Assessing the Spatio-temporal Trends of Selected Toxic Substances from E-waste Recycling Facilities in Pakistan

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Assessing the Spatio-temporal Trends of Selected Toxic Substances from E-waste Recycling Facilities in Pakistan

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DEDICATION

To
Almighty ALLAH and the Holy Prophet MUHAMMAD (P.B.U.H)

&

My loving family

DECLARATION

I *Mureed Kazim*, PhD scholar in the Department of Environmental Science enrolled under registration No. 53-FBAS/PHDES/F18, hereby declare that the knowledge contributed by data collection and results derived to draw conclusion presented in this thesis titled "*Assessing the Spatio-temporal Trends of Selected Toxic Substances from E-waste Recycling Facilities in Pakistan*" is my own original work and has not been submitted as research work or thesis in any form in any other university or institute in Pakistan or abroad for the award of any degree. However, three research papers on the basis of this research have been published in ISI indexed journals and the other one research paper have been submitted for publication.

Dated: 20-12-2024 **Deponent**
Mureed Kazim

FORWARDING SHEET BY RESEARCH SUPERVISORS

The thesis entitled "Assessing the Spatio-temporal Trends of Selected Toxic Substances from E-waste Recycling Facilities in Pakistan" submitted by Mureed Kazim in partial fulfillment of PhD degree in Environmental Science has been completed under my guidance and supervision. I am satisfied with the quality of student's research work and allow him to submit this thesis for further process of graduation with PhD Degree from Department of Environmental Science, as per IIU rules & regulations.

Date: 14-12-2024 ______________________________

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Table of Contents

List of Figures

List of Tables

List of Appendices

Details of Appendices **Pg#**

List of Plates

Details of Plates **Pg#**

List of Abbreviations

ADD	Average daily dose
BFRs	Brominated Flame Retardants
CRT	Cathode ray tube
DD	Dry deposition
DMA	Digital mercury analyzer
EEE	Electrical and Electronic Equipment
EPA	Environmental protection agency
FRs	Flame Retardants
GEM	Gaseous Elemental Mercury
HBB	Hexabrominated bipihenyls
HBCDD	hexa-bromocyclododecane
HFRs	Halogenated Alternative Flame Retardants
HMs	Heavy Metals
HWM	Hazardous waste management
ICP-MS	Inductively coupled plasma-mass spectrometer
ICTs	Information and communication technologies
IDL	Instrument detection limit
ITU	International telecommunication union
KP	Khyber Pakhtunkhwa
LAD	Lifetime average dose
LCD	Liquid crystal display
LED	Light emitting diode
MDL	Method detection limit
MRL	Minimal risk level
MoCC & EC	Ministry of Climate Change and Environmental Coordination
NBFRs	Novel Brominated Flame Retardants
PAS	Passive Air Sampling
PBBs	Polybrominated Biphenyls
PBDEs	Polybrominated Biphenyl ethers
PCBs	Polychlorinated Biphenyls
PMD	Pakistan meteorological department
POPs	Persistent Organic Pollutants
PUF	polyurethane foam
RfDs	Reference doses
SR	Sampling rate
UNEP	United nations environment program
WEEE	Waste Electrical and Electronic Equipment
WHO	World health organization

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Mureed Kazim

Abstract

The prevalent presence of electrical and electronic waste (e-waste) is highlighted as global environmental challenges due to the increase of irregular and poor system of e-waste management, especially in developing countries. The consequences include the release and emission of toxic compounds into environmental compartments which ultimately poses significant risks to human health and ecosystem. In the current research study, the concentration levels of persistent organic pollutants – flame retardant (POP-FR), heavy metals (HMs) and gaseous elemental mercury (GEM) in air, dry deposition particles and soil samples were investigated for a period of one between September 2020 and December 2021 (During one season (spring), the designated sampling duration was exceeded due to COVID-19 lock down). Samples were carried out at 40 informal e-waste recycling facilities and background sites in major urban cities such as Rawalpindi, Faisalabad, Lahore, Gujranwala and Multan from Punjab Province, Peshawar from Khyber Pakhtunkhwa (KP) Province, Karachi and Hyderabad from Sindh Province and Quetta from Baluchistan Province, Pakistan. The results showed that the chemicals investigated within the scope of the study were at detectable levels in air, airborne particles, and soil samples, like the concentrations reported in studies conducted in other parts of the world. Informal e-waste recycling facilities act as "point source" for the air and soil environment for the chemicals of interest. To measure GEM, continuous measurements of seasonally resolved concentrations were conducted using 132 Hg-passive air samplers (Hg-PAS) across thirty-two (32) e-waste recycling facilities (informal) and a background area. Among the studied cities, higher concentrations were measured in Karachi (mean ± S.D: 17.0 ± 22.0, range: 4.20 – 92.0 ng m^{-3}), Lahore (16.0 ± 4.20, 8.20 – 22.0 ng m^{-3}) and Peshawar (15.0 ± 17.0, 4.90 – 80.0 ng m^{-3}), while lower levels were measured in Hyderabad (6.90 ± 6.20, 3.10 – 25.0 ng m^{-3}), consistent with a higher rate of informal recycling activities in metropolitan areas. Seasonally, higher GEM levels occurred during autumn (15.0 ± 16: 3.30 –92.0 ng m^{-3}) and summer (13.0 ± 8.70: 1.80 – 80.0 ng m^{-3}) than in winter (12.0 ± 8.40: 2.50 – 49.0 ng m^{-3}) and spring (9.20 ± 7.30: 1.80 – 80.0 ng m^{-3}), possibly reflecting enhanced volatilization at higher temperatures and/or varying magnitude of recycling operations in different seasons. A total of 164 dry deposition (PAS-DD) and 164 surface soil samples were analyzed for selected (07) heavy metals (HMs) near 40 informal e-waste recycling sites and one background site during the study period. Findings revealed that Zn (1410), Pb (410) and Mn (231) exhibited the higher mean deposition fluxes (µg/m^2.day), derived from air samples, particularly in Karachi. Similarly, soils showed higher mean concentrations (µg/g dw) of Mn (477), Cu (514) and Pb (172) in Faisalabad, Lahore, and Karachi, respectively. Temporally, HMs concentrations were found to be higher in winter or autumn and lower in summer season. In addition, HMs concentrations were significantly (p=0.05) higher at recycling sites compared to background sites year-round, highlighting the e-waste recycling operations as the major source of their emissions. The I_{geo} index indicated moderate to extremely contaminated levels of Cu, Pb, Cd, and Ni in Karachi, Lahore and Gujranwala. Ingestion was found as a leading human exposure route, followed by dermal and inhalation exposure, with Pb posing the greatest health risk. The cumulative incremental lifetime cancer risk (ILCR) model suggested moderate to low cancer risks for workers. Similarly, a total of 164 dry deposition (PAS-DD), 164 gaseous passive air samples (gaseous-PAS) and 164 surface soil samples were analyzed for 30 brominated flame retardants (BFRs) near 40 informal e-waste recycling sites and one background site during the study period. In soils, concentration levels (mean (range) ng/g) of 27PBDEs, 2PBB, HBB and γ-HBCDD were detected as follows: 176 (0.76 – 11141), 31.0 (0.65 – 58.0), 1.39 (0.01 – 42.8) and 12.0, (0.22 – 461), respectively. The levels were six to ten-fold higher to their respective levels at background sites. Among cities, Karachi, Faisalabad, Gujranwala, and Lahore were prominent cities with PBD-209 (45.5 (0.13 – 1152)) was the most prominent in all soil samples. Seasonally, concentrations of ΣBFRs were higher ranked as follows: Winter (11620) >Spring (3874) >Autumn (3139) >Summer (1207). Average daily dose for soil ingestion was estimated for BDE-209 (0.10973 ng/kg/day) at Faisalabad, followed by BDE-47 (0.08616 ng/kg/day), BDE-99 (0.06788 ng/kg/day) at Karachi city but lower than RfDs values suggesting minimal ingestion risk. While in air samples, yearly average (range) flux (ng/m^2.day) of PBDEs were measured as 8.68 (0.23 – 721) in particulate and 9.21 (0.23 – 864) were calculated for gaseous phase (pg/m^3). In both phases, the prevalence of lower PBDEs such as BDE-47 and BDE-28 and deca-BDEs (BDE-209), exceeded that of octa-BDEs in the atmosphere. In case of non-PBDEs, HBB and HBCDD was calculated as 3.68 (0.22 – 106) ng/m^2.day and 14 (3.92 – 69) ng/m^2.day for particulate phase, while 3.02 (0.34 – 59.9) pg/m^3 and 21.3 (4.09 – 248) pg/m^3 for gaseous phase. In both phases BFRs were found higher in Karachi, Gujranwala, Lahore, Faisalabad and might be associated with scale of recycling operations and high-temperature seasons. In summary, our findings indicate that informal e-waste recycling operations significantly contaminate soil and air in urban centers in Pakistan. Thus, implementing specific e-waste regulations, policies, and capacity-building programs is crucial. Comparative research on e-waste management strategies and government incentives for proper recycling is recommended. Future studies should also address additional toxic chemicals from these informal operations.

Keywords: E-waste; Informal recycling; HMs; GEM; BFRs; Passive air sampling; Urban areas

Chapter 1

Introduction

1.1 What is e-waste?

Electronic waste, usually recognized as (e-waste), refers to waste electronics and electrical equipment (WEEE). Pucket *et al.* (2005) define WEEE more generally as an increasing variety of electronic appliances including huge equipment like refrigerators, air conditioners to small and personal equipment such as computers, mobile etc., all of which have been thrown away by their users. E-waste comprises various equipment, containing nearly any business or household item or containing electrical or circuitry or apparatus powered with means of battery or electricity (Baldé *et al.*, 2015).

1.2 E-waste, a Global challenge

E-waste highly ranked among emerging international challenges due to its growing generation volume and related complex nature in waste stream (Xu *et al.*, 2020; Baldé *et al.*, 2017). During the last few decades of the 20th century, there was an enormous increase of consumption-based economy all over the world and this leads to an increasing risk for environmental and ecological sustainability. E-waste is an interest of concern since elevated usage of electrical and electronic equipment (EEE) and its short existence durations result in considerable portion to become outdated and redundant all over the globe. E-waste is the fastest expanding flow of waste on global scale (Shittu *et al.*, 2021; Ilankoon *et al.*, 2018). It is estimated that global generation in 2023 was 62 billion kg, expressing ~6 % growth compared to 2019 while 82 billion kg expected till 2030 if present trend continues (Baldé *et al.*, 2024). Worldwide, only 15 – 16 % of the total was formally recycled in 2014, 20 % in 2016 and dropped in 2019 to 17.4 % (Forti *et al.*, 2020; Sahajwalla & Gaikwad, 2018; Baldé *et al.*, 2017). It is critical to recognize the circumstances behind the elevating flow of e-waste. There are numerous crucial aspects involve with the issue of e-waste management comprising advancement in technology, increasing demands by consumers, behaviors, and consumption incentives which drastically decrease the lifetime and boost quicker replacement rates (Borthakur & Govind, 2017). These issues are briefly discussed below.

The escalating demand for EEE is forced by many interconnected factors like enhanced networks, faster speeds, new services, and applications, have prominently increased the usage of EEE. Additionally, communication, administrative, and industrial domains and entertainment services also boost the process. The situation coupled with increasing incomes, purchase power, and the industrialization and urbanization in developing countries, has surged in EEE bank (Baldé *et al.*, 2017). High growth rate in EEE consumption was observed between the year 2000 to 2016 in new devices while high internet dispersion rates in developing nations accelerate the demand (Adedoyin *et al.*, 2020). Expansion of online e-commerce additional demand for EEE (Baldé *et al.*, 2017). Pakistan being considered among the high populus country, with increased purchasing power have promoted the demand for EEE through several sectors such as telecommunications, IT and home appliances (Iqbal *et al.*, 2015). Chinese manufacturers accelerated the affordability of low-income groups to purchase EEE (International Telecommunication Union, 2016).

Elevated growth of e-waste is intensified due to high technology adoption, results in obsolescence of EEE by manufacturers (McMahon *et al.*, 2021; Gollakota *et al.*, 2020; Cayumil *et al.*, 2016). This conditioned obsolescence is accelerated by limited innovative cycles in both software and hardware, where latest applications claim high memory and speed (Berkhout & Hertin, 2004), in result, equipment shortened its lifespan significantly (Babbitt *et al.*, 2009; Robinson, 2009). More oftenly, functional devices are also replaced prematurely, due to obsolescence of technology, leading to a disposal of second-hand devices in waste. For example, a study conducted 2012 highlighted that 60 % of TVs were marked obsolete which were still functional due to the modification of Liquid Crystal Display (LCD) or Light Emitting Diode (LED) from Cathode Ray Tube (CRT) (Ala-Kurikka, 2015). This trend indicates the small lifespan of EEE which result of rapid advances in technology.

