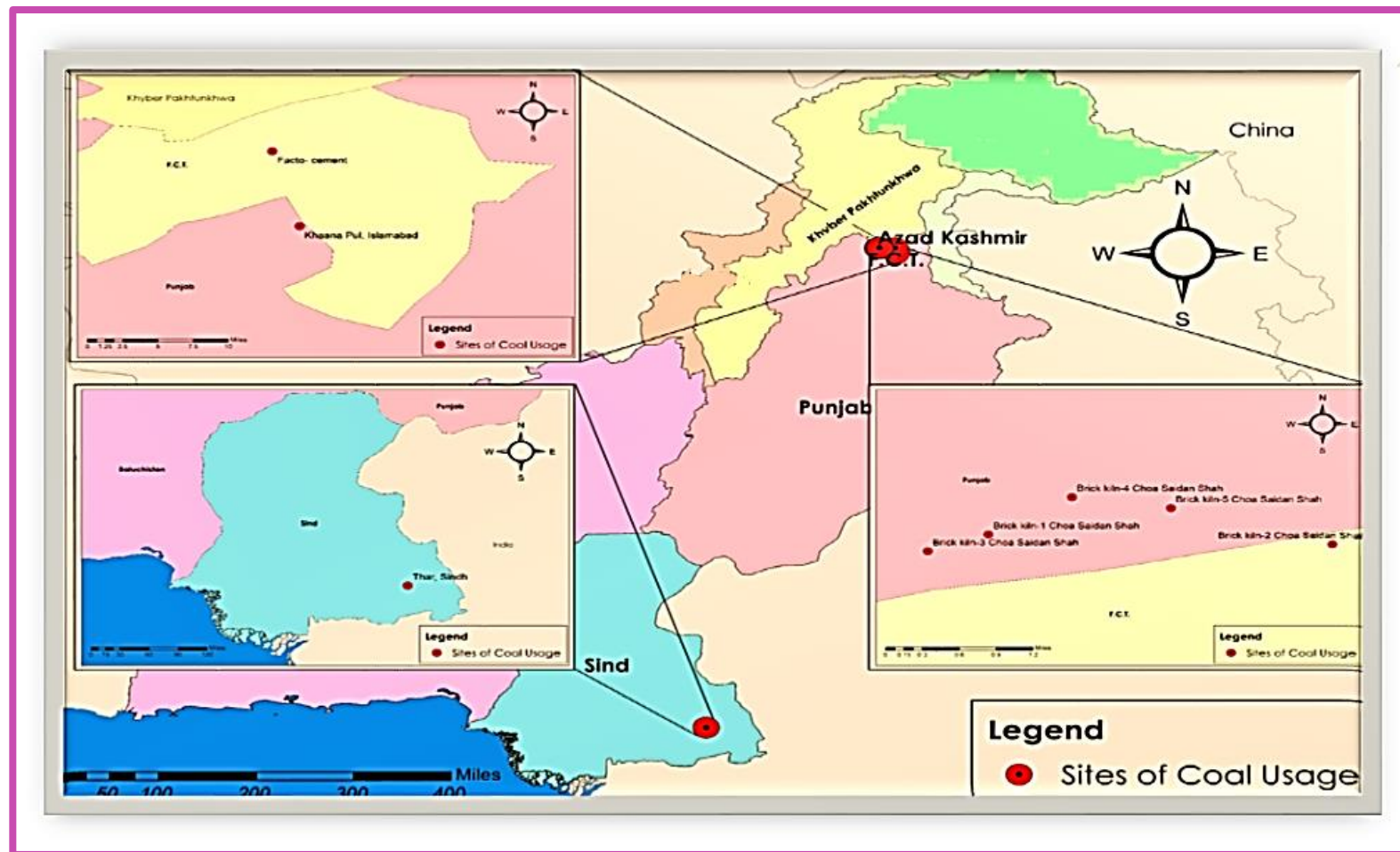
Figure 2.1. Study area map

2.2   Sampling sites

Four specimen sites were selected, one location in Punjab province, two locations in the territory of Islamabad and one location in Sindh. Sampling location detail is given in Table 2.2. A total of nine samples were collected from selected four locations. The coal samples in solid form were collected physically and packed in polythene bags and further brought to the lab for further analysis of organic and inorganic elements.

Table 2.2. Sampling sites description for coal collection.

Sampling locations description			
Site No.	Locations	GPS Coordinates	
01	Facto- cement industry Islamabad	N $33^0$72.148	E $73^0$04.329
02	Five brick kilns (Choa Saidan Shah)	N $33^0$71.887	E $72^0$79.691
03	Sindh (Thar Area)	N 24^0 87.767	E $70^0$24.08
04	Khanna Pul, Islamabad	N $33^0$62.605	E $73^0$07.14

2.3   Methodology

The following chart shows the complete methodology opted for the study.

Figure 2.3. Methodology flow chart

2.4 Instrumentation

2.4.1 Inductively coupled plasma spectroscopy

It is a technique for doing multi-component flame emission spectroscopy (FES) however under predominant condition. An electrically-conducting gas is a plasma that contains electrons and ions besides neutral atoms and molecules. Very hot flames, electric releases and radiofrequency releases can create plasmas. ICP usually uses a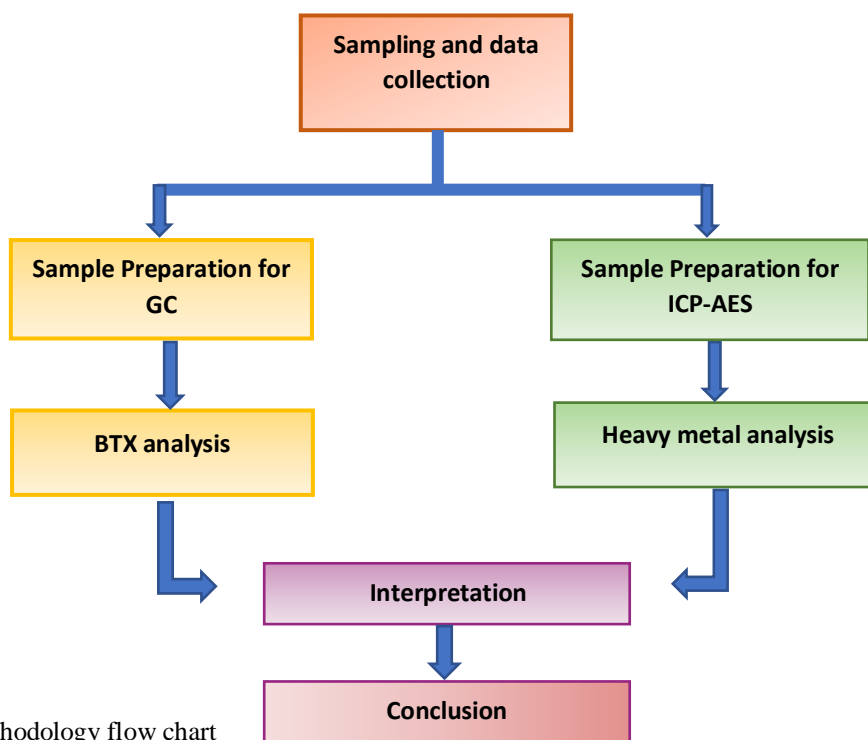rgon particle plasma which is ignited by radiofrequency liberation. It contains argon in gas form or argon radical and electron. It is an extremely spotless fire that has little background release. The flame itself cause some discharge. Correct for background utilizing double-channel recognition measure discharge power at the outflow wavelength of the analyte and again a few nm away (Greenfield, 1994).

2.4.2 Gas chromatography

Gas Chromatography is a chromatographic technique or a system where the mobile phase is a gas. GC is one of the most well-known technique for isolating and examining compounds. The main factors that increase its efficiency are high resolution, low limits of detection, speed, precision, and reproducibility. GC can be applied to the separation of any compound that is either naturally unstable (i.e., freely goes into the gas phase) or can be transformed into an unstable derivative. This makes GC useful in the parting of a number of small organic and inorganic compounds (Grob et al., 2004).

2.5 Sample preparation/analysis for coal

2.5.1 Sample preparation

The local coal samples and imported samples were obtained from industry, Thar, brick kiln and local market ground to a fine powder and the portion which passed through a 100 mesh sieve was retained for analysis. The coal powder was homogenized manually. The Eastern Coal, a standard reference material SRM-1632-a was obtained from the National Bureau of Standards, USA. The samples were dried in an oven at 105°C for 4 hours to remove moisture.

2.5.2 Ashing

Accurately weighed amounts of coal samples were taken in a pre-cleaned silica crucible and heated in an electric furnace in successive steps at temperatures of 110, 300, 400, 550 and 750°C in conformity with the ASTM D6357-11 methods. The residue

left after the last heating step was retained and used as the coal ash sample. Weights were taken and ash produced were as below (Wiersma et al., 1986).

Table 2.5.2: Ashing procedure of coal samples

Site No.	Sample	Weight Taken (g)	Ash Produced (g)	Ash Produced (%)
1	Local market	2.988	0.354	10.5
2	Fecto cement 1	3.427	0.431	14.4
3	Fecto cement 2	3.090	0.381	12.1
4	Thar	4.017	1.281	31.9
5	Brick kiln 1	2.874	0.339	9.9
6	Brick kiln 2	3.104	0.390	12.4
7	Brick kiln 3	3.388	0.418	13.8
8	Brick kiln 4	3.701	0.459	15.5
9	Brick kiln 5	2.912	0.349	10.3

Two samples must be kept for a further time at 500ºC till no noticeable proof of carbonaceous material.

2.5.3 Digestion of coal

Digestion was done according to US-EPA 2007 for solid samples to test by Inductively Coupled Plasma – Atomic Emission Spectrometry (ICP-AES) as follows.

Quantitatively transferred the sample (ash) to a measuring glass (beaker) and added 4ml (1+1) HNO_3 and 10 ml (1+4) HCl. secured the lid of the beaker with a watch glass and placed the beaker on a hot plate. The heat was adjusted to keep up the reflux temperature to 95ºC. Continued with reflux for 30 minutes. Permitted to cool and quantitatively transferred to a100 mL volumetric flask. Diluted with deionized water to volume and mixed carefully. Allowed the samples to stand overnight to get clear supernatant. Centrifuged the samples with suspended solids. Still, unclear samples were filtered (Wiersma et al., 1986).