Expectedly, a crucial factor manipulating demand as well disposal practices are concerns with regulations that government enforce. Involvement of government authorities is impactful in importing, domestic generation, carrying and recycling practices of e-waste (Liu *et al.*, 2023; Abalansa *et al.*, 2020; Borthakur & Govind, 2018; Iqbal *et al.*, 2015). In many regions of the world especially developing countries marked with lack of regulations, handling standards, environmental protection procedures, recycling mechanism, policy implementation, and undocumented trade stream from developed to developing countries results in facilitation and adaptation of informal recycling practices (Baldé *et al.*, 2017; Ismail & Hanafiah 2017).

According to the Global e-waste monitor (GEM-2020), national e-waste policy and legislation is implemented on 73 % of the world's population in 81 of the 193 countries till 2023 (Balde *et al.*, 2024). In Asia, the most populous countries, such as India and China, have national policies in place and ratified e-waste rules (Honda *et al.*, 2016; Yu *et al.*, 2010). A large part of the African, Eastern and Central part of Asia, and Caribbean countries entirely lacking with their national e-waste regulations (Patil *et al.*, 2020; Forti *et al.*, 2020; Osibanjo & Wath *et al.*, 2011). Therefore, there is lack or absence of policy efficacy from collection to recycling operations which ultimately results in poor actions (Forti *et al.*, 20 20; Baldé *et al.*, 2017).

On the global scale, Basel Convention is an international treaty aiming to regulate hazardous waste with its transboundary movement and disposal, which was initially regulated in March 1989 (United Nations Environment Program 2011). The convention came into imposing next to the finding of toxic waste imported into Africa and other regions of the developing nations. The primary goal of the convention is to safeguard human health and the environment due to harmful outcomes of hazardous and toxic waste matters (United Nations Environment Program 2011). Basel decisions were adopted by 29-OECD countries to restrict toxic waste to non-OECD countries in 1998 (Basel Action Network 2011).

1.3 Why e-waste is important

E-waste contains several hazardous chemicals like brominated flame retardants (BFRs), mercury and several others heavy metals creating considerable environmental and health consequences due to insufficient discarding and recycling methods. Each year, an expected 71 kilotons of BFRs and 50 tons of mercury from undocumented e-waste streams add to environmental pollution properly collected and processed (Figure 1.1). Approximately $57 billion worth of e-waste raw material is generated in 2019, while only $10 billion was recovered formally. Copper, iron, and gold were the most contributing metals in total worth (Forti *et al.*, 2020). Out of total e-waste generation on global scale, undocumented volume counts for 82.6 % which is mostly streamed out into the developing countries, while only 17.4 % is WEEE is a combination of metals, ceramics, glass, and plastics, and all these materials may restrain poisonous chemicals like Brominated flame retardants (BFRs), polychlorinated biphenyls (PCBs), novel brominated flame retardants (NBFRs), halogenated alternative flame retardants (HFRs), metals, and many further potentially harmful chemicals (Robinson, 2009).

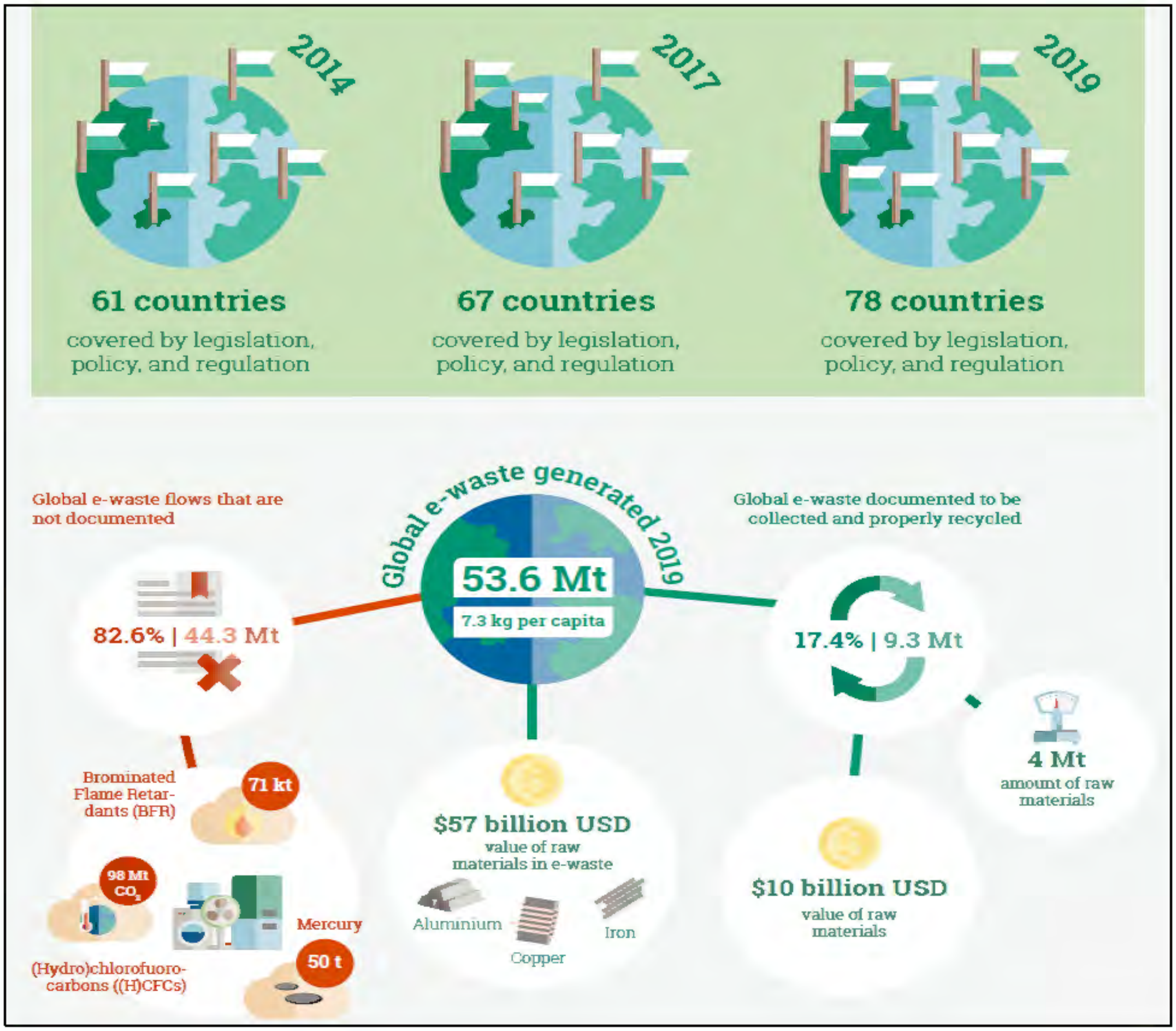


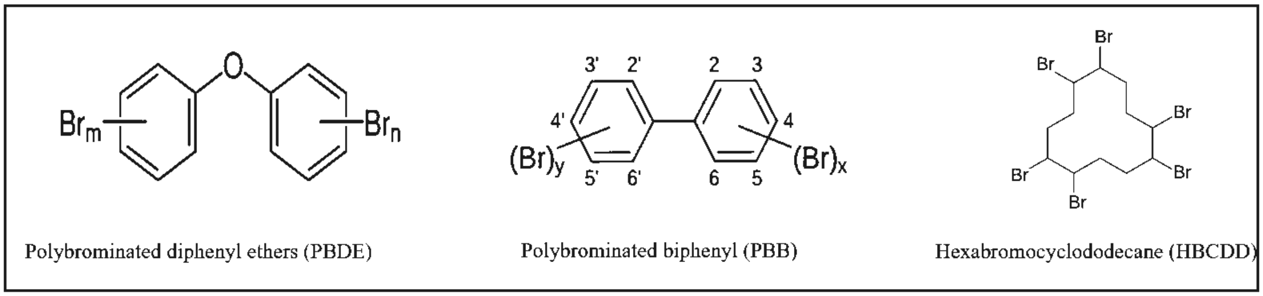
Figure 1.1: Global e-waste database and streaming with potential environmental concerns (Adopted from Forti *et al.*, 2020)

To diminish the flammability of various polymers including synthetic fiber, plastics, polystyrene, polyurethane foam, and some other few plastics that are mostly utilized in textiles, circuit boards, vehicles, furniture, electronic equipment and in plastic materials (Matsukami *et al.*, 2015) the FRs are used. Bromine containing (BFRs), chlorine containing flame retardants (CFRs) and Phosphorus containing flame retardants (PFRs) has commonly been utilized in electronic equipment (Bergman *et al.*, 2012) but polybrominated diphenyl ethers (PBDEs) were the most extensively used FRs chemicals used recent decades (Alcock *et al.*, 2003). Most numerous FRs that are used extensively are hexa-bromocyclododecane (HBCDD), tetra-bromobisphenol A (TBBPA) derivatives and (PBDEs) (De Wit, 2002). Many of these FRs are extremely constant in the ecosystem and a cause for ecological pollution due to use of commercial consumer products, emission from production units and during discarding (Shaw *et al.*, 2010; Imm *et al.*, 2009).

Since the 1960s, PBDEs have been used and are set up in a variety of user stuffs, including mattresses, TVs, toasters, drapes, and mattresses. They are synthetic chemicals used as additives to slow down the rate of catching fire and give people more time to escape or put out the fire. There is a relatively weak carbon-bromine bond in the structure. Due to thermal instability of the bond, bromine radicals release quickly by thermal energy and this radical combines with carbon radical and reduces flammability by producing carbon monoxide (Hooper *et al.*, 2000; Szymanska, 1996).

There exist about 209 theoretical PBDE congeners, categorized into ten congeners from mono - deca Bromo-diphenyl ether. Commercial polybrominated diphenyl ether is made from a mixture of diphenyl ethers in different percentages. PBDEs have the potential of bioaccumulation in humans and wildlife and are suspected of their adverse effects on human health (Shaw *et al.*, 2010; Fernandez *et al.*, 2007) and endocrine disorder (Yang *et al.*, 2022). Therefore, it has attracted international attention (Legler, 2008). HBCDD is also used as an additive flame retardant to provide fire protection for vehicles and construction materials, especially in expanded and extruded polystyrene foam insulation. It has also been used in textile applications and electrical and electronic equipment, but to a lesser extent (Stockholm Convention, 2017). Polybrominated biphenyl (PBB) is widely used in plastic products and textiles. PBBs were banned a long time ago and are no longer used or produced. However, when it is widely used, there may still be products of the time. In the 1970s, HBB was mainly used as a flame retardant (Stockholm Convention, 2017). The chemical nature of the target chemicals of interest in the present study are given in Figure 1.2.

The accumulation tendency of metals in the human body is a matter of concern. For example, lead and cadmium are related to bone, blood, cardio-vascular and nervous system diseases (Jarup, 2003). Exposure of excessive amounts of copper may have poisonous impacts on the human body (Brewer, 2010). Beryllium can affect the lungs and/or skin and respiratory system (U.S. Toxic Substances and Disease Registry, 2008). Mercury with excessive accumulation in human body may be fatal and lower amount can also cause bad effects on the reproductive, immune, cardiovascular, and nervous systems (Env -Health, 2017).



Polybrominated diphenyl ethers (PBDE) Polybrominated biphenyl (PBB) Hexabromocyclododecane (HBCDD)

Figure 1.2: Chemical structure of target compounds i.e., POP-FRs selected in current study

In recent years, the international scientific community has expressed concern about the adverse health effects of halogenated or non -halogenated organic flame retardants (FR) that are releasing from electronic waste recycling to the environment and humans. Therefore, Stockholm Convention's Annex A (Stockholm Convention, 2017) included these FRs i.e., commercial poly-brominated diphenyl either (commercial pentabromodiphenyl ether for furniture foam), commercial octa-bromodiphenyl ether (for electronics) and commercial deca-bromodiphenyl etiher (for plastics/composites/polymer) materials, adhesives, sealants, textiles, coatings and HBB and HBCDD. So, it is officially recognized as POPs. Therefore, persistent organic pollutants polybrominated diphenyl ethers would prohibit its export/import, use, and production. In addition, the Stockholm Convention (Article 6) discusses the management of POPs originating from waste to protect humans and environmental health. Therefore, the signatories of the convention need to minimize (remove) the discharge of figured chemicals in stocks and wastes. Being the signatory of the Stockholm convention, Pakistan starts to force its implementation in 2008.

1.4 Scenario of e-waste in Pakistan

Pakistan being the 6th most populus country in the world while developing infrastructure and economy is still compromised (Wang *et al.,* 2022). Most of the people have a limited purchasing resource of new and advanced electrical equipment, so they mostly buy secondhand products (Iqbal *et al.,* 2015). Such a situation generates a market demand for less expensive secondhand items to be imported into the country. Where crude recycling practices are implemented like open burning, physical dismantling, acid bath, and use of blowtorches to obtain valuable materials, all these procedures are very cost efficient.

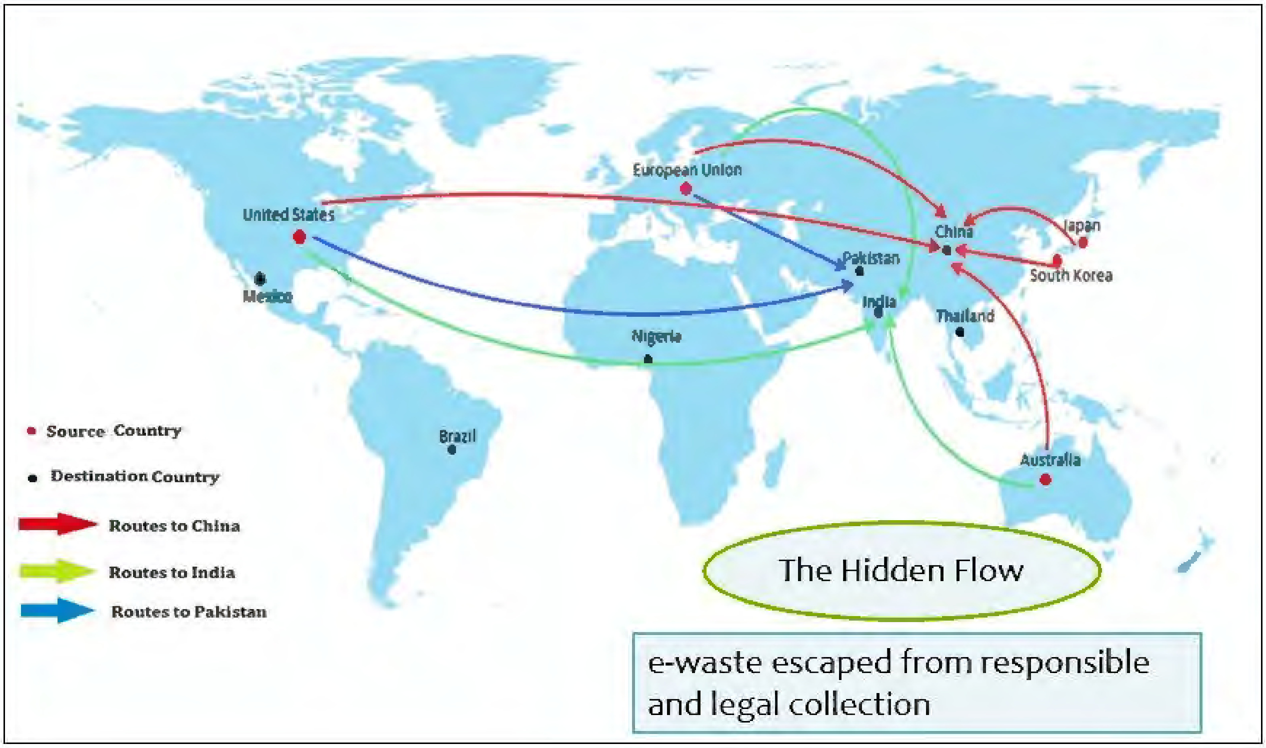


Figure 1.3: Global flow of e-waste (Iqbal *et al.*, 2015)

The scale of informal recycling is growing day by day in Pakistan and is grown in all over the country (especially in mega-cities) as large- and small-scale business (Umair *et al.*, 2013). While availability of cheap labor, potential of resource recovery and availability of raw material encourages the informal sector to grow with speed (Imran *et al.*, 2017). We cannot ignore the advantages of employing e-waste recycling from a socio-economic perspective due to employment opportunities and material recovery output for the people involve in this business. Pakistan is documented as a dumping base for e-waste from different overseas regions (Figure 1.3) with increasing import quantity (Baldie *et al.*, 2024; M; Puckett *et al.*, 2005).

E-waste contains precious and harmful materials, producing valuable social and environmental consequences. However, it also signifies commercial prospect given its capability for formal recycling operations (Perkins *et al.*, 2014; Robinson, 2009). Many developing countries including Pakistan produce a significant amount of e-waste domestically, while a huge volume is imported with the title of second-hand item and sometime in the name of charity. Despite the lack of formal recycling facilities such waste is treated informally with local unregulated methods (Abid *et al.*, 2019; Sajid *et al.*, 2019; Umair *et al.*, 2016; Iqbal *et al.*, 2015), which pose environmental and human health related consequences (Kazim *et al.*, 2023: Shakil *et al.*, 2023;

Iqbal *et al.,* 2017). Pakistan generates a significant volume of e-waste, with approximately 559 kt produced in 2022 compared to 433 kt in 2019, representing a ~40 % rise and ranking it as the 20th biggest e-waste producer globally (Forti *et al.*, 2020).

1.5 E-waste Streaming in Pakistan

The e-waste streaming in Pakistan is explained in Figure 1.4 using a flow chart. The import of EEE and domestic generation, whether legal or illegal, are Pakistan's two major sources of e-waste (Iqbal *et al.,* 2015). Pakistan generated 559 kilotons (kt) of e-waste in 2022 as data reported in United nations report "The Global E-Waste Monitor 2024" (Balde *et al.,* 2024. The primary entrance point for e-waste is Karachi's marine port (Imran *et al.,* 2017). E-waste is collected by sellers and scrapers, after being disposed of from these sources. These individuals may then break down the e-waste into different valuable components, which are subsequently sold to extractors and dismantlers. By using informal procedures including open burning, manual disassembly, acid baths, and use of blow torches, recyclers and dismantlers recover valuable metals from this waste (Hameed *et al.,* 2020).

1.6 Policy/Regulation dealing e-waste in Pakistan

In addition to Pakistan Environmental Protection Act (PEPA)-1997, which adress some of the hazardous waste, Pakistan has recently formulated National Hazardous Waste Management (HWM) Policy in 2022. The policy is formulated to facilitate the execution of international conventions & treaties to progress the definition & implementation of HWM for improved environmental management, explain institutional duties and management related hazardous & other wastes. Additionally, some other policies and laws which address hazardous material, and their environmental concerns in Pakistan on national level are, National Environmental Policy 2005, Hazardous Substance Rules 2003, and Pakistan Penal Code. While the Import Policy Order 2007-08 and Trade Policy 2006-07 also prohibit the importation of toxic waste. Though all these rules and regulations exists but still no policy and regulation are available which specifically adress e-waste management in Pakistan. The country, being the signatory of the Basel Convention and other national and international agreements, the execution is still questionable. Consequently, Pakistan receives large volumes of e-waste from developed nations by trade which is treated informally (Kazim *et al.*, 2023; Shakeel *et al.*, 2022; Imran *et al.*, 2017; Umair *et al.*, 2016; Iqbal *et al.*, 2015).

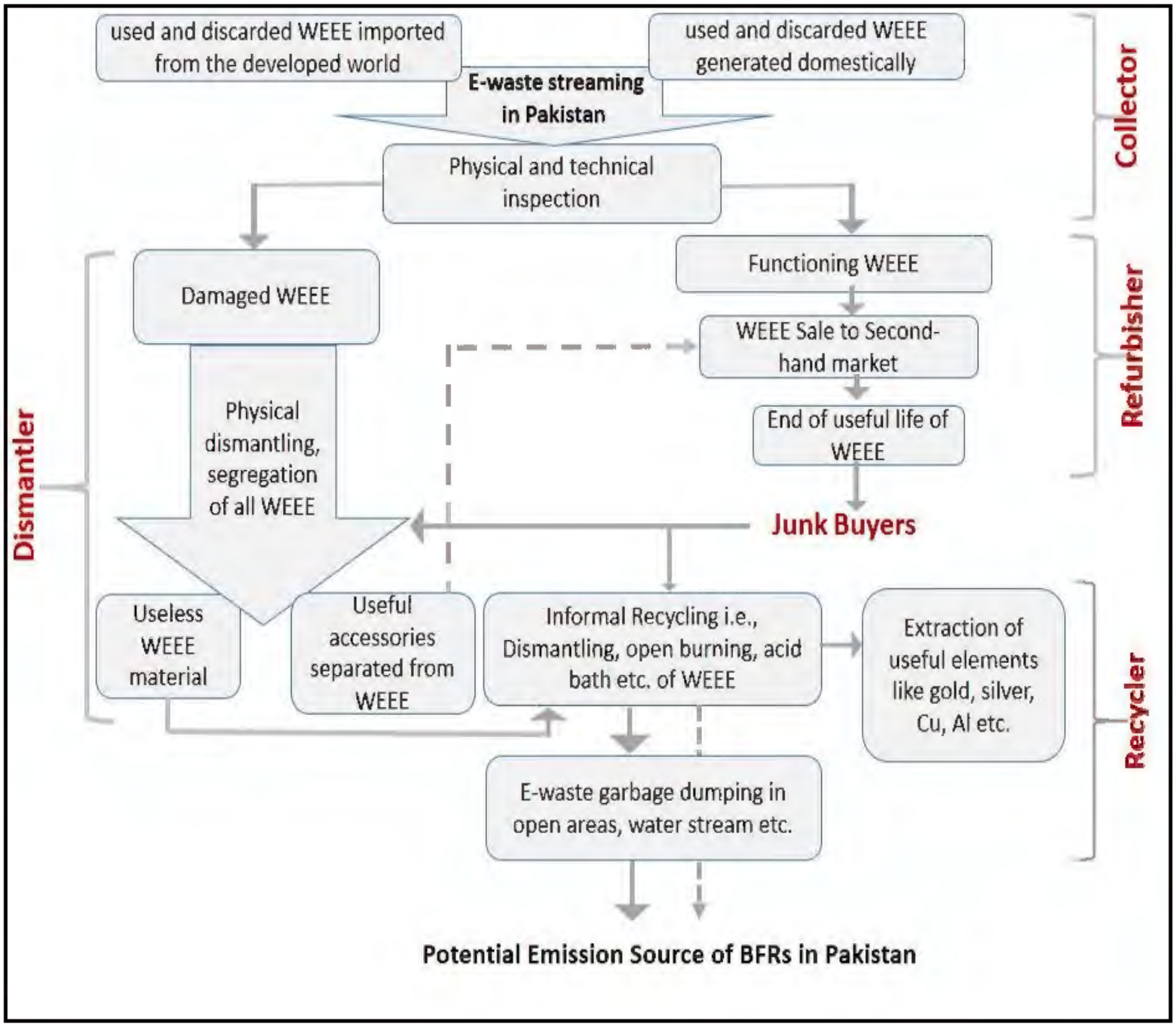


Figure 1.4: Flow of e-waste streaming in Pakistan

Management of e-waste is an increasing interest and concern all over the world. However, developing countries are considered particularly vulnerable due to informal recycling, poor management of recycling facilities and/or import from developed countries (Puckett *et al.*, 2002, Cobbing, 2008). However, lack of proper recycling technologies, waste treatment systems, contamination management and poor safety measures for workers and resident living in proximity of these operations have directed the environmental contamination and increased human exposure to hazardous substances like heavy metals, toxic gases, and various organic pollutants. Up till now, there is no formal e-waste recycling facility available in Pakistan; all the e-waste is recycled through illegal and/or informal means (Imran *et al.*, 2017; Iqbal *et al.*, 2015). Such ways to treat this toxic and hazardous waste (e-waste) contaminate the environmental matrices and human health related issues (Ádám *et al.*, 2021; Alabi *et al.*, 2021; Rautela *et al.*, 2021; Krishnamoorthy *et al.*, 2018). The following section elaborates the global and regional overview of the e-waste related chemicals of interest in the present study and their behavior in different environmental matrices.

1.7 Key environmental challenges due to informal e-waste operations

E-waste is becoming an increasing problem as due to advances in production technology and substitutes, and more unknown waste components enter the municipal waste stream. The country's absence of an organized management system, as well as low environmental laws and regulations, resulted in an increase of e-waste invading the country's environment. It has opened the way for unregulated, informal recycling processes to extract precious metals from garbage. In Pakistan, informal recycling practices are more common includes dismantling, open burning, acid bath and repairing and refurbishing methods without earlier familiarity of their composition and harmful material. Such informal practices can possibly pose a significant risk to humans and the environment.