2.5.4 Analysis

After the initial equipment startup, calibration curve was readied utilizing multi-element standard solution at three levels in the same acid matrix as samples. The prepared samples were analyzed by inductively coupled plasma-atomic emission spectroscopy. Elements for which results were beyond quantifying range were diluted with the same acid strength deionized water. ICP-AES revealed results in mg/L which were calculated and provided details regarding, "As is Basis" (crude Coal Basis) taking into account dilution, amounts of samples taken and volume of digested solutions (Chen and Chen, 2011).

2.5.5 GC with FID detector

A HP 6890A gas chromatograph is utilized with FID (Flame Ionization Detector), Agilent 6890 PLUS Software, which has an HP-INNOWAX column; 30 m x 0.5 mm and ID 0.25 um. Also, an analytical scale with 0.0001 g precision and a Vortex mixer were utilized (Chen and Chen, 2011).

2.5.5.1 Selection of extraction solvent

Extracting analyses of concentration from the adsorbing material requires a solvent limit of extracting investigations from the matrix and making them soluble as indicated by solubility and polarity of compounds.

The experiment was made with acetone, methanol, and carbon disulfide. Refinement of extraction solvent among the solvents utilized (acetone, methanol, and carbon disulfide), that are important for separating benzene, toluene, ethylbenzene and xylene's compounds of activated charcoal, it was decided to utilize the carbon disulfide (CS_2), regardless of activated charcoal (Chen and Chen, 2011).

2.5.5.2 Preparation of standard solutions

From benzene, toluene, ethylbenzene and xylene certified standard of 2000 µg/mL, preparation of work standard solutions was made at known concentrations of carbon disulfide and the internal standard was added. The internal standard work solution (Fluorobenzene) is prepared in acetone from its certified standard of reference. At that time, each BTEX standard and the sample extract are added with a similar amount, so that it keeps a constant concentration in all solutions. Standards are stored in amber glass vessels and retained under refrigeration and the individual injections of each analysis (BTEX). During the specificity tests, a blank extracted from the sample

(activated charcoal) is injected with the purpose of checking that there is no interfering or that another compound does not co-elute with the examines of interest (Chen and Chen, 2011).

2. 5.5.3 Extraction and chromatographic analysis

The extraction and analysis process are performed as follows:

The adsorbing material (activated charcoal sample) is taken to a 4.0 mL vial and is then added with 3.0 mL of purified CS_2 and a volumetric amount of fluorobenzene standard (internal standard) of known concentration. In the present study, five VOCs were checked by utilizing the Synaptic Spectra's gas chromatography. This instrument is generally used to screen BTEX and has been approved as per 138 Service specifications EN 14662-3. The samples were drawn in through the inlet feeder operated flow rate of 5 ml/min connected at the back of the instrument (Chen and Chen, 2011).

CHAPTER 3
RESULTS AND DISCUSSION

3.1   Inorganic /trace elements

Figure 3.1 showed that Fe concentration ranged 1000-29600 mg/kg with an average value of 6446 mg/kg. Further, the result showed that high Fe concentration is found in the coal which is collected from brick kiln 3 with a concentration of 29600 mg/kg. The coal is purchased from the Khushab city near to Chakwal region, whereas, coal is also bought from other cities like Quetta and Chakwal. The coal purchased from Quetta is considered the best coal in Pakistan because of its better quality and astounding spark. It is a common practice in brick kilns that coal of the best quality is blended with other coals to improve overall quality and productivity. Thar coal has Fe concentration of 10500 mg/kg among other coals samples.
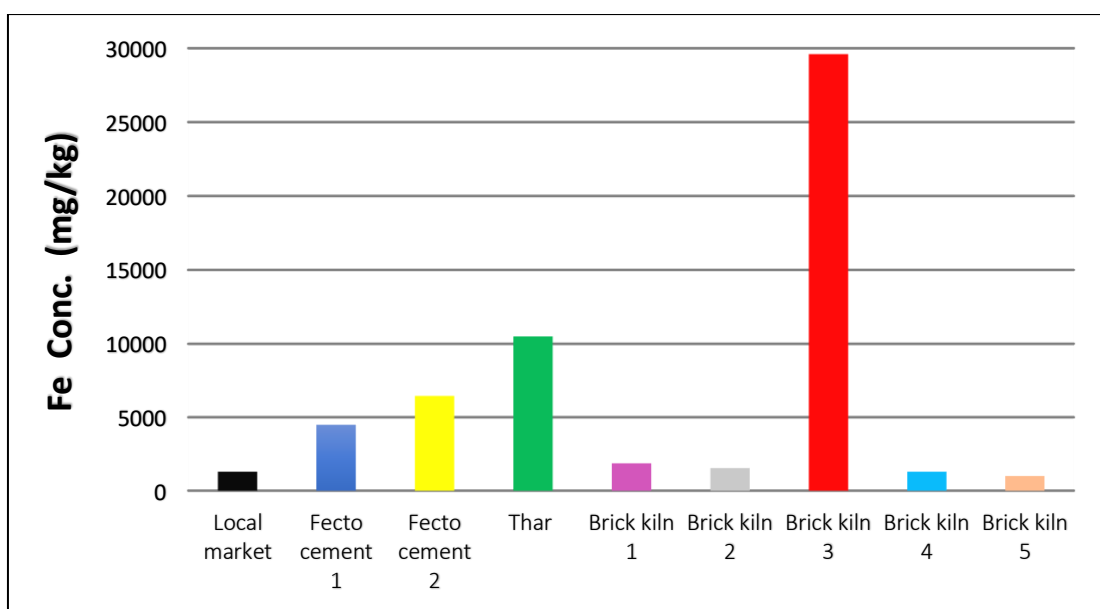
Figure 3.1. Concentration of iron in coal samples

Crosby reported in 1970 that iron in body exceeded in limits so, it will abnormally be absorbed and necessarily put into storage. Injury of the storage organ results and such patients develop cirrhosis, diabetes, heart failure, impotence, sterility, pigmentation of the skin and hemochromatosis. Fe can enter into air or water during the burning of coal or become part of particulate matter. No standard value is specified for drinking water by Pak EPA but WHO threshold limit is 0.5-50 mg/l. So the result showed that all samples contain high Fe concentration which is harmful to environment.

The utilization of coal and its effect on the earth is a noteworthy concern since coal contains high concentrations of trace elements, for example, As, Cd, Co, Cu, Pb, Ni, Hg, Si, and Zn that can be discharged into the water, soil, and in the air at raised and potentially dangerous level (Fernández-Turiel et al., 1994; Hower et al, 2005). Huang and co-workers in 1994, conducted a study on Iron concentrations in coal and concluded that it was not truly a trace constituent and might act as an intermediary in causing common lung disorders of coal minors. Further acid-soluble ferrous iron could cause lung tissue damage leading to disease emphysema. The impact of the acid-soluble ferrous iron has tempered the presence of carbonate minerals in the coal that neutralize the acids and allow the oxidation of the ferrous iron to benign ferric iron.

The lead concentration in all coal samples ranged from 1.98-5.53 mg/kg with an average of 3.18 mg/kg and brick kiln 3 (Khushab coal) showed high concentration whereas 3.121 mg/kg concentration is found in the brick kiln 2 (Peshawar coal). Table 3.1 showed that samples from the Fecto cement industry have Pb concentration below the detection limit. According to Pak-EPA, the allowable limit for Pb concentration in ambient air is 1 μg / m^3. For drinking water, the permissible limit of lead is ≤ 0.05 mg / l and the WHO permissible limit is 0.01 mg / l (Pak-EPA, 2016). The coal samples from brick kilns showed high concentration of lead and it can be discharged into air, water and soil during coal utilization. The study was conducted in the Netherlands by Van et al. (1987) to analyze the trace elements and it was observed that Pb was an element normally considered as volatile, but it was not detected in the gas phase. Due to binding capacity with other elements, and sometimes with glassy solid, which was more resistant to leaching. According to Shetty in 2003, during the combustion of coal, Pb can go into the vicinity and through the drainage system, it will be bound to the soil and transferred from the soil to the plants. Further from the soil, it can be transferred to plants and then to humans through plants. Lee conducted a study in 1981 at the University of Manchester, the United Kingdom to find out the features of lead clinical poisoning and depict the general symptoms developed due to lead poisoning.
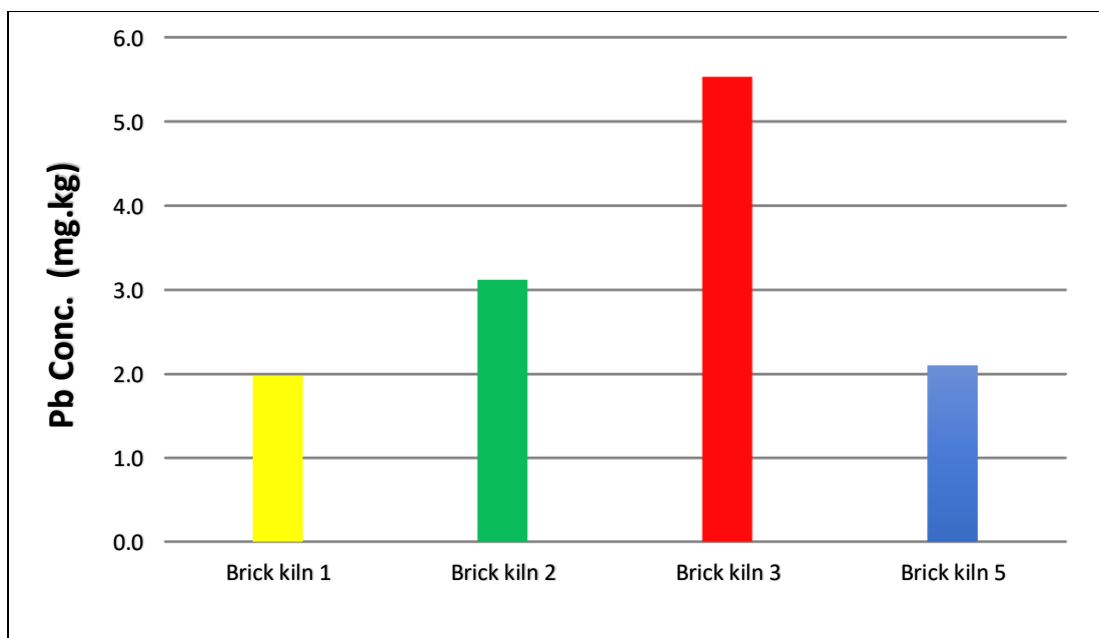
Figure 3.2. Concentrations of lead in coal samples

He was conducted his study on the workers at mines and non-workers and found out that lead exposure can cause kidney damage, muscle discomfort, bone loss, loss of intelligence, artery diseases (nausea) in workers. Youravong in 2011, conducted a study in the US and found out that dental diseases among children had also been detected with lead levels greater than 10 µg / dl. Therefore, the present study showed that lead, a heavy metal present in brick kilns coal samples with high concentration, whereas the minor concentration can be harmful.

Figure 3.3 showed that Hg concentration ranged from 2.08-7.2 mg/kg with an average of 4.55 mg/kg. A high concentration of Hg is found in brick kiln 1 (Mianwali coal) whereas the second-highest content of mercury is found in local market coal (Layyah coal) with a concentration of 6 mg/kg. Thar coal and Fecto cement samples (imported coal) showed the Hg concentration below the detection limit. The threshold limit defined by WHO and Pak EPA for drinking water is <0.001 mg/l. The result should Hg concentration is high in indigenous coal which is being utilized in different sectors as compare to imported coal.

Ito et al., conducted a study in 2006 related to the emission of mercury during coal combustion in Japan and reported that in indigenous coal of Japan the Hg concentration was 0.045 mg/kg whereas imported coal from China and South Africa has Hg concentration 0.21 mg/kg which was high as compared to world standards. Mercury had the highest emission ratio among the trace elements in the previous study,

with a fraction of about 27%. So, when the result of the present study was compared to the previous research it reveals that Hg concentration is very high in indigenous coal which is bought from different areas of Pakistan Further, the result of this study was compared to previous study it is revealed that Pakistan import coal from South Africa has better quality than coal which was import in Japan. Hg is a heavy metal of major concern and there are many researches on the Hg in literature. Meij et al. (2001) studied the content of mercury in coal used in coal-fired power plants in the Netherlands and gave 0.11 mg/kg as the mean concentration with the range 0.02 to 1.8 mg/kg. In continuation of this study, further research was conducted by Kizilshtein and Kholodkov (1999) to summarize the mercury content in coal used in coal-fired utility electric boilers in the US and showed that the mean concentration in bituminous coal was 0.11 mg /kg and the range was from 0.0 to 1.3 mg/kg. When the results of the current study are compared with previous studies it showed that the mean concentration in current result is 4.550 mg/kg with the range 2.080-7.120 mg/kg which is very high in the coal of Pakistan. According to Sandhya in 1994, coal combustion was considered an important human activity for the release of mercury in the surrounding environment for the production of electricity. Due to the mercury being more toxic, it was ranked by the National Research Council in 1980 as a "major concern."

Slimmer and Langer (1992) reported that an increase in the concentration of Hg resulted due to the emission of coal combustion in the northern hemisphere due to the trend for increasing coal consumption. The release of mercury into the natural environment is a global concern in light of its serious fatal effects. Severe mercury poisoning depends on the mixture of poison pollution that causes damage to various internal organs. In the 1950s, mercury has received considerable attention as an environmental hazard when it was determined that many symptoms, for example, lack of coordination, tremors, lowered discrimination, and dementia was found in the people living nearby Minamata Bay in Japan and exposed to mercury poisoning.
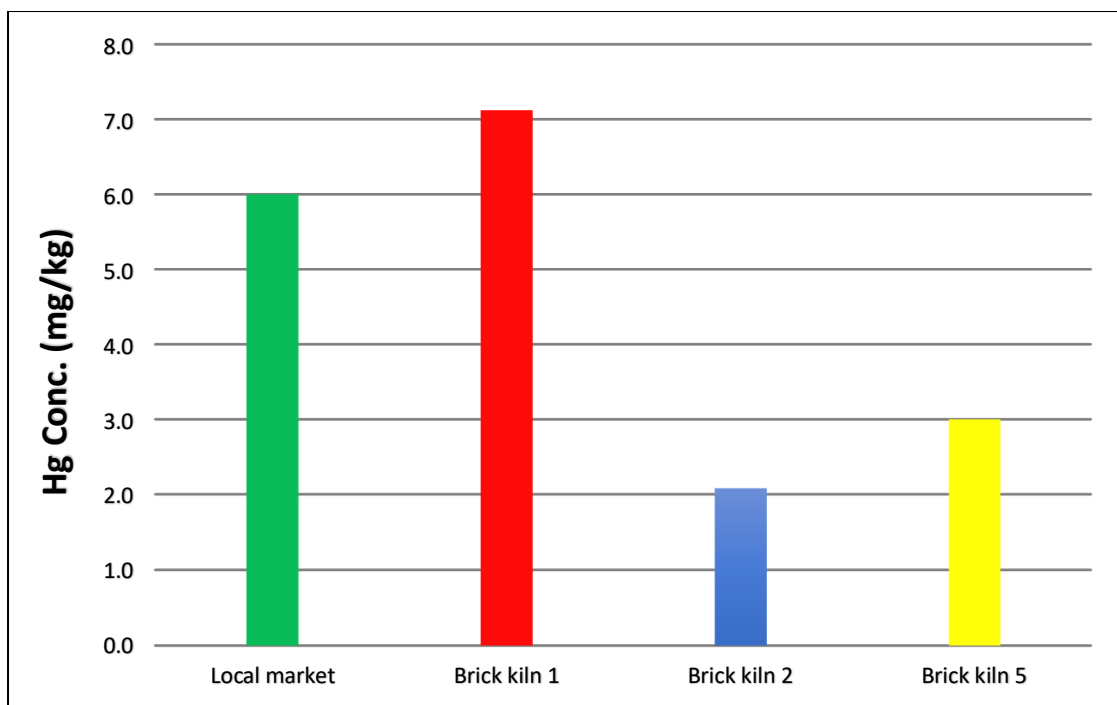
Figure 3.3. Concentration of mercury in coal samples

Figure 3.4 showed that each coal sample collected from nine locations contains Zn concentration ranged from 8.99-25.22 mg/kg, whereas, high concentration is found in the brick kiln 3 (Khushab coal). The second highest concentration of Zn is observed in Fecto cement sample 2 (South Africa coal). As per Pak-EPA permissible limit for drinking water is 5.0 mg / l (Pak-EPA, 2016) and the WHO limit is 3 mg / l (Pak-EPA, 2016). Table 3.1 results showed nine coal samples collected from four different locations have a high concentration of Zn except the sample collected from brick kiln 4 (Dalwal coal). Fosmer et al. (1990) described that according to the periodic table of elements, zinc is found in Group II-B, which contains two toxic metals, cadmium and mercury. However, zinc is deliberated to be comparatively non-toxic to Cd and Hg.
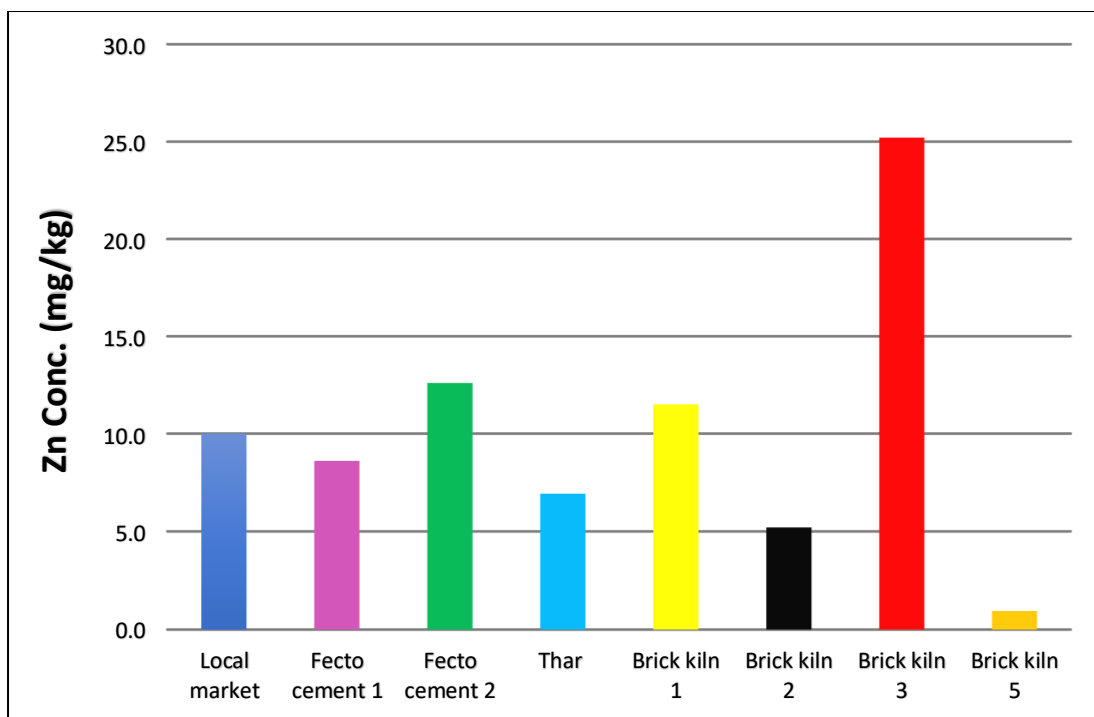
Figure 3.4. Concentration of zinc in coal samples

Fukada et al. (2011) reported that Zn homeostasis causes growth retardation, immunodeficiency, neuronal and sensory dysfunctions. According to Swaine in 1975, Industrial activities, minerals and climates are potential sources of Zn metals enrichment. Zinc is primarily mineralized in coal and is particularly associated with sphalerite (Prasad et al., 1961; Cowder et al., 1983).