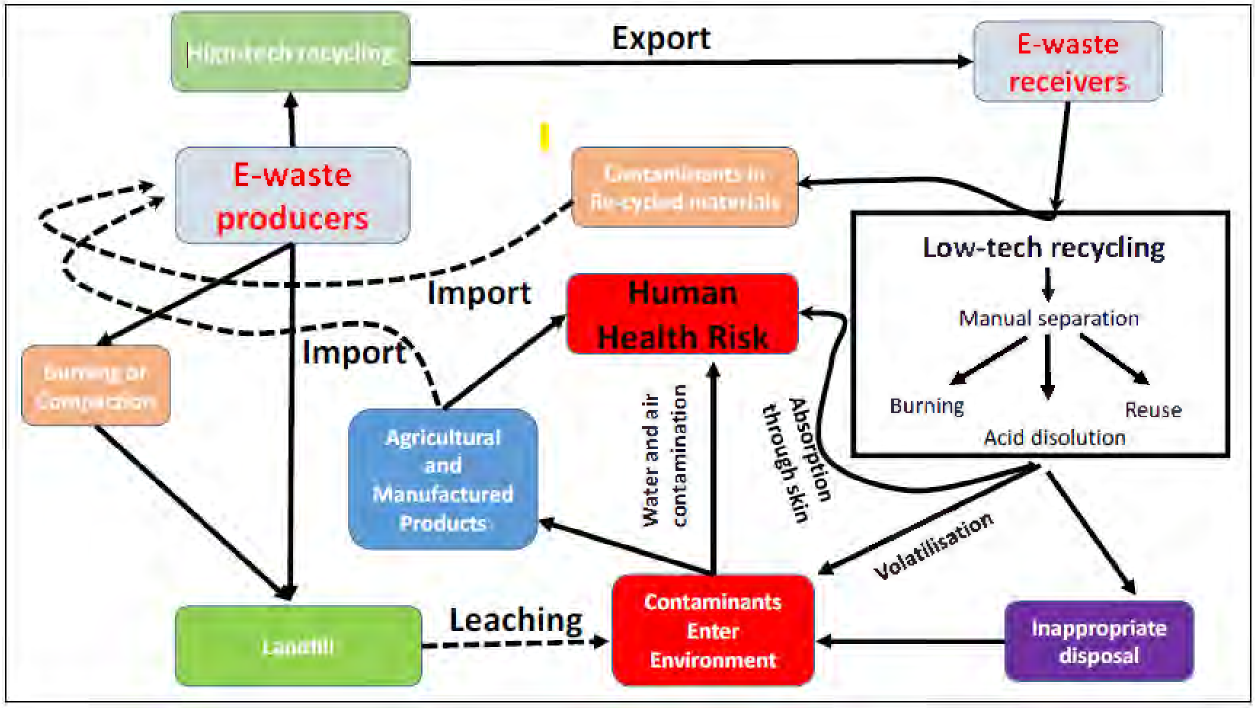


Figure 1.5: Human and environmental health implications of e-waste

Information about the outcomes of e-waste recycling is still developing, stakeholders naturally do not take the consequences of informal e-waste recycling procedures into account. While numerous research findings on the toxicity, composition, and health risks correlated with inappropriate recycling (Lin *et al.,* 2022; Ohajinwa *et al.,* 2019). While very few research investigations have been carried out in Pakistan to determine the pollution level of contaminants resulting from such operations (Shakil *et al.,* 2023; Iqbal *et al.,* 2017; Rafeeq, 2020), and the most of which lack in-depth insight and spatial scale limitations. Presently, there is no comprehensive research studies on the contamination posed by e-waste in any environmental matrices in Pakistan, similarly exposure routes have not been evidently identified nor understood, and the impacts on environment and human health are unknown. Such unhealthy practices influence the distribution of hazardous chemicals and other related pollutants in the atmosphere thereby polluting the environmental matrices (Figure 1.5).

1.8 Aims of the study

The current study was carried out with aim to quantitatively explore the impact of Stockholm Convention listed flame retardants i.e., POP-FRs and selected hazardous/toxic metals emissions from WEEE facilities in metropolitan cities of Pakistan. Contamination of e-waste related hazardous compounds were monitored seasonally from soil and atmospheric media all around the year to investigate the level of contamination and their impact on human health.

1.9 Objectives

The following objectives have been outlined to achieve the aim of this study:

(i) Quantify the levels and human exposure assessment of GEM in air from nearby and background site of selected informal e-waste recycling facilities in Pakistan.

(ii) Determine soil contamination and particle-bound deposition fluxes of selected heavy metals levels from nearby and background sites of selected WEEE processing facilities in Pakistan.

(iii) Quantify the levels and human exposure assessment of BFRs in soil and air from nearby and background sites of selected informal e-waste recycling facilities in Pakistan.

1.10 Thesis Outline

Chapter 1 Provide the introductory section of e-waste management issue at global level and more specifically to Pakistan. This chapter includes mega issue of informal e-waste operations related environmental and human health impacts, Objectives of the current research and possible outcomes.

Chapter 2 provides review on the sources and invasion of e-waste practices in Pakistan, the review includes human health and ecological impact of such processes, exposure pathways and risk models employed in examining contamination levels. The studies were reviewed with the reason of justifying the research theme.

Chapter 3 provides methodological framework of the e-waste related compound which are the subject of interest. The chapter also details the study area, sample collection and preparation, analytical procedures and statistical approach to present the data. Additionally, detailed methodology for the ecological and human health related assessment are presented.

Chapter 4 presents the results and discussion part of the thesis. In detail all target compounds are discussed in different parts with publication. Part-1 comprises of results and discussion section of GEM emission into air, while Part-2 contain Heavy metals pollution in air and soil and Part-3 includes BFRs toxicity in soil near e-waste recycling facilities in Pakistan.

Lastly, **Chapter 5** brings the dissertation to a close by going over the study's limits, implications, suggestions, and visions for beyond research.

Chapter 2

Review of Literature

2.1 Gaseous Elemental Mercury (GEM)

Worldwide, there is a massive export of e-waste from some developed to developing nations, where employees could be subjected to elevated levels of mercury (Hg) because of informal and uncontrolled e-waste processing (Wilson *et al.,* 2018; Gravel *et al.,* 2020). In some parts of the world, like Europe and North America, mercury emissions to the environment have fallen; however, in other regions, such as Africa and Asia, emissions have risen (Streets *et al.,* 2019). As reported by Bagnati *et al*. (2015), human-induced releases of mercury to the atmosphere in the world are expected to have reached 2225 tons yearly in 2015. Mercury concentrations are rising much over their natural limits. Mining, extracting precious metals, burning coal, producing chemicals, producing items that contain mercury, and processing e-waste informally are among the activities which generate these emissions (Pirrone *et al.,* 2010; Pacyna *et al.,* 2010; Moody *et al.,* 2020; Anselm *et al.,* 2021; Amponsah *et al.,* 2022).

The dispersion through space and time, as well as its eventual transfer to other environmental matrixes, are all established by its chemical form. GEM may travel long distances and stay in the atmosphere for an extended period i.e., up to a year before distributing to remote areas. PBM and GOM, on the other hand, are immediately deposited locally and regionally into aquatic and terrestrial ecosystems and have a shorter atmospheric existence (Pirrone *et al.,* 2010; Driscoll *et al.,* 2013).

Investigating GEM levels in air is fundamental because of its widespread dispersion and persistent nature in the atmosphere. It has been determined that long-term average GEM concentrations in air could reliably acquire applying passive samplers (Jeon *et al.,* 2020; Naccarato *et al.,* 2021). These samplers may be installed in large quantities and concurrently to provide high spatial resolution measurements of GEM air concentrations at and near possible sources since they are easy to handle, affordable, and do not require a active energy requirements (McLagan *et al.,* 2018a). Therefore, this makes it possible to find out the traces of GEM concentrations into the atmosphere (Tao *et al.,* 2017; Streets *et al.,* 2017) and to evaluate such levels (McLagan *et al.,* 2019).

Although Pakistan ratified the Minamata Convention on October 10, 2013, the accomplishment of programs to reduce Hg emissions has been hampered by a lack of regulatory mechanisms and baseline data (Sattar, 2020; Hina *et al.,* 2021). Numerous significant sources of Hg in Pakistan have been assessed in current years by monitoring research studies. These research studies were mainly conducted on emission sources at chlor-alkali plant near Lahore (Jamil *et al.,* 2015), ship-breaking yard in Gadani (Baluchistan Coast) (Kakar *et al.,* 2021) dental clinics (Khwaja & Abbasi, 2014), and few gold mining sites (Khan *et al.,* 2012; Biber *et al.,* 2014). However, at present there is lack of evidence in Pakistani literature about air monitoring and GEM source identification. Table 2.1 provides the overview of previous studies conducted worldwide for the monitoring of GEM emission to the atmosphere due to informal e-waste recycling operation. Additionally, this table provides the results of present study conducted on nine major urban cities of Pakistan to make a comparison. With previous studies to understand how such informal practices contributing to the overall emission in Pakistan. The details are also discussed in results and discussion session.

Table 2.1: Current average GEM concentrations (ng m^{-3}) and comparision with earlier global studies

Site	Region	Sampling location	Monitoring period	GEM (Mean ± SD) Range	References
Background levels					
Rawalpindi (this study)	Pakistan	Background	2020 − 2021	2.99 ± 0.71 (1.94 − 3.84)	This study
Summit of Mt. Leigong	South China	Air	2008 − 2009	2.80 ± 1.51 1.88 − 3.59	Fu *et al.,* 2010
Popocatépetl	Mexico	Rural/Volcanic	2019	1.72 ± 0.83 0.51− 5.5	Schiavo *et al.,* 2020
Kodaikanal*	India	Countryside	2012 − 2013	1.53 ± 0.25 0.83 − 3.25	Karthik *et al.,* 2017
		Air	2015 − 2016	1.53 1.38 − 159	Karuppasamy *et al.,*2020
Southern Hemisphere		Reference site	2016	1.1−1.3 (range)	Sprovieri *et al.,* 2016
Northern hemisphere		Reference site	2015	1.5−1.7 (range)	Venter *et al.,* 2015
E-waste Recycling Sites					
Peshawar, Faisalabad, Lahore, Rawalpindi, Karachi, Multan, Gujranwala, Quetta & Hyderabad	Pakistan	e-waste location	2020 − 2021	11.88 ± 2.12 (1.78− 92.07)	This study
Dar-es-Salaam city	Tanzania	e-waste location	2019	2.13 ± 1.57 0.79 − 5.34	Nipen *et al.,* 2022
E-waste recycling facility	Norway	e-waste location	2018	(5) Geomean 0.9 – 1140	Snow *et al.,* 2021
Taizhou*	China	e-waste location	2015	30.7 ± 9.9 16.7 − 43.4	Tang *et al.,* 2015
Others					
Mexico	Main city	Municipal town	2021.	5.60 ± 2.33 0.20 − 30.23	Schiavo *et al.,* 2022
Hefei	China	Municipal town	2016	2.53 ± 1.28 0.32 − 15.10	Yue *et al.,* 2021
Mexico City	Mexico	Municipal town	2019	3.80 ± 1.34 0.50 − 11.90	Morton-Bermea *et al.,* 2021

			2020	5.04 ± 2.95 0.50 − 32.60	
Chennai city*	India	Ambient Air	2015 − 2016.	4.68 3.62 − 5.40	Karuppasamy *et al.,* 2020
Zhongshan city*	China	Urban, EEE production unit	2019 − 2019.	2.4 ± 3.5 0.37– 49	Luo *et al.,* 2021.
Abbadia San Salvatore city	Italy	Hg mining sites	2016 − 2016.	1030 ± 1420 17 – 4200	Monaci *et al.,* 2022.
Presidente Plutarco Elías Calles city	Mexico	Coal power Units	2013.	2.8. 0.3 − 14	Garcia *et al.,* 2017.
Guangzhou	China		2010.	5.07 ± 2.89 1.87 − 29.9	Chen *et al.,* 2013.
		River sites		4.60 ± 1.36 2.7 − 11	
Guiyang city*	China	Cement & coal Units	2000 − 2001	7.39. 1.7 − 147	Feng *et al.,* 2003.