Table 3.1 showed that Ni concentration ranged from 0.12-38.9 mg/kg with an average of 15.198 mg/kg. The concentration of Ni is highest in the brick kiln 3 (Khushab coal) whereas second-highest Ni concentration is found in the Fecto cement industry sample 2 (South Africa coal) (Figure 3.5). The allowable concentration of Ni by Pak-EPA in drinking water is <0.02 mg /l and the WHO value for drinking water is 0.02 mg/l (Pak-EPA, 2016). The results showed a high Ni concentration in imported coal and coal used in brick kilns. Goldsmith in 1935 described that nickel is present in coal as an organic complex, as indicated by the initial work on the elements contained in coal. Finkelman (1993) has discovered that a large part of nickel in coal is physically bounded. Mukherjee et al. (1988) discovered that nickel is, at least incompletely, as a natural chelate. Doll in 1958 conducted research in South Wales, Australia, when lungs and nose disease issue was emerging. It was common in labors who had involved in refining Ni. Cancer of the nose and lungs had been prescribed as an industrial disease

when it was occurring in a certain class of nickel workers. It was estimated that the risk of death from cancer of the lung to be five times the normal rate, and from cancer of the nose. Further excessive amounts cause cancer of lungs, nose, kidney and prostate, dizziness, respiratory failure, congenital defects, asthma and interstitial bronchitis, allergic reactions and heart failure.
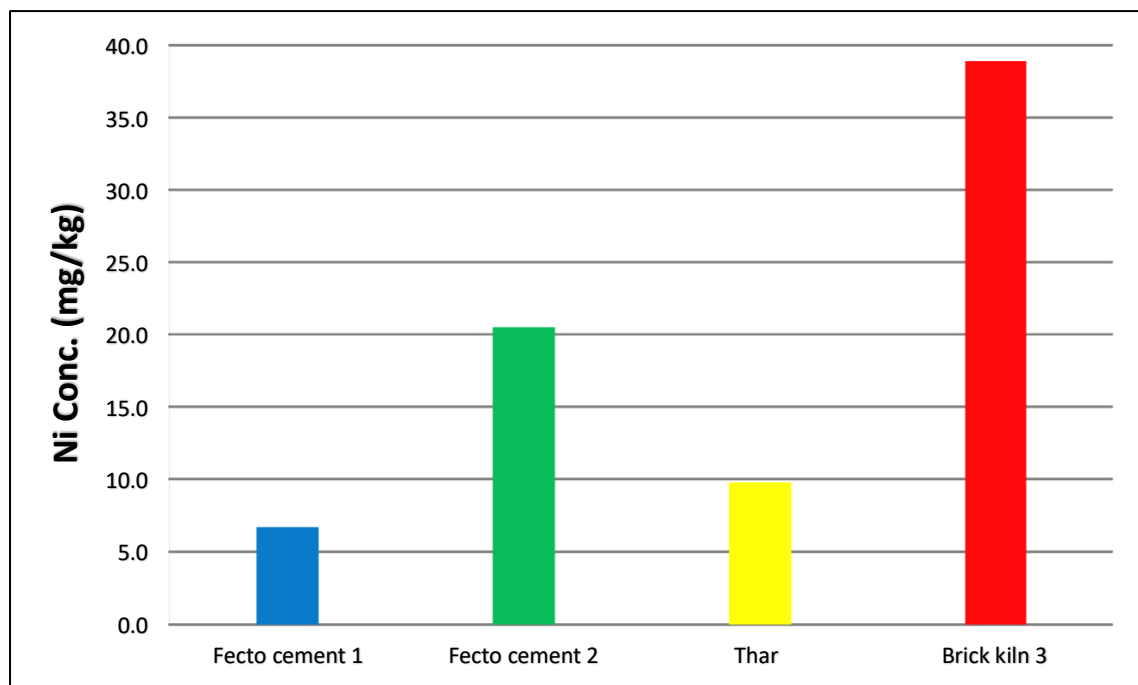

Figure 3.5. Concentration of nickel in coal samples

Table 3.1 showed that the concentration of Cd is below the detection limit in all nine samples whereas Cd is carcinogenic substances (Sun et al., 2000).

Table 3.1 showed that Copper concentration ranged 0.100-13.7 mg/kg with an average of 3.375mg/kg while figure 3.6 showed that high concentration of copper is found in the brick kiln 3 (Khushab coal). On the other hand, coals from Indonesia and South Africa showed Cu concentration of 6.1 mg/kg and 4.1 mg/kg concentration respectively. The permissible limit of copper for drinking water as per Pak EPA is 2 mg/l and the WHO limit is 2 mg/l. Johnson and Larry in 2008 described that copper is an important determinant of human health, so absorption of copper is essential. Despite the fact that people can handle a disproportionate amount of copper, excessive amounts of copper can cause significant health problems. But if the concentration of copper is increased to some extent, people experience a variety of diseases. Similarly, people living in homes that use coal at home are also more likely to be exposed to high levels

of copper than those who use other sources of energy in their homes. Tisato et al. (2010) reviewed copper causing diseases and therapies treatment and observed that many kinds of cancers including prostate, breast, colon, lung, and brain were due to elevated levels of copper.
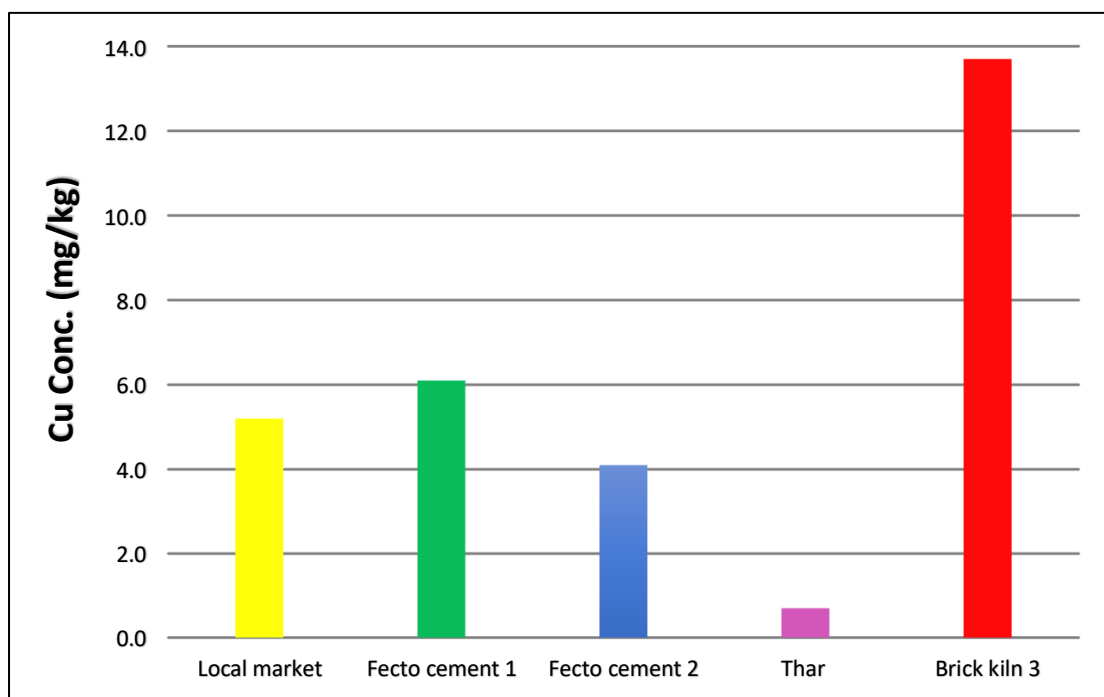

Figure 3.6. Concentration of copper in coal samples

From the result, it is obvious that when coal residue will discharge into the soil (industries, brick kilns, and mining) nearby area because if a high concentration of Cu will enter into the soil it will affect the productivity of plants. Araya et al. (2004) reported that only a restricted variety of plants have the chance to tolerate copper-rich land. This is a major reason there is no abundant plant variation close to the copper dispensing industrial unit.

Table 3.1 shows that Chromium concentration ranged between 0.28-70.7 mg/kg whereas the high concentration is found in Khushab coal being used in the brick kiln 3, while Thar coal has Cr concentration of 4.54 mg/kg. Other coal samples also showed chromium concentration of 3.700 mg/kg and 2.840 mg/kg respectively in South Africa and Indonesia coal (Figure 3.7). As per Pak EPA and WHO limit for chromium in drinking water is 0.05 mg/l. the study was conducted by Xiaoyan et al. (2015) at Pingdingshan, North China enriched Cr in the atmosphere was believed to be associated with coal combustion and retarded oxidation of coal gangue at waste dumps. The

TD$_{50}$ values of soluble fractions were positively correlated with soluble Cr concentrations, but no correlation was observed for intact whole samples, indicating that the Cr toxicity in PM$_{10}$ is caused mainly by its soluble fraction. And Cr was present in a soluble and insoluble form and soluble form of Cr is associated with PM10 causing DNA damage in people. Huang et al. (1991) conducted a study to investigate the level of chromium in the hair of patients with coronary heart disease. It was concluded that excessive chromium intakes or exposure can cause chromium accumulation in the liver and damage liver function. Further, the study suggested that excessive chromium levels may cause injury to blood vessels, hypertension and neurological dysfunction.
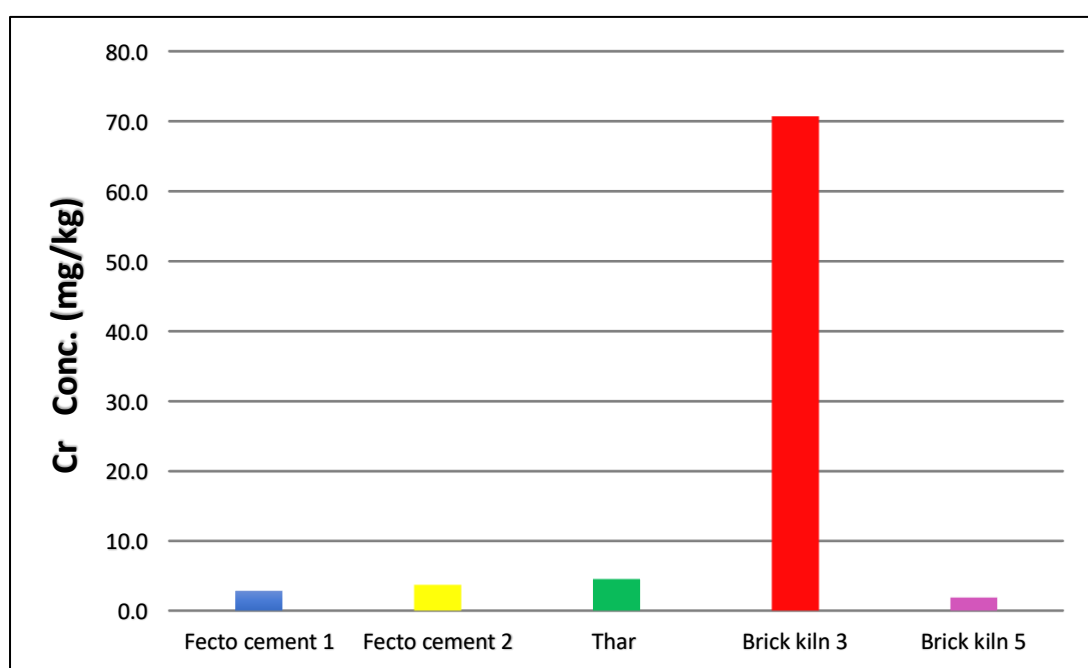
Figure.3.7. Concentration of chromium in coal samples

The result showed (Table 3.1) that arsenic concentration is below the detection limit in all samples collected from four locations.

The figure 3.8 showed the concentration of soluble sulphate ranged 0.054-5.800 with an average of 1.08 mg/kg. The Dahwal city coal showed a high concentration used in brick kiln 4 (5.800 mg/kg) and Thar coal has a concentration of 2.028 mg/kg. It has been observed that soluble sulphate is present in all coal samples collected from four different locations. Ribelles reported in 1995 that there is partial information about soluble sulphate respiration and oral, chronic and toxic, carcinogenic, growth and reproductive toxicity in humans and animals.
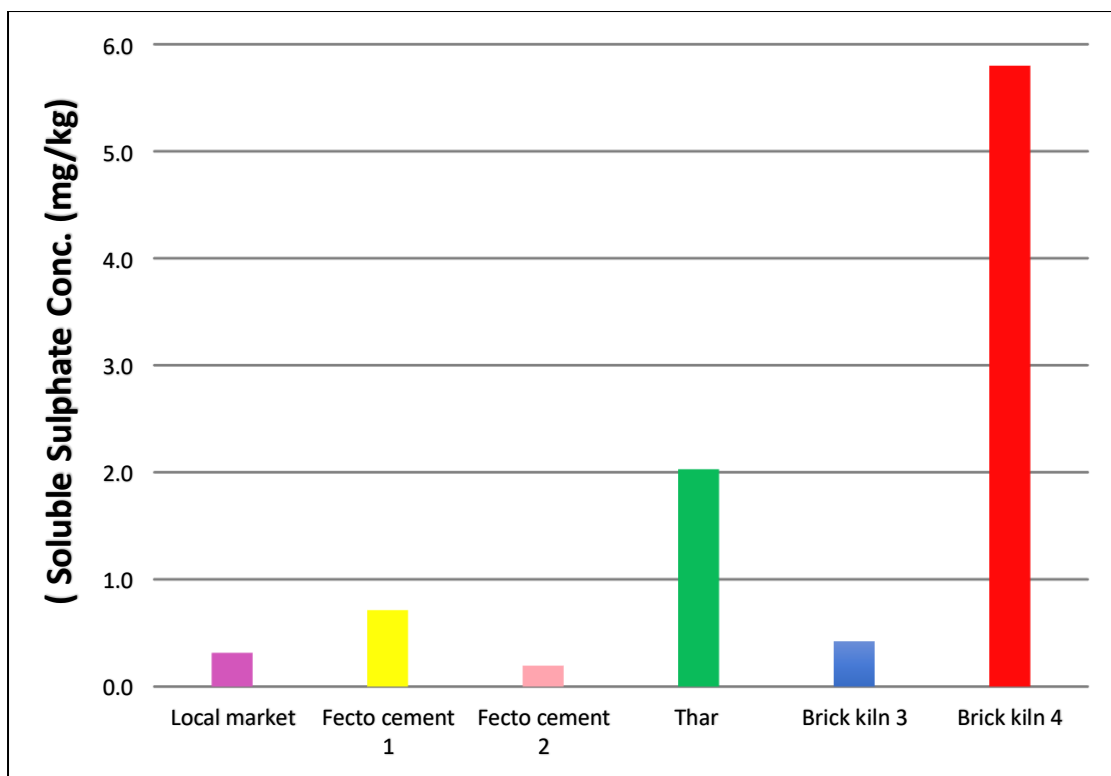
Figure.3.8. Concentration of soluble sulphate in coal samples

Result showed (Table 3.1) that inorganic sulfide is not detected in all samples collected from four locations.

The results (Table 3.1) and figure 3.9 showed that Al concentration ranged 0.010-5.87 mg/kg with an average 1.183 mg/kg whereas the coal is being used in brick Kiln 3 and purchased from the Khushab with a high concentration of 5.870 mg/kg. The South Africa coal has Al concentration of 2.100 mg/kg and Indonesia coal has 1.167 mg/kg Al concentration respectively. As per WHO the permissible limit for drinking water for Al concentration is < 0.2 mg/l. Al has not been classified with respect to carcinogenicity but Al production has been classified as carcinogenic to humans by the International Agency for Research on Cancer (IARC). Occupational limits exist in several countries for exposures to aluminium dust and aluminium oxide. For non-occupational environments, limits have been set for intake in foods and drinking water. Workers in the aluminium production and user industries, as well as aluminium welders, experience considerable exposures to the metal and its compounds (Xavier et al., 1994).
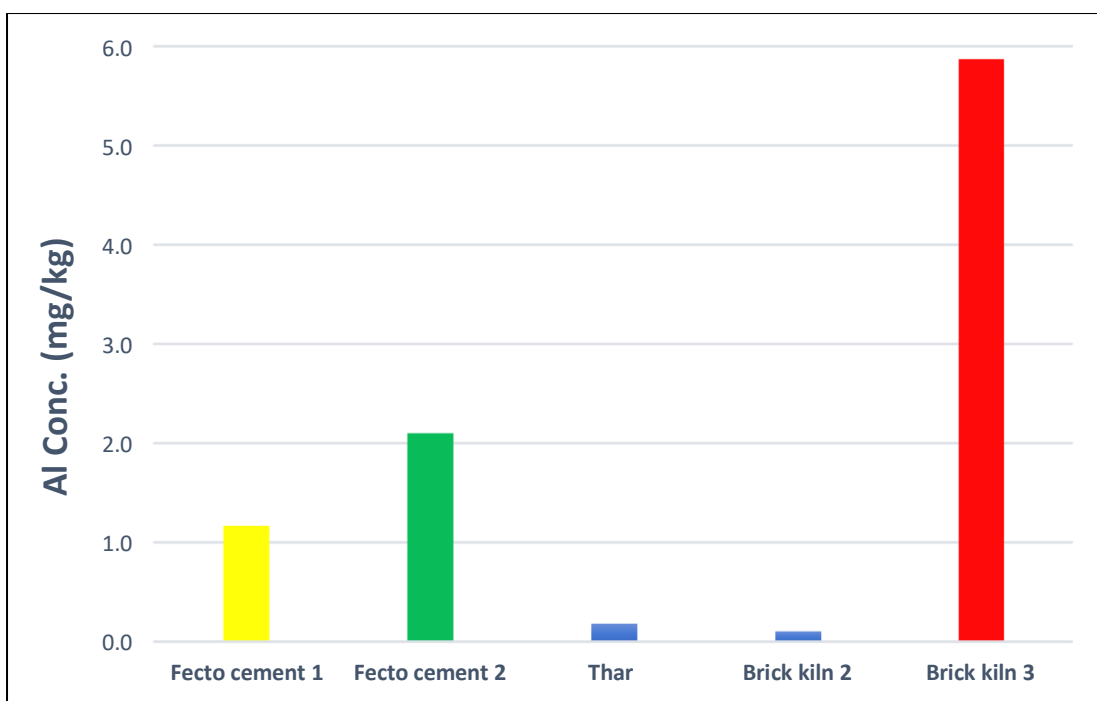
Figure.3.9. Concentration of aluminum in coal samples

Willhite et al. (2014) reported that Al has harmful effects and is usually found in combination with other ions as a pollutant, for example, Al-chlorine. Long-lasting Al concentrations can have serious health effects, for example, damage to the central nervous system, memory loss, severe trembling and lung problems. When entering the body during kidney dialysis, it can cause complications for kidney patients. This effect, called shaver disease, is complicated by the presence of silica and iron oxide in the air. Al can accumulate in plants and cause health problems for the animals that consume it.