* **Total gaseous mercury (TGM)**

2.2 Heavy Metals (HMs)

Informal e-waste recycling practices include acid baths, stripping/shredding and open-air burning, grilling, chipping, and melting plastics, disposing of unusable material in open fields and water bodies, etc., Through these activities, several heavy metals such as Pb, Cd, Ni, Cu, and other toxic chemicals such BFRS can be emitted into the surroundings. Thus, exposure of theses toxic elements to humans and their effects are of great concern (Song & Li, 2014). For example, exposure to Pb can affect the liver, kidney, and nervous system and impair cognitive development (Obeng-Gyasi, 2018; Bellinger, 2011). Cr can cause respiratory irritation, kidney, and liver damage, weakened immune systems, and cancer of the nose, sinus, or lung (Tchounwou *et al.,* 2012). Ni may contribute to dermatitis and bronchial asthma (Kuntawee *et al.,* 2020).

Recently, many studies have been conducted on harmful human health impacts induced by e-waste handling and recycling procedures. These research studies are continuously reporting the risks that reveal the toxicity of hazardous compounds. Unrestrained e-waste recycling procedure has been correlated to an increasing harmful health impact. Such human health related complexities includes negative birth outcomes (Zhang *et al.,* 2018), altered neurodevelopment (Huo *et al.,* 2019), hostile learning outcomes (Soetrisno *et al.,* 2020), DNA damage (Alabi OA *et al.,* 2012), negative cardiovascular issues (Cong *et al.,* 2018), respiratory effects (Amoabeng Nti *et al.,* 2020), immune system effects (Huo *et al.,* 2019), skin disorders (Eckhardt & Kaifie, 2024), hearing loss (Xu *et al.,* 2020), and cancer (Davis *et al.,* 2019).

Numerous studies have been reported on HMs emission into air contamination due to e-waste recycling worldwide Table 2.2, while only few studies in Pakistan are conducted in (Saleem *et al.,* 2018; Khan *et al.,* 2015; Mahmood and Malik, 2014; Shakil *et al.,* 2023) as per recent literature.

Table 2.2: Comparison of heavy metals (mean) concentrations in air from this study with previous studies (µg/m^2.day)

Location	**Site description**	**Cr**	**Mn**	**Ni**	**Cu**	**Zn**	**Cd**	**Pb**	**References**
Peshawar, Faisalabad, Lahore, Rawalpindi, Karachi, Multan, Gujranwala, Quetta & Hyderabad (µg/m^3)	e-waste recycling, dumping sites	0.016	0.11	0.037	0.085	0.64	0.002	0.097	This study
COMSATS University Islamabad (µg/m^3)	Background site	0.005	0.029	0.009	0.022	0.147	0.0001	0.044	This study
Guiyu, China (µg/m^3)	PCB recycling workshop	-	0.16	0.08	0.57	3.32	0.08	4.4	Bi *et al.,* 2010
Guiyu, China (µg/m^3)	E-waste recycling	.004	.08	-	-	-	.05	.016	Zheng *et al.,* 2016
Jiangsu, China (µg/m^3)	PCB recycling workshop,	0.17	-	-	1.22	-	0.028	1.4	Xu *et al.,* 2012
Bangalore, India (µg/m^3)	E-waste recycling	18	59.6	-	111	191	1.48	89	Ha *et al.,* 2009
Chennai, India (µg/m^3)	E-waste recycling	14	31.6	-	8.98	221	6.84	73	Ha *et al.,* 2009
Moradabad, India (µg/m^3)	E-waste recycling	3.6	-	5.1	76	66.8	-	9.6	Gangwar *et al.,* 2019

In addition to the air contamination of HMs, numerous studies have been reported on the contamination into soil due to e-waste recycling worldwide Table 2.3, while only few studies in Pakistan are conducted in (Khan *et al.,* 2015; Shakil *et al.,* 2023) as per recent literature. Soil is a valuable environmental component that can provide facts on the distribution, amount, and fate of pollutants in the surface environment (Bi *et al.,* 2011, Labunska *et al.,* 2013, Ma *et al.,* 2009).

Leung *et al.* (2008) reported that higher mean concentrations of Pb 110,000, Cu 8360, Zn 4420, and Ni 1500 mg/kg were present in workshop soil, and Pb 22,600, Cu 6170, Zn 2370, and Ni 304 mg/kg were present in the dust on nearby roads. The Pb and Cu levels in the road dust were 371 and 155 times higher, respectively, than for non-e-waste sites located 8 and 30 km away. Furthermore, while comparing with previous research (Fang *et al.,* 2013, Xue *et al.,* 2012, Zhu *et al.,* 2012), the average Pb concentrations in workshop soil were much higher.

A possible explanation for this inconsistency might be due to earlier e-waste recycling procedures employed informal procedures. Bi *et al.* (2011) investigated the concentration levels of Sb and As in indoor dust from thirteen Guiyu e-waste recycling operational sites. In contrast, the As levels in the soil (5.4 – 17.7 mg/kg) were similar to the control locations' reference sites. Similarly, Zhu et al. (2012) analyzed HMs levels in soil from family-run workshops in a Guiyu neighborhood affected by e-waste recycling. Of all the heavy metals, Pb had the high concentration (892 mg/kg) in the dust, although it was still lower than in previous research and even lower than in official e-waste recycling companies (Fang *et al.,* 2013, Xue *et al.,* 2012). Pb was more promptly discharged into the recycling lines' atmosphere than Cr, Ni, Cu, and Cd, according to Fang *et al.* (2013). There was a noticeable differentiation in the results among manual workshops and mechanical workshops: the mechanical processes present higher Cr, Cd and Ni concentrations, while manual dismantling produced more Cu and Pb.

Table 2.3: Comparison of heavy metals (mean) concentrations in soil from this study with previous studies (ug/g dw)

Location	Site description	Cr	Mn	Ni	Cu	Zn	Cd	Pb	References
Peshawar, Faisalabad, Lahore, Rawalpindi, Karachi, Multan, Gujranwala, Quetta & Hyderabad	E-waste recycling, dumping sites	49.4 (25 - 112)	371.8 (299 - 477)	37.3 (19 - 79)	155.2 (17 - 457)	219.9 (62 - 514)	0.6 (0.1 - 1.3)	63.1 (12 - 172)	This study
COMSATS University Islamabad	Background site	19.5 (16.5-23.)	210 161-296	12.2 8.3-18.8	11.9 8.9-13.63	45.5 41.6-49.3	0.11 0.10-0.14	7.97 4.87-9.16	This study
Delhi, India	E-waste recycling sites	-	-	-	1883.55	226.14	1.55	596.93	Arya *et al.*, 2021
Lagos, Nigeria	E-waste recycling	23 - 35.5	92 – 255	23 – 41	3165 – 5880	863 - 10641	8.67 - 26.4	911 – 2418	Isimekhai *et al.*, 2017
Qingyuan, China	Dismantling Site	20.5 – 297	88.7 – 728	6.27 – 269	78.7 – 13640	-	0.18 - 57.2	45 – 1688	Han *et al.*, 2019
	Burning Site	36 – 262	69 – 377	6.63 – 129	71 – 29650	-	0.26 - 29	52 – 10993	
Ashaiman, Ghana	Dumping & burning sites	21 - 77.3	-	-	48.4 - 114.9	-	0.39 – 4.1	77 – 341	Teye *et al.*, 2023

2.3 Brominated Falme Retardants (BFRs)

Persistent in nature and resistant to environmental degradation, POPs are synthetic organic chemicals/compounds (Eqani *et al.,* 2012; Khairy & Lohmann, 2013; Zhang *et al.,* 2008). PBDEs, OCPs (e.g., DDT, Chlordane, Endosulfan, Hexachlorocyclohexane, Hexachlorocyclobenzene, Adrin, Endrin), PCBs, and Polychlorinated dibenzo-p-dioxin and-furans (PCDD/Fs) are among the several groups of POPs. POPs have been extensively used in industrial sectors across the world for many decades (Ali *et al.,* 2014; Kurt-Karakus *et al.,* 2018). BFRs are entirely used as additives in diverse plastic applications such as EEE. BFRs have the capacity to be released into the environment during disposal (McGrath *et al.,* 2018), production (Li *et al.,* 2016), and use at any other stage (Choi *et al.,* 2017). Table 2.4 presents the contamination of soil with BFRs due e-waste operation in different regions of the world.

E-waste is a heterogeneous combination of metals, plastic, ceramics and glass (Robinson, 2009). Plastic in WEE is considered to contain largest share of POP-BFRs in waste stream (Petreas & Oros, 2009; Schlummer *et al.,* 2007; Wager *et al.,* 2010, 2012, Stockholm Convention, 2012). Contamination of air, soil, water, sediments and food in Asia have been reported in various studies (US EPA, 2016 b; Woo *et al.,* 2016; Tansel, 2017; Chen *et al.,* 2011, Li *et al.,* 2011, Luo *et al.,* 2011, Wong *et al.,* 2007, Zheng *et al.,* 2013).

PBDEs have been used since the 1960s and are found in a variety of consumer products, from TVs and toasters to mattresses and drapes. They are synthetic chemicals used as additives to slow the rate of ignition and fire growth, allowing people more time to escape from a fire or extinguish it. There is a relatively weak carbon-bromine bond in the structure and this bond is thermally labile, hence the thermal energy releases bromine radicals that intercept carbon radicals to decrease flame, while simultaneously reducing heat and carbon monoxide production (Hooper *et al.,* 2000; Szymanska, 1996).

Ling *et al*. (2022) conducted a study on the 55 soil samples taken from abandoned and a newly built e-waste dismantling zone in China. The concentrations of PBDEs ranged from 78.0 to 13,300 ng/g dw, while BDE-209 was the most dominant congeners among all in both sites. In soil samples taken from 20 various soil locations, Zhang *et al.* (2021) investigated 18 HFRs from an e-waste recycling site. Levels ranged from 0.24 to 153 mg/g and 600 to 14,200 particles/kg, for plastic and soil samples respectively, which were at the high compared to literature.

Various hazardous elements including POPs are commonly known to have capability to migrate and/or move into the environment, persist for long time, and may accumulate to some extent which could be dangerous to human and biota. POPs, with special features, have unique physical and chemical properties, upon releasing into the environment; they remain altogether due to their potential to oppose degradation phenomenon (Buccini, 2003; Wang *et al.,* 2005). Various hazardous elements including POPs are commonly known to have capability to migrate and/or move into the environment, persist for long time and may accumulate to some extent which could be dangerous to humans and biota. POPs, with special features, have unique physical and chemical properties, upon releasing into the environment; they remain altogether due to their potential to oppose degradation phenomenon (Buccini, 2003; Wang *et al.,* 2005). BFRs used in the greatest quantities are tetrabromobisphenol A (TBBPA) derivatives, PBDEs and HBCDD (De Wit 2002; Lassen *et al.,* 1999). Many of these FRs are highly persistent in the environment and a cause for environmental contamination because of discharges from production plants, from the use of commercial consumer products and from the end-of-life materials (Allen *et al.,* 2008; Imm *et al.,* 2009, Shaw *et al.,* 2010, Wong *et al.,* 2007).