The result (Table 3.1) and figure 3.10 showed that Ca concentration ranged 100-2800 mg/kg with an average of 828 mg/kg whereas a high concentration of the Ca is found in the brick kiln 4 which purchased coal from Dalwal city and being utilized in brick kiln. Whereas the South Africa coal has concentration of 1500 mg/kg and local market coal (Layyah coal) which is used in the local market contain Ca concentration 1090 mg/kg. The most significant contributors to calcium emissions are stationary combustion such as brick kilns and coal power plants, quarrying and mining of coal minerals, and residential coal combustion. Calcium emissions have decreased by 74% since 1990, due to using alternatives for energy production though that sector was still the source of 55% of UK emissions of calcium in 2017. Some abatement of emissions is also likely through efforts to reduce particulate matter emissions from large industrial processes and coal power stations (Xavier et al., 1994).
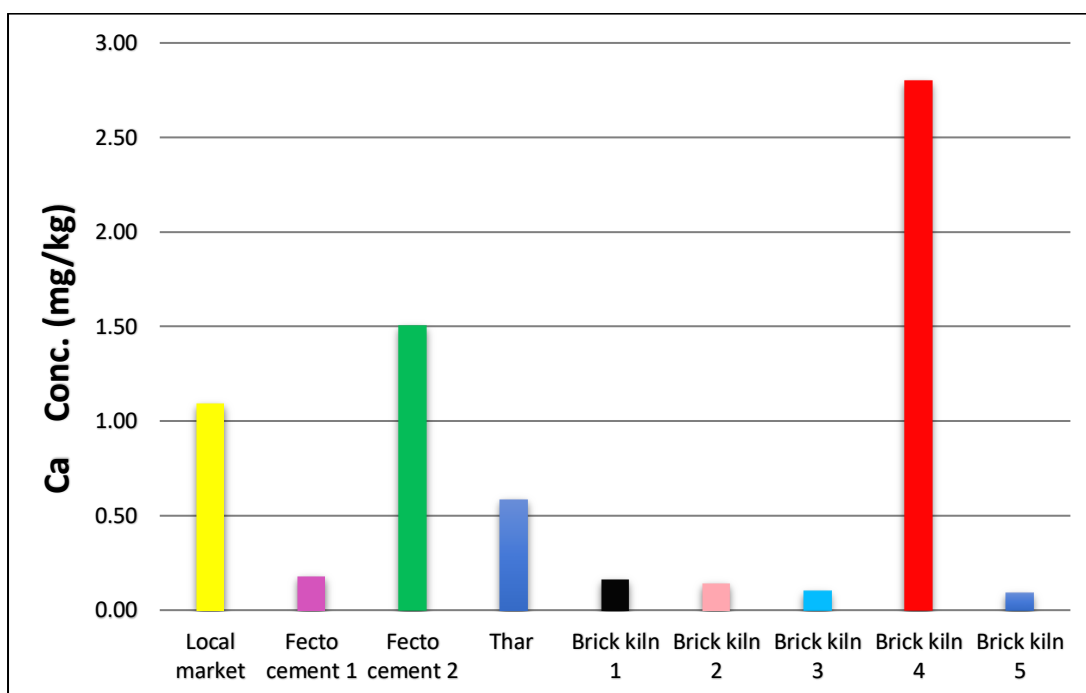
Figure.3.10. Concentration of calcium in coal samples

Balk et al. (2017) reported that an excess amount of Ca can create the gas, bloating, nausea, vomiting, memory loss, confusion, muscle weakness, increased urination, dehydration, bone disease and kidney stone.

The result (Table 3.1) and figure 3.11 showed that Mg concentration ranged 272-2556 mg/kg with an average value of 1130 mg/kg whereas a high concentration of the Mg is found in Thar coal. The brick kiln 4 (purchased from Dalwal city) has a concentration of 2219 mg/kg and imported coal (purchased from South Africa) has Mg concentration of 1581 mg/kg.

Mg is less toxic and is not considered as unsafe for health. If inhaled, dust-containing Mg can damage mucous membranes, upper respiratory tract, mechanical injury or particulate matter can be injected into the eye. However, a large amount of magnesium powder can cause itch injury. Magnesium is no longer inspected, but it is not suspected to be carcinogenic, mutagenic or teratogenic. This substance can also flare up upon contact with air or moisture producing toxic fumes. It was long assumed that the major source of Mg in the air was emission from coal combustion and further patterns of concentrations in air and precipitation also suggest significant emissions from urban and industrial sources. Emissions of magnesium have fallen by 82% since

1990 in UK, mainly due to a reduction in emissions from coal combustion. Further investigation revealed that the most significant source of magnesium emissions in 2017 were coal used for fireworks at homes which were responsible for 29% of emission in air (Yasui et al., 1992).
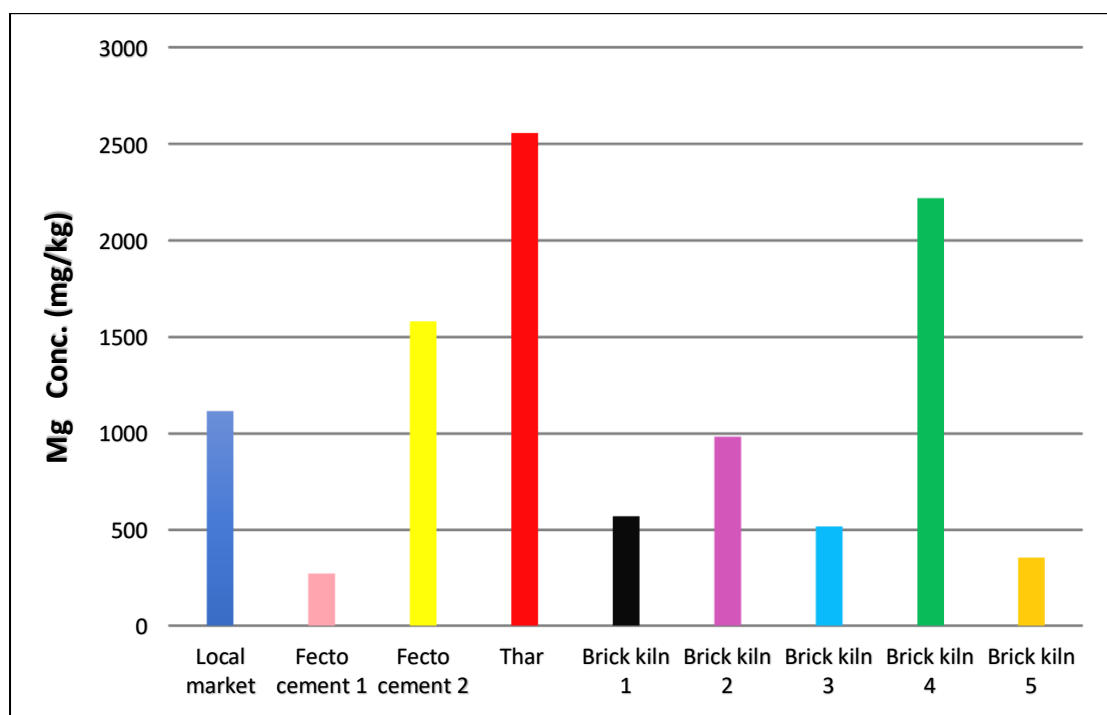

Figure.3.11. Concentration of magnesium in coal samples

Figure 3.12 showed that Na concentration ranged 255-1294 mg/kg with an average value of 572 mg/kg, Whereas a high concentration of the Na is found in Thar coal. The brick kiln 4 (Dalwal coal) has a concentration of 1033 mg/kg and brick kiln 3 (Khushab coal) has a concentration of 777 mg/kg. As per the WHO limit in drinking water for sodium is 200 mg/l, while it is generally found in < 20 mg/l of freshwater. Sodium is a relatively minor element in coal and is nevertheless of great importance in combustion because of its association with boiler fouling and corrosion. Much of the available evidence on the mode of occurrence of sodium in coals has been obtained from aqueous leaching experiments. Previous studies and work showed differences in the rates of release of sodium during coal combustion. Previous studies suggested that Na occurrence is heavily dependent on chorine present in coal due to its association with chorine. Subbaru et al. (2003) had demonstrated that over 90 percent of the sodium in UK coals was readily be removed by aqueous extraction. This case of removal indicated that only a trace amount of sodium was present in the aluminosilicate

(clay) minerals. Excess sodium increases blood pressure, stroke, heart failure, osteoporosis, stomach cancer and kidney disease (Subbaru et al., 2003).
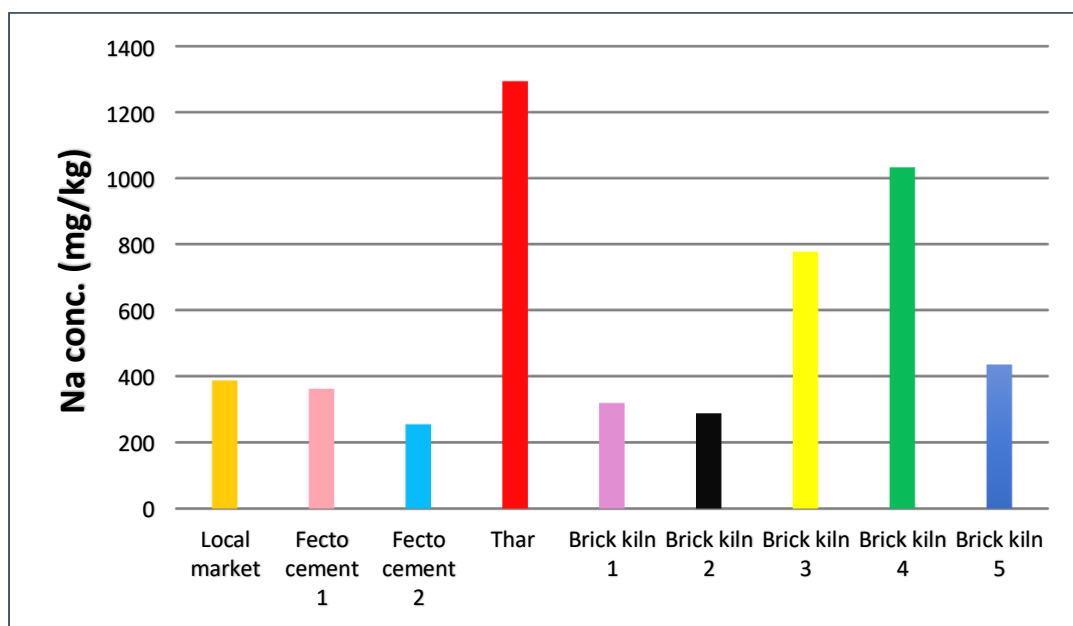
Figure.3.12. Concentration of sodium in coal samples

3.2 Trace element classification

The resultant elements are further grouped into three most important classes when compared with the classification given by NRC, 1980.

3.2.1 Class 1: major concern elements

Arsenic (As), Cadmium (Cd), Lead (Pb) and Mercury (Hg) are classified as major concern elements present in nine coal samples. Arsenic, cadmium, lead and mercury are highly toxic to most biological systems at concentrations above critical levels. Whereas As and Cd are found below the detection limit in all coal samples. This study showed that indigenous coal contains the Hg concentration high whereas imported coal does not contain Hg. The figure 3.13 demonstrated that Hg concentration is high as compared to Pb concentration but both heavy metals are harmful and making coal hazardous for utilization.
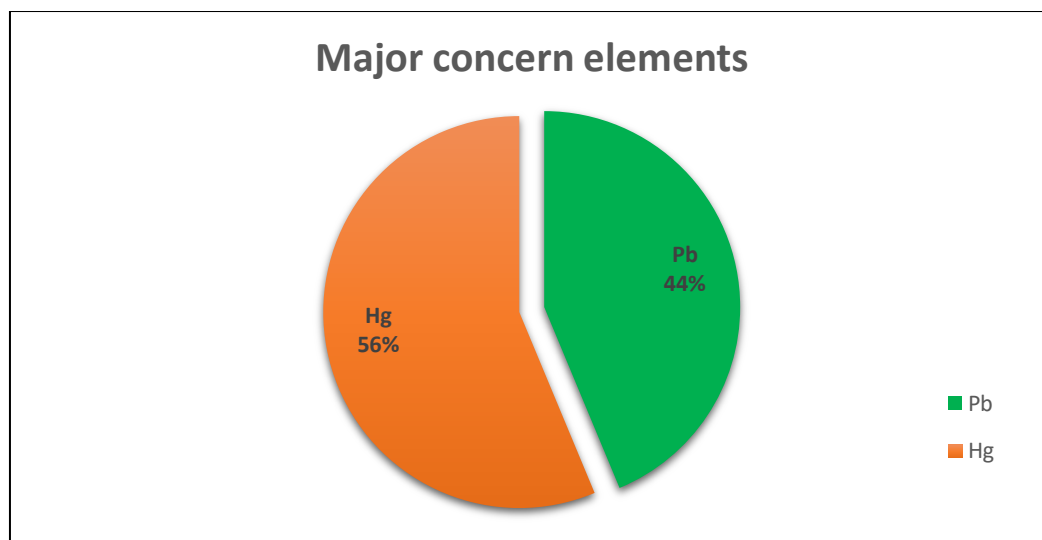
Figure 3.13. Concentration of major concern elements in coal samples

3.2.2 Class 2: moderate concern elements

The result showed (Table 3.1) that Chromium (Cr), Copper (Cu), Zinc (Zn), Aluminium (Al) and Nickel (Ni) are of moderate concern. These elements are potentially lethal and are available in coal-burning residues at raised levels of bioaccumulation. The figure showed that among moderate elements the Cr percentage is very high as compared to other elements and is represented by the yellow color in the graph.
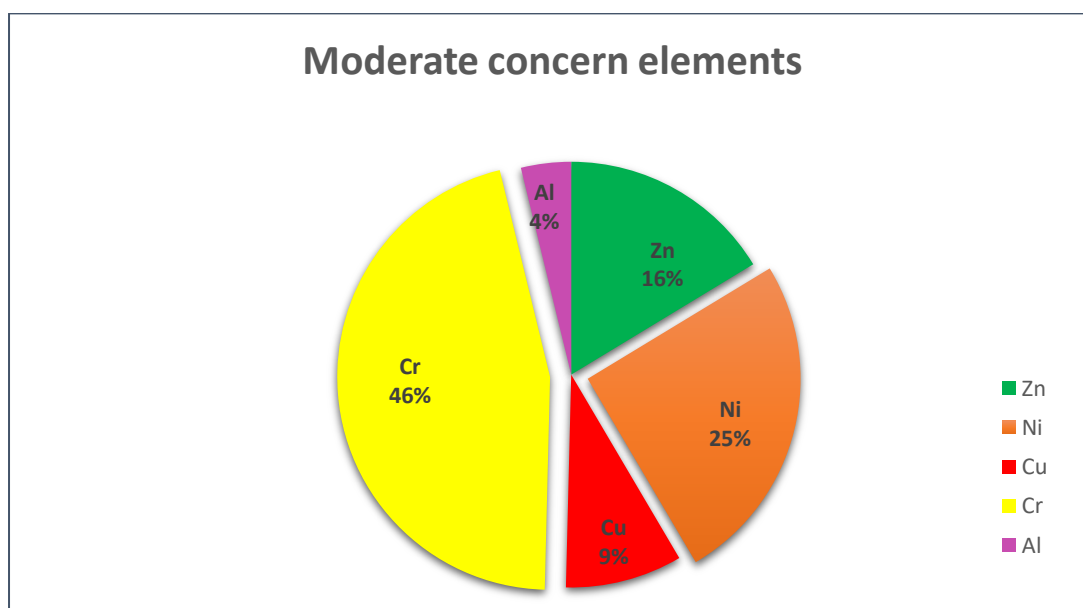
Figure 3.14. Concentration of moderate concern elements in coal samples

3.2.3 Class 3: minor concern elements

Result showed that Sodium (Na), Manganese (Mg), calcium (Ca), inorganic sulfide and soluble sulphate are of minor concern. These elements are of minimal ecological concern. They are categorized generally on the basis that they are available in residues. The low level of these elements has an insignificant effect (National Research Council, 1980). Among minor concern elements Ca concentration is high and represented by the green color whereas the red color represents Mg concentration second highest in coal samples.
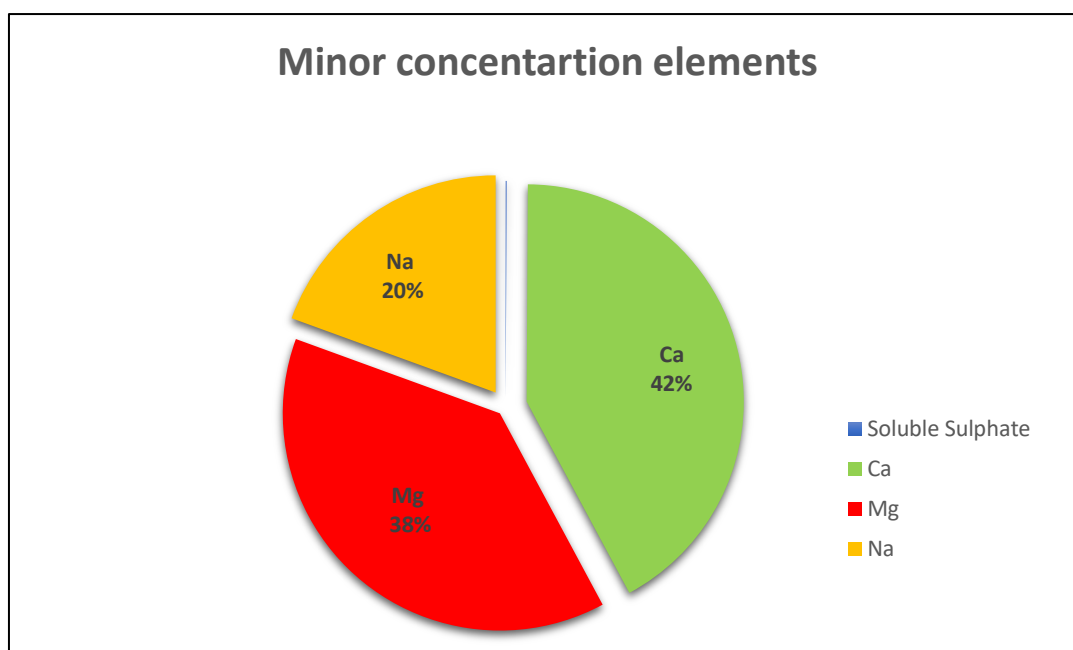
Figure 3.15. Concentration of minor concern elements in coal samples

Table

3.3 Hydrocarbons (benzene, toluene and m-xylene)

Hydrocarbons i.e. benzene, toluene, and m-xylene concentration is analyzed by using GC method and each coal sample run through the instrument at a regular time interval to get average concentration. Figure 3.16 showed that the red color bar presents high concentration of toluene in coal extracted from Thar as compared to other samples. Whereas the green bar shows that the second-highest concentration of toluene is found in a sample collected from the local market (Layyah coal). The yellow color bar shows that the concentration of toluene is third highest in the imported coal sample that is collected from the Fecto cement industry as an imported sample 2 (South Africa coal) that also showed the percentage of toluene near the same as in local market coal (Layyah coal). The result (Table 3.3) and figure 3.16 showed the same concentration of toluene in Fecto cement 2 (Indonesia coal) and coal samples collected from brick kilns where coal is purchased from different cities of Pakistan i.e. Layyah, Mianwali, Peshawar, Khushab, Chakwal and Dalwal.