Table 2.4: E-waste originated levels of BFRs in soils from different regions of the world (ng/g dw)

Regions/Sampling Year	Compounds	Concentrations	Description of sampling sites	References
PBDEs				
9 cities of Pakistan/2021–22	Σ_{27}PBDEs	Informal e-waste recycling sites: 0.76 – 1.1×10^3 Background sites: 3.26-82.5	32-informal e-waste recycling sites in mega-cites Nine background sites in each sampling city	This Study
Hangzhou, China	Σ_{10}PBDEs	Without BDE-209: 0.34–69.3 BDE-209: 0.33–68.5	E-waste dismantling site	Zhou et al. (2021)
Guiyu, China/2018	Σ_{20}PBDEs	E-waste dismantling park: 1.54×10^3–3.10×10^5 Surrounding area: 11.6−3.60×10^4	An e-waste dismantling park and surrounding area	Ge et al. (2020)
Melbourne, Australia/2017	Σ_8PBDEs	Site A: 34−5.00×10^3 Site B: 8.3−9.80×10^4 Reference sites: 0.10−44	Samples were collected from the vicinity of two e-waste A and B, and reference sites	McGrath et al. (2018)
Tianjin, China/2015	Σ_{14}PBDEs	5.9−2.70×10^3 Central area: 138 (mean) Surrounding area: 16 (mean)	Ziya e-waste recycling area including central area and surrounding area	Wu et al. (2019)
Lagos, Ibadan, and Aba, Nigeria/2015	Σ_{17}PBDEs	City of Lagos: 4.67 ± 4 (control), 2.09×10^3 (burning sites), 1.58×10^3 ± 7.40×10^3 (dismantling sites), 3.19 ± 3.19 (repair sites) City of Ibadan: 1.05×10^3 (control), 6.97×10^3 ± 9.24×10^3 (burning sites), 1.80×10^3 ± 639 (dismantling sites) City of Aba: 77.7 ± 61.8 (control), 206 ± 206 (burning sites)	Three cities with different functions	Ohajinwa et al. (2019)
Ghana/2015	Σ_8PBDEs	e-waste: 15.6 - 96.8	e-waste dump site in the Greater Accra Region	Akortia et al. (2017)
Guiyu, China/2004 & 2014	Σ_{13}PBDEs excluding BDE209	Year of 2004: 0.64−670 Year of 2014: 12−2.10×10^3	The whole sampling area and a reference site	Li et al. (2018)
Yen Province, northern Vietnam/2012	Σ_{13}PBDEs	e-waste-processing workshop: 37–9200 open-burning sites 1.6–62 refernce site footpath: 0.048–12	e-waste sites	Matsukami et al. (2017)
South Korea/2012	$\sum_{23}$BDEs	e-waste site: 1.3-17,	e-Waste recycling	Li et al. (2016)
Vietnam/2012	Σ_{23}PBDEs	E-waste sites =68^a	e-waste recycling sites	Li et al. (2016)
China/2012	Σ_{23}PBDEs	e-waste sites: 60-14000	Factory region of e-waste	Li et al. (2016)
Guiyu, China/2009	Σ_{37}PBDEs	E-waste disposal area: 13−1.01×10^3 Two background sites: 4.3 and 5.7 Three adjacent towns: 8.7, 2.6 and 10	Sampling area included e-waste disposal area, two background sites and three adjacent towns	Xu et al. (2017)
Guiyu, China/2012	Σ_{10}PBDEs	Residential area: 168−6.54×10^3 Agricultural area: 10−4.45×10^3	Sampling area included residential area and agricultural area	Zhang et al. (2014)
Guiyu/2004	Σ_{23}PBDEs	e-waste site: 893-2890, reference site:2.0−6.2	proximity to the dismantling workshops dismantling and recycling of e-waste	Leung et al. (2007)
Taizhou, China/2008	Σ_8PBDEs	1.20×10^3, 27.9, 131, 1.89×10^3, 3.13×10^3, and 64.4 (reference site)	Five sites adjacent to e-waste recycling activity sites and a reference site	Tang et al. (2013)
Guangdong Province, china/2011	Σ_{41}PBDEs	e-waste dismantling site: 13.9−13300	Samples taken near 1300 e-waste recycling workshops	Wang et al. (2014)
Guangdong Province, china/ 2005-2006	Σ23PBDEs	e-waste dismantling site: 190.8–9156	Samples taken near 1300 e-waste recycling workshops	

Guiyu, China/2004	Σ_{13}PBDEs	$219-1.42\times10^3$	From a large e-waste open burning site	Luo et al. (2012)
PBBs				
China/2018	PBBs	47.9 (reference soil: 0.58) [b]	e-Waste recycling	Ge et al. (2020)
Dali, China/2016	PBBs	58-8700	e-waste recycling sites	Zeng et al. (2016)
Dali, China/2016	HBBs	10-160	e-waste recycling sites	Zeng et al. (2016)
Australia/2014	HBBs	ND-0.34 (reference soil: ND)	Incinerator	McGrath et al. (2017)
China/2018	HBBs	249 (reference soil: 0.57) [b]	e-Waste recycling	Ge et al. (2020)
Karachi, Pakistan/2014	HBB	e-waste sites: N.D.-461	Four e-waste recycling sites	Iqbal et al. (2017)
γ -HBCD				
Guangdong Province/2006-08	γ -HBCD	QY- Area:8.42−215 GY Area: 0.15−1.64 Industrial area: 0.474−0.518	e-waste recycling site	Gao et al. (2011)

[a]= mean, [b]=median

Chapter 3

Materials and Methods

3.1 Study Area

Nine mega cities including Lahore, Faisalabad, Gujranwala, Multan and Rawalpindi from Punjab province, Karachi and Hyderabad from Sindh province, Peshawar form KPK province and Quetta from Baluchistan Province along with sampling sites presented in Figure 3.1. Individual sampling sites (Table 3.1) were selected based on the following criteria: (1) conducting field surveys to locate sites involved in e-waste repair, dismantling, and refurbishment; (2) identifying national entry points; and (3) referencing previous studies (Shaikh, 2021; Sajid *et al.,* 2019; Imran *et al.,* 2017; Iqbal *et al.,* 2017, 2015; Umair *et al.,* 2016). Informal e-waste recycling sites were determined through the Air and soil samples were collected to calculate the contamination level of chemicals of interest from informal e-waste recycling facilities starting from September 2020 and December 2021. The detailed description of the sampling cities is given in the following sections.

Karachi city ranked 1st in population round 20 million people, is in Southern Pakistan and country's most important business Centre. Karachi being, the South Asia's biggest and busiest seaport, receive 85,251 tons (89 % in total) of e-waste annually (Imran *et al.,* 2017), which is then sold from sellers to scrap dealers and then to dismantlers who recycle it for secondary use and metal recovery (Iqbal *et al.,* 2015: Umair *et al.,* 2015). Karachi and is the biggest junkyard of Pakistan where all kind of used electronic and locomotive parts are dismantled, re-paired / recycled and then transported to entire country. Most of the city’s waste dumped into the Lyari River, which eventually makes its way through the mangroves and into the Arabian Sea. These wastes are a serious threat for coastal areas which become polluted for marine environment, marine life as well as human health (Tahir, 2017).

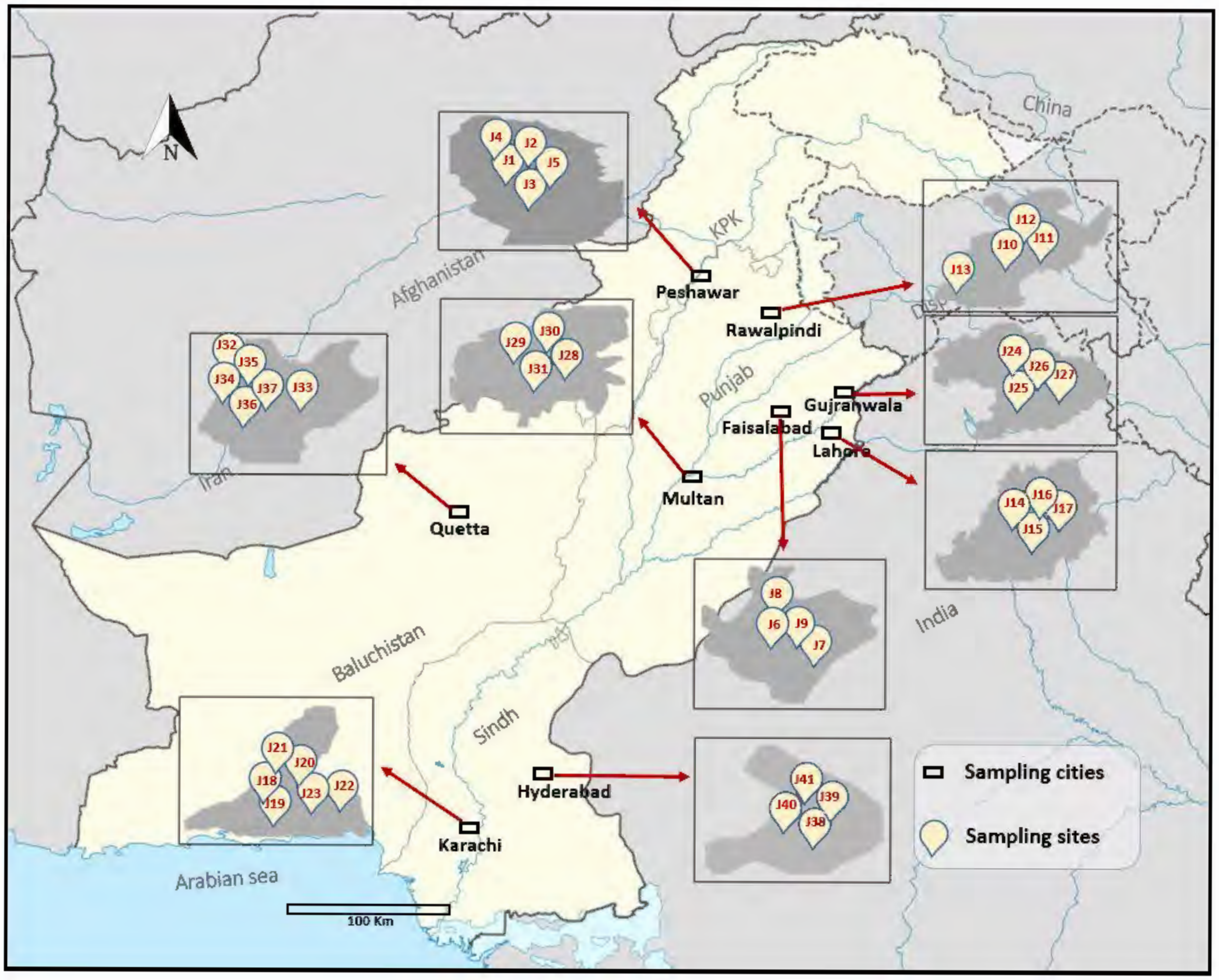


Figure 3.1: Study area map showing e-waste recycling facilities and background site in nine cities in Pakistan

Lahore stands among the largest business centers of e-waste which imports an average of 5807 tonnes (6.09 % of total) per year (Imran *et al.,* 2017). Hall road is the biggest electronic market in Lahore, where tonnes of second-hand equipment are offered for cheap prices by local vendors (Mehmood, 2022). The recycling processes are carried out by various factories and warehouses with non-ventilated rooms spread across all recycling sites. The hazardous chemicals used in the recycling, as well as domestic e-waste generated, are frequently dumped into the Ravi River via sewage (Rafique *et al.,* 2020). Although, many small informal recycling units were previously prohibited by local enforcement agencies to limit the emission of toxic materials into the atmosphere, hidden work is still on its way (Raza, 2010).

Peshawar is the capital and most populous city of Khyber Pakhtunkhwa, located near the Afghan border where most of the e-waste along with other equipment are illegally imported (Miankhel *et* *al.,* 2016). The city receives 1075 tonnes (1.13 % to total) of e-waste import from Taiwan with leading exporter followed by Japan, USA, and Europe (Imran *et al.,* 2017). Mostly, recycling activities at Peshawar city are carried out by teen-aged and women without any safety or protective measures.

Gujranwala city located at northeastern Punjab's is a center for small and medium based steel and metal extraction industries primarily functioning in urban areas (Ilyas *et al.,* 2017). According to Faiz *et al.* (2015), heightened air pollution in Gujranwala is due to industrial emissions, e-waste burning, tanneries, chrome plating facilities, and metal smelters.

Rawalpindi is located near the capital city (Islamabad), where e-waste recycling and disposal is far lower/small-scale compared to Lahore and Karachi (Iqbal *et al.,* 2015; Imran *et al.,* 2017). This city highlighted for various recycling activities include dismantling, repairing, refurbishing and metal recovery operations also reported by Hameed et al. (2020); Shaikh et al. (2020). Abbas et al. (2015) reported 624 tons of only computer waste was being generated in the twin cities (Islamabad & Rawalpindi) per year. Capital development authority (CDA) and Rawalpindi development authority (RDA) that are responsible for solid waste management in the twin cities, have not devised some management for e-waste so far. E-waste is being dealt with as municipal waste dumped in nearby areas without treatment (Dino & Mustafa, 2015). Many teen-age workers have been reported to be suffering from Asthma who were employed on these reported sites of Rawalpindi city involved in e-waste recycling (Saeed, 2013).

Faisalabad, known for the textile industry, which generates over 20 % of the country's GDP. The city has become a highly polluted hotspot site because of increasing industrialization, getting status of national commercial zone and rapid urbanization (Tabinda *et al.,* 2020). Most of the e-waste is dismantled here, and individual components are sold to recyclers.

Multan is located in south of the Punjab and many informal e-waste recycling including refurbishment, dismantling, and recycling for recovery of precious metal from laptops, mobile phones, printers, monitors, and other electronic gadgets were observed during survey study. While most of the e-waste illegally imported in Quetta from South-West (Chaman-Border) with Afghanistan and Pakistan Iran border (Sharif *et al.,* 2000). The imported e-waste then treated informally with involvement of low-income families including children and women to generate their revenue. According to Khoso *et al.* (2018), most of Hyderabad’s e-waste along with other solid waste lacks an effective management system from collection to disposal creating health and environmental problems.

Table 3.1: Brief description of individual sampling sites in each city with codes for all target compounds

Province	City	Site Name	Site Code	Latitude	Longitude	General description about site
KPK	Peshawar	Hazrat Jan road- b, d	J1	34.05597	71.55845	Small to medium dismantling, repairing and refurbishing industries and markets.
		Gula Ji- a, b, c, d	J2	34.00995	71.50159	Dismantling, sale/purchase of used ICTs, Printers, Air conditioned and all type of electrical and electronic equipment
		P. Saddar- a, b, c, d	J3	33.99993	71.53891	Buying/selling of second-hand ICT, equipment, scrap collection. Manual dismantling and refurbishing.
		Ring Road- a, b, c, d	J4	33.97421	71.46718	Dismantling and repairing of used equipment with refurbishment practices
		Karkhany- a, b, c, d	J5	34.00019	71.41028	Buying/selling of e-waste/second-hand ICT equipment imported from Afghanistan route, refurbishing & manual dismantling.
Punjab	Faisalabad	Qaim sain road- b, d	J6	31.42994	73.06833	Dismantling, repairing shops and markets.
		Rax City- a, b, c, d	J7	31.40606	73.10017	Largest sale/purchase of used electronic devices, printers, mobiles, LCDs and computer devices. Dismantling of ICTs.
		Sargodha road- a, b, c, d	J8	31.4374	73.08761	Sale virgin and second hand EEE & repairing of Imported used large/small electronic devices, dismantling and metal extraction.
		Motor market- a, b, c, d	J9	31.40989	73.05386	Manual dismantling, refurbishing and informal metal extraction, rewinding, repairing of electronic equipment.
Punjab/Federal	Rawalpindi/Islamabad	Dubai Plaza- a, b, d	J10	33.64107	73.07495	Buying/selling of second-hand ICT, equipment, and refurbishing. Manual dismantling of e-waste.
		Collage Road- a, b, c, d	J11	33.61112	73.05945	Buying/selling of second-hand ICT, equipment, scrap collection/ refurbishing, equipment. Manual dismantling and refurbishing.
		Pindi Sadder- a, b, c, d	J12	33.60065	73.05208	Buying/selling of second-hand ICT, equipment, scrap collection/ refurbishing.
		COMSATS Uni	J13	33.651592	73.156456	Overall, less populated, semi-agriculture zone, the university area is defined as the green campus.
Punjab	Lahore	Jail Road- b, d	J13	31.49682	74.29279	Manual dismantling, rewinding, repairing of electronic equipment.
		Hall Road-a, b, c, d	J14	31.56411	74.31662	Selling small second-hand ICTs, Mobile phones, laptop equipment/parts, repairing and dismantling
		Misri Shah-a, b, *c, d	J15	31.58978	74.3328	Informal recycling of Printed circuit boards, acid bath and dismantling practices.
		Abid Market-a, b, c, d	J16	31.55061	74.31429	Repairing and dismantling market of small and large electronic equipment.
Sindh	Karachi	Surjani road- b, d	J17	24.88934	67.34691	Small to medium dismantling and refurbishing factories and shops.
		Sher Shah-a, b, c, d	J18	24.88558	66.99342	The biggest junkyard of Pakistan for used electronic and locomotive parts dismantling and recycling.
		Bhens Colony-a, b, c, d	J19	24.83702	67.24817	Commercial areas surrounded by heavy industries and e-waste piling, dismantling site.
		Layari-a, b, c, d	J20	24.87855	67.00657	Densely populated area of the city with mixed residential and commercial areas in close proximity of Sher Shah site.
		Gulshan-e- Haded-a, b, c, d	J21	24.88934	67.34691	Suburban, close proximity of industrial area, chemical and wastes recycling, repairing and open burning

		Orangi Town- a, b, c, d	J22	24.94945	66.98943	The site is located in close proximity of the largest industrial area, e-waste refurbishment, dumping, repairing
Punjab	**Gujranwala**	Canal Road- b, d	J23	32.09603	74.1838	City's busy center for e-waste recycling mainly, refurbishing and recycling practices.
		Kamoki- a, b, c, d	J24	31.9653	74.27164	Small villages with open burning and dismantling practices. Imports containers of e-waste from China and Europe.
		Parao road-a, b, c, d	J25	32.15138	74.18317	Manual dismantling and refurbishing. Informal recycling, precious metal extraction factories.
		Industrial Estate- a, b, c, d	J26	32.11371	74.16846	Biggest zone of the buying/selling of e-waste. Informal recycling PCBs, include acid baths, open burning etc.
Punjab	**Multan**	Sui Gas Road- b, d	J27	30.1486	71.43522	Dismantling markets and sale/purchase center of e-waste.
		Aziz hotel- a, b, c, d	J28	30.18477	71.45181	Densely populated area with dismantling and repairing of electronic devices
		Rasheed abad- a, b, c, d	J29	30.21375	71.48829	Hub of small home-based informal recycling activities, open burning of PCBs to recover precious metals.
		Khan Plaza- a, b, c, d	J30	30.19147	71.4375	Centre of the city, repairing/resale practices of laptop, mobile, printers, monitors and related devices.
Balochistan	**Quetta**	Sariab Road- b, d	J31	30.12138	66.96135	e-waste repairing and dismantling sites. Few site were also recognized as used for dumping
		Western bypass- a, b, c, d	J32	30.17228	66.91665	The activities here include stone crushing and all e-waste recycling practices
		Suraj gang- a, b, c, d	J33	30.19893	67.01394	Commercial area known for electrical instrument segregation and repairing
		Wapda Colony- a, b, c, d	J34	30.25425	67.02094	Near to WAPDA workshop, where the major repairing of the transformers is done. It is located on the main airport road north of the valley
		Madrsa Road- a, b, c, d	J35	30.20263	67.03323	Commercial area well-known for dumping ACs, laptops, mobile phones and printers.
		Sabzal Road-a, b, c, d	J36	30.19213	66.97942	e-waste is transported, collected, stored, and segregated for reuse and recycling purposes.
Sindh	**Hyderabad**	Bypass road-b, d	J37	25.38501	68.36268	Dismantling markets in the vicinity of this location. E-waste trading is common here.
		Sepa office-a, b, c, d	J38	25.38399	68.34724	The site is behind another smaller mobile market in Hyderabad city where mobile phones and other electronic gadgets are being repaired.
		Metha Ram-a, b, c, d	J39	25.38876	68.36306	The site is main mobile and computer markets of Hyderabad City which deals with repairing of cell phones, desktop computers, iPad and laptops.
		Naseem market- a, b, c, d	J40	25.38501	68.35611	This location covers the major electronics market of Hyderabad City where the all the electronic goods i.e. TV, fridge, ACs etc. are repaired and resale.

a= Active sites for GEM, b= Active sites for HMs in air and soil, c= Active sites for BFRs in soil, d= Active sites for FRs in air

3.2 Sampling Scheme/Design

3.2.1 Air sampling

For air sampling of target compounds (gaseous + particulate), Passive Air Samplers (PASs) were employed during four subsequent continuing deployments i.e., Autumn, Winter, Spring and Summer) at chosen informal e-waste recycling locations throughout the country. Plate 3.1 showing the installation of different air samplers at random sites in the study area. Additionally, background site / sites were also selected at different location varying for selected compounds of target in this study. The average deployment timeframe for PASs was 100 days, with a range of 62 to 135 days. The three-month aim was periodically surpassed by sample intervals because of Covid-19 travel constraints during a couple of sampling seasons. Meteorological parameters (Average temperature and wind speed) are presented in Appendix-1.

GEM: For sampling of GEM, Passive Air Samplers (Gem-PASs) were placed at a height of around 10 meters on the rooftops of double-story buildings. The polypropylene jars were sealed with polytetrafluoroethylene tape and sealed at the sampling locations once the target time had passed. The sealed samplers were then placed in Ziplock bags and a closed container for transportation to COMSATS University Islamabad, where they were kept in a clean room until being sent to Bursa Technical University in Turkey for analysis. Details on sampling periods, meteorological conditions, and site-specific sampling rates for sapling GEM in study area are presented in Appendix-2

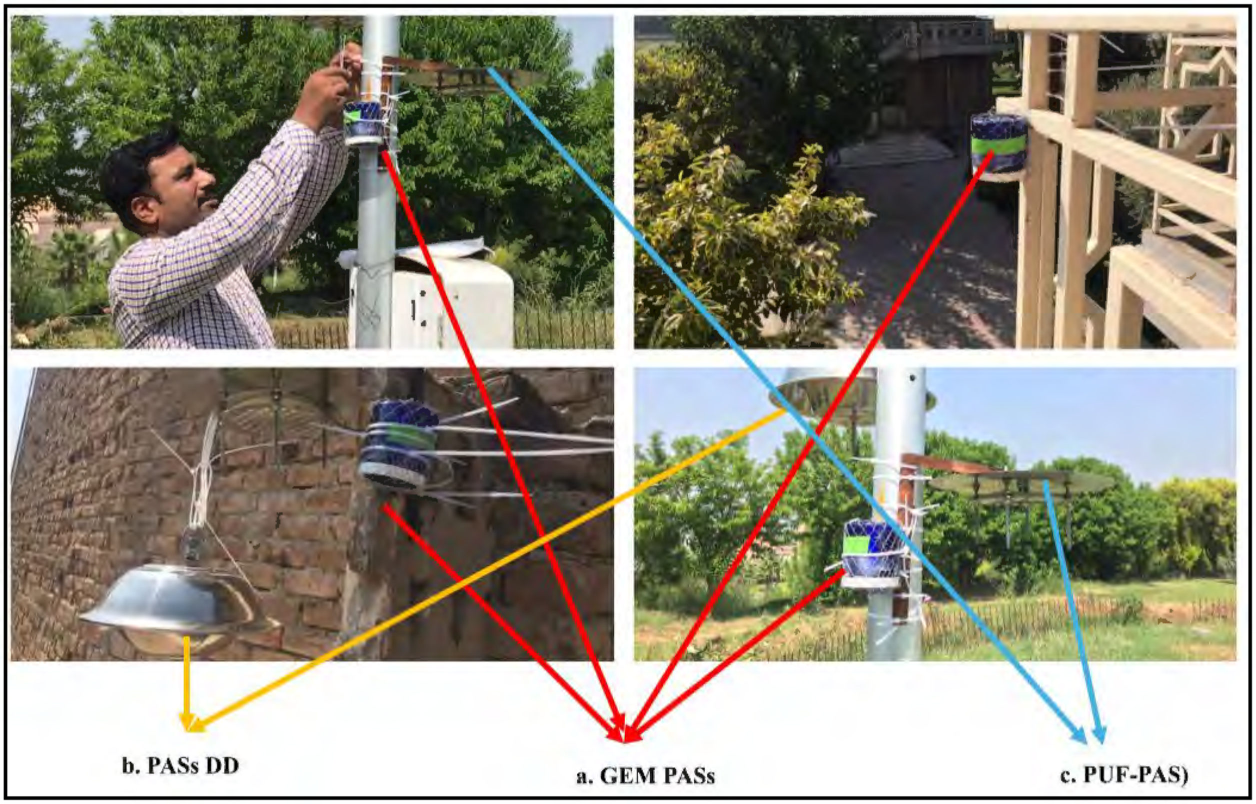


Plate 3.1: Passive sampler installed for target compound at study area

HMs: Sampling of air deposition of HMs are mainly associated with particulate matter, was performed by deploying passive dry deposition (PASs-DD) using a polyurethane foam disk (PUF-disk). PASs-DD have successfully been used to determine the flux of polycyclic aromatic hydrocarbons (PAHs) (Eng *et al.,* 2014) and HMs (Gaga *et al.,* 2019) in urban environments and collect both particle-phase dry deposition and gas-phase. Seasonal deployment duration of PAS-DDs at each sampling location are given in Appendix-3**.** The information about detailed design and sampling rate of PAS-DD can be found elsewhere (Gaga *et al.,* 2019; Eng *et al.,* 2014). PUF disks were precleaned prior to deployment in accordance with the standard clean-up procedure applied for persistent organic pollutants (POPs) analysis (Birgul & Karakus, 2024). After harvesting at the sampling locations, PUF disks were tightly closed in aluminum bags, transported to COMSATS University Islamabad after tightening it within zip-lock bags and a locked container for transport. At the university, the tighten PASS-DD were kept in a dry, sanitized room till they could be shipped to Turkey (Bursa Technical University) for sample preparation. Prepared samples were analyzed for HMs in Dokuz Eylul University.