Figure 3.16. Concentration of toluene in coal samples

Benzene concentration is below the detection limit (Figure 3.17) in all samples besides coal is being utilized in Fecto cement industry sample 2 and brought from South Africa and the result also indicates that minor percentage of benzene is present in coal samples collected from brick kilns.
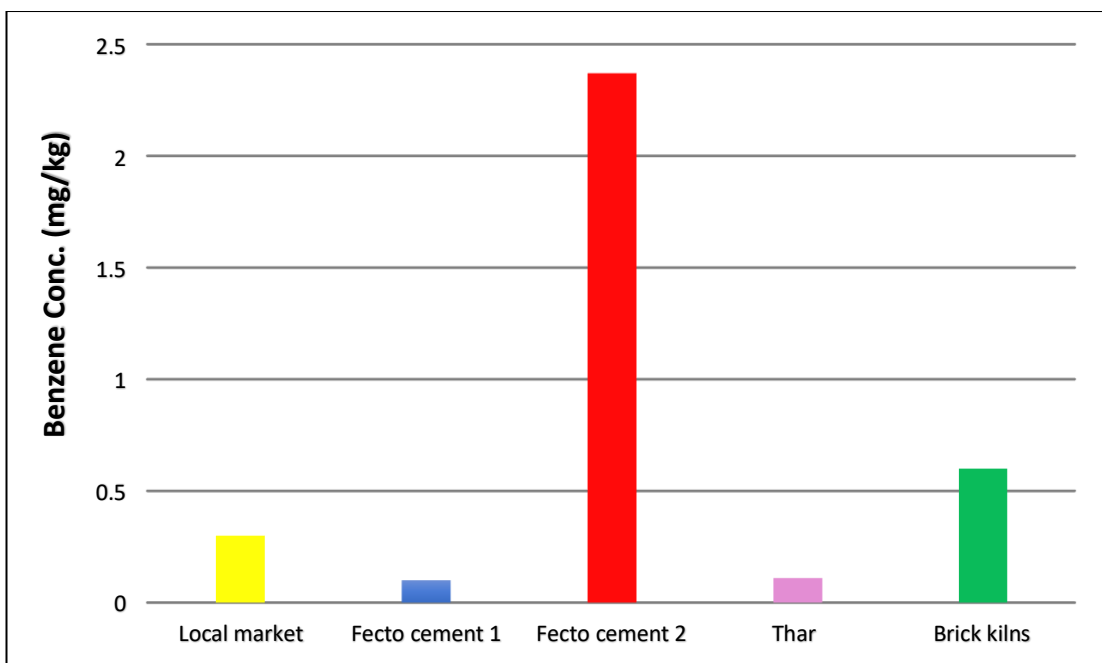
Figure 3.17. Concentration of benzene in coal samples
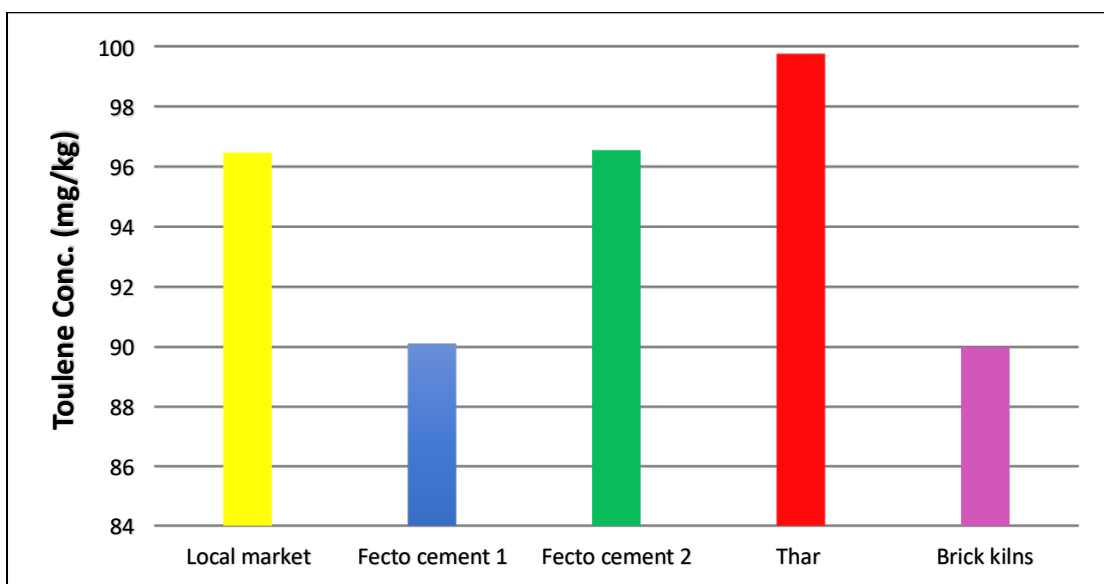
Further, the result of the present study was compared with the same study was conducted in Calcutta by Chattopadhyay in 1996. The results of the previous study were compared with the current study that showed an average value of benzene in present study is less than previous research whereas the toluene concentration in our coal samples is exceeded than previous study results. In the current study m-xylene concentration is also very high than found in previous studies. The values of BTX was compared with threshold limits of WHO, US-EPA and Australian drinking water quality standards the concentration of benzene, toluene and xylene is lower than the guideline for drinking water quality.

The result showed (Table 3.3) that second high concentration of m-xylene is found in the coal being utilized in brick kilns located at Choa Saidan Shah, Chakwal District whereas local market coal showed of 2.74 mg/kg m-xylene. M-xylene concentration is found high in Fecto cement 1 (Indonesia coal sample) (Figure 3.18). Whereas minor concentration is showed in Thar coal sample. It belongs to the family of toluene and its compounds containing a benzene ring which bears a methane group. The excess amount can cause eyes, skin, nose, throat disturbance, faintness, excitement, incoordination, nausea, vomiting and abdominal pain (Chang, 1989).
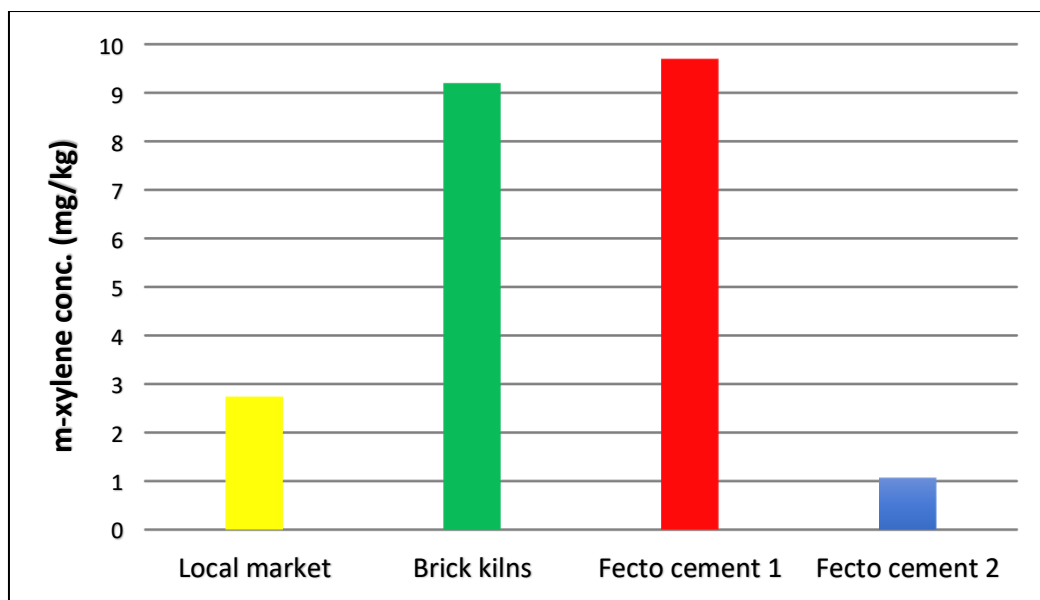
Figure 3.18. Concentration of m-xylene in coal samples

Table 3.3: BTX concentration in coal samples

Site No.	Samples	(Concentration in mg/kg)		
		Benzene	Toluene	M-Xylene
1	Local Market	0.3	96.46	2.74
2	Thar	0.11	99.75	0.12
3	Fecto cement 1	0.1	90.12	9.7
4	Fecto cement 2	2.37	96.55	1.07
5	Brick kilns (1,2,3,4,5)	0.6	90	9.2
6	Max.	2.37	99.75	9.7
7	Min.	0	90	0.12
8	Average	0.69	94.57	4.56
9	WHO DWG	10	700	500
10	US NPDWS	5	1,000	10,000
11	A-DWG	1	800	600

WHO = World Health Organization (WHO, 2008), DWG= Drinking Water Guideline (US EPA, 2003), US NPDWS = United States National Primary Drinking Water Standards, Australian Drinking Water Guideline (NHMR

CONCLUSIONS

The present study was conducted for analysis of organic and inorganic constituents of local and imported coal which is being utilized in different sectors of Pakistan. Following are the main conclusions of the study;

1. The content of Fe is in a range about (100-2960), Pb (1.9-5.5), Hg (2.0-7.1), Zn (0-25.2), Ni (0.1-38.9), Cu (0.1-13.7), Cr (0.2-70.7), Soluble Sulphate (0-5.8), Al (0-5.8), Ca (100-2800), Mg (272-2556), Na (255-272) and As, Cd, inorganic sulfide are shown under below the detection limits in all coal samples.

2. Coal is being utilized in brick kilns brought from other cities of Pakistan i.e. Layyah, Chakwal, Dalwal and Khushab cities whereas Khushab city coal has a high concentration of the inorganic elements i.e. Fe, Pb, Zn, Ni, Cr, Cu, and Al.

3. Imported coal is less toxic as compared to the indigenous coal.

4. Coal from Thar and Dalwal city has the same quality as imported coal.

5. Toluene concentration is found a high as compared to benzene and m-xylene.

RECOMMENDATIONS

On the basis of current study following recommendations are given;

1. There should be standards or permissible limits defined by concerned authorities i.e. Pak-EPA and US-EPA.

2. In order to control pollutants the best method is source correction method i.e. International coal is less toxic as compared to indigenous coal.

3. More than 90 % coal is being utilized in brick kilns which do not have modern technologies to control the emission during burning of coal and gases emission discharge direct into air. Government agencies should survey and installed new equipment to control the emission.

4. Coal mined at Thar and brought from Dalwal city have same quality as coal imported from the other countries like South Africa and Indonesia, and therefore for economical concern it is suggested to utilize Pakistani coal instead of importing from other countries.

5. Hg concentration is found to be very high in most of samples especially purchased from different cities of Pakistan. Due to increase in pollution of mercury and as heavy metal of global concern further investigations and researches on coal are suggested and precautionary measures and substitutes should be adopted.

6. There should be awareness programs for knowledge of the local people, mines workers, and people living near the vicinity of those areas. The areas of coal reserves or coal are being used as an energy source that can be avoided by people when has knowledge about the concentration of trace elements in coal, especially heavy metals.

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APPENDICES

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