BFRs: For the monitoring of FRs air, the PASs was deployed for the monitoring of atmospheric (particulate and gaseous) at various closeness from, however they were placed in a radius of ~ 200m of e-waste recycling units. Figure 3.2 indicate PASs sampler installed on the roof-tops of double-story buildings with a height of approximately 10m.

a) ***Gaseous BFRs*****:** Air samples to determine gaseous concentrations of BFRs were collected using polyurethane foam disk passive samplers (PUF-PASs) designed by Shoeib & Harner (2002) and Harner *et al.* (2004). The PUF-PASs are well-characterized samples which have been used in many other field investigations (Gouin *et al.,* 2005; Jaward *et al.,* 2004; Motelay-Massei *et al.,* 2005; Pozo *et al.,* 2004; Wang *et al.,* 2009, 2010, Kurt-Karakus *et al.,* 2017). In this technique, PUF disks are suspended between two stainless steel bowls where a gap between upper and lower bowls maintain airflow between the bowls hence exposure of PUFs to air.

b) ***Particle bound BFRs*****:** Particulate matter samples for analysis of particle bound BFRs were collected using PAS-DD samplers (Eng *et al.,* 2017). The PASs-DD sampler comprises two parallel flat plates and a quartz filter as the sampling medium. The edges of the open plate promote unobstructed flow of air between cover plate and open plate with minimal turbulence (Davidson *et al.,* 1985). As reported by Eng *et al.* (2017), even a gap opening as small as 2 cm allows the full-size range of particles to deposit onto sampling medium. A total of 328 samples were collected i.e., 160 samples + 4 background sites from each sampling matrix i.e., air + dry deposition. Air samples (PUFs) after collection, wrapped in aluminum foil and stored in sealed plastic bags at −20 °C. All samples were stored at COMSATS University Islamabad and then transported to Bursa Technical University for further analysis (Plate-3.2).

Plate 3.2: Sample collection and storage before analysis

3.2.2 Soil Sampling

HMs: Total of160 samples were collected for assessing the soil residues of HMs in four seasons. A hand-held corer mase of stainless steel was used to collect soil samples between 0-10 cm depth. At least 10 cores were collected randomly at individual sampling locations and a composite sample was obtained after mixing all-together. Soil samples collected were sieved through a 2 mm mesh metal sieve. Moisture and organic content in soil samples were determined according to ASTM D-2974-87 (ASTM, 2000) method and soil pH measurements were made according to EPA method 9045-D (US EPA, 2004). Methods to determine soil moisture content, soil organic matter content and soil pH values (Appendix- 4).

BFRs: Soil samples were collected within ~200 - 500-m distance from e-waste recycling sites. Surface soil samples were collected using a hand-held core made of stainless steel from 0-10 cm depth. Similar to the HMs sampling in soil, at least 10 cores were collected at each sampling site

Plate 3.3: Sample preparation and analytical procedure

and mixed to obtain a composite sample. Soil samples collected for FRs analysis were sieved through a 2 mm mesh metal sieve. Meteorological parameters, soil moisture, pH and organic matter content for sampling sites are presented in (Appendix- 5).

3.3 Sample Preparation and analysis

GEM: Hg obtained on the sorbent was assessed using a Direct Mercury Analyzer (DMA-1; Milestone Srl, Italy), which works on the laws of thermal breakdown, Hg amalgamation, and atomic adsorption detection. The sorbent from the stainless-steel mesh cylinder was poured into a pre-weighed Eppendorf tube (2 mL), and the amount was weighed. A sorbent sample was placed into the DMA-1 instrument's quartz cell for Hg measurement. During the analysis, the sample is weighed into a quartz vial and dried in the instrument's sample cell before being thermally decomposed in an oxygen-rich stream.

Mercury and other combustion products are liberated from the sample and passed through a catalyst tube, which takes away any interfering compounds. The gold amalgamator selectively captures Hg, while other combustion products are executed from the system. The amalgamation furnace is heated to quickly release the Hg, which is then carried into several measurement cells along the spectrophotometer's optical path and measured using atomic absorption at 253.65 nm.

By dividing the blank-corrected mass of sorbed Hg (ng) by the result of a sampling rate SR (m^3 day-^{1}) and the deployment period t (day), volumetric GEM concentrations C (ng m^{-3}) were determined: (Equation 3.1)

$$C = m / (SR\ t) \qquad \text{(Eq. 3.1)}$$

The SR is unchanged by relative humidity, although it does rise slightly with temperature (by 0.001 m^3 day^{-1} or 0.7 % for every 1K increase) since temperature affects the molecular diffusivity of GEM. The SR rises by 0.003 m^3/day^{-1} for an increase of 1 ms^{-1} at wind speeds greater than 1 ms^{-1} (McLagan *et al.,* 2017b). By adjusting the thickness of the boundary layer around the Radiello diffusive barrier, wind speed affects the diffusion route length (Zhang *et al.,* 2013).

Eq. 3.2 was hence employed to adjust the general SR of 0.135 m^3 day^{-1} for temperature and wind speed, which was detected during a global-scale calibration investigation of the PASs (McLagan *et al.,* 2018; McLagan *et al.,* 2017a).

$$SR_{adj} = SR + (T - 9.89\ °\mathrm{C}) \cdot 0.0009\ \frac{m^3}{day \cdot °\mathrm{C}} + \left(WS - 3.41\ \frac{m}{s}\right) \cdot 0.003\ \frac{s \cdot m^2}{day} \qquad \text{(Eq. 3.2)}$$

where WS and T are the average wind speed (m s^{-1}) and temperature (°C) for the period of the deployment of every PASs. The value ranged from 0.132 - 0.179 m^3 day^{-1} for adjusted SR. The facilities at Pakistan Meteorological Department (PMD) were used to get meteorological data during every sampling period.

Plate 3.4: Different analytical procedure of target compounds

HMs: Weight of each PUF disk was recorded before and after deployment in the field, hence approx. dust amount collected was determined (0.04 g - 4.39 g). Subsamples taken out of each PUF disk that were deployed for approx. 3 months at the sampling sites were used to analyze heavy metals. A stainless-steel corer was used to cut 1 cm diameter cores from 5 randomly selected points on each disk to obtain sub-samples. The PUF disk was weighed again after 5 cores (∑0.11 g) were taken out to determine the weight of the cores as well as weight of dust collected in these 5 cores (0.02 - 0.22 g). Wet digestion method was applied to prepare the samples for instrumental analysis. The subsample consisting of 5 cores were placed in a 40 mL glass vial, 2 mL of H_2SO_4 and 6 mL of nitric acid HNO_3 and were added into the vial. Vials containing PUF disk subsamples and acid mixture were placed on an aluminum heating block and digestion was carried out by heating samples at temperatures ranging from 160 °C to 180 °C until the formed brownish fume disappeared and the solution became clear. After the digestion was completed, the samples were kept in the fume hood until they are cooled to room temperature and diluted to 50 mL using ultrapure water. To remove any impurities an aliquot of 15 mL of the digested sample was filtered through a 0.45 µm pore size Teflon syringe filter. Filtered samples were placed in 15 mL volume plastic falcon tubes, the caps of the tubes closed tightly and refrigerated at -18 °C until instrumental analysis.

Analysis of heavy metals was conducted using an Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) (Agilent 7700x). The operational parameters of the device were as follows: RF power set to 1550 W; carrier gas flow rate at 0.90 L/min; plasma gas flow rate at 15 L/min; plasma sampling depth of 8 mm; nebulizer flow rate set at 1.01 L/min; extractor lens potential at -160 V; conical spray chamber temperature maintained at 2°C; nebulizer pump operated at 0.10 cycles/second; nebulizer type used was micro-mist; and the ion lenses model employed was x-lens. Readings were taken as three replicates and average value of three readings were used as the concentration value of a sample.

Fluxes were presented as mass per unit area per unit time (1) (i.e., µg/m^2.day) in Eq. 3.3 as follows:

$$Deposition\ Flux\ (F) = \frac{m}{t} \times A \qquad \text{(Eq. 3.3)}$$

Where m is the quantity of HMs determined in the PAS-DD sample (µg), t is the total deployment duration of the sampler in the field (days), A is the surface area where deposition of particles occurred (0.00785 m^2, as edges and bottom of the DD-PAS sampler sampling medium holder unit is relatively closed, therefore it was assumed that deposition occurred mainly on to the top side of PUF disk). Plates 3.3 and 3.4 shows the procedural streaming of target compound from sampling to analysis.

BFR (Air): Soxhlet extraction (addition of surrogate standards, i.e., for PBDEs: BDE-77 and 13C$_{12}$PBDE209; for HBCDD: 13C labeled or deuterated-HBCDD; for HBB: 13C$_{12}$-HBB) (for at least 16 hrs)+Volume reduction + column clean up (Option 1: 1 cm i.d. glass column filled with approx. 20 cm of 70-230 mesh silica gel that were baked at 450 °C overnight, topped to 21 cm with baked granular sodium sulphate; elution with 70 mL hexane and 80 mL of 1:1 DCM-hexane. BFRs were analyzed on GC (Agilent 7890B) coupled with an MSD (Agilent 5977 MSD). Column: HP5; Oven temp: 80°C, 2 min., 7°C/min110 °C; 3°C/min 230°C; 20 °C/min 340 °C 5 min. Carrier gas: helium; Injector, ion source, quadrupole and auxilary: 280°C, 250°C ve 150°C ve 310 °C, respectively. Instrument operating mode: negative chemical ionization (NCI).

Prepared samples were subjected to GC-MS analysis to determine their POP-FR contents. Analysis of representative compounds were analyzed in the Agilent brand 7890 gas chromatography-5975 mass spectrometer (GC-MS) instrument in the laboratory of Bursa Technical University Environmental Engineering Department. The instrument was operated in electron bombardment (EI) mode to ionize the analytes, while the MS part was operated in the selected ion tracking (SIM) mode. The analysis of target POP-FR pollutants was analyzed in the Agilent brand 6890 N gas chromatography-5973 model mass spectrometer (GC-MS) device in the laboratory of Dokuz Eylül University Environmental Engineering Department. The instrument was operated in negative chemical ionization (NCI) mode and the MS part was operated in selected monitoring mode (SIM) mode.

BFRs (Soil): Approximately 5 g soil sample was placed in an amber vial and mixed with ~5 g anhydrous Na_2SO_4. Approx. 30 mL of acetone (ACE): DCM (1:1 v/v) was added in the vial, surrogate standards were spiked (PBDE-77, 13C12-PBDE-209, 13C6-HxBBz, 20 ng each), the vial was sealed, and the sample was kept in dark overnight. Ultrasonic extraction was conducted for 30 min; the supernatant was transferred into a round bottom flask. Ultrasonic extraction step was repeated twice more using 30 mL ACE/DCM mixture (1:1, v/v) at each time, and all supernatants were combined. Extracts were concentrated using rotary evaporator to about 1 mL. Extracts were cleaned up on a chromatography column using 1.1 cm i.d. glass columns with 3 g alumina (baked at 450 °C for 4 hours, 6 % deactivated). Analytes were eluted using 35 mL of dichloromethane DCM: HEX (20:80 v/v). The final volume was collected into 1 mL in isooctane under nitrogen gas and 12 ng of $13C_{12}PCB_{105}$ was added as internal standard.

Instrumental analysis of PBDEs, ∑HBCDD, PBBs and HBB was carried out on a GC (Agilent 6890N) coupled with an MSD (Agilent 5973 inert MSD). A 15 m HP-5 MS capillary column (0.25 mm i.d., 0.10 μm film thickness) was used for chromatographic separation. Oven program: 90°C, 1 min; 20°C/min to 340°C, 3 min. Temperature of transfer line, source, quadruple, and injection port was 320°C, 230°C, 150°C and 280°C, respectively. Helium was carrier gas with a constant flow rate of 1.8 mL/min while methane was reagent gas. Targeted chemicals were monitored in selected ion mode (SIM) and ionization was achieved in negative chemical ionization (NCI) mode. 1 μL of sample was injected in pulsed-spitless mode (pulse time: 1.80 min) (Cetin & Odabasi, 2007). All analytes, surrogate standards, and the internal standards were completely separated based on their retention times, target, and qualifier ions (Appendix-6 and appendix-7) except PBDE 171 and 190 and HBCDD isomers (α, β, γ) that were co-eluted and could not be separated based on their ions. These were reported as sum of these congeners/isomers.

3.4 Quality Assurance and Quality Control (QA/QC)

Accurate quality assurance and quality control practices were pursued from sample collection through to analysis. The details of the practices are discussed in detail in the given section for chemicals of interest.

3.4.1 GEM

DMA-1 instrument's auto calibration, correct quartz sample cell cleanup, and the observation of blanks (both field and lab) and sample duplicates are various QA/QC procedures for GEM analysis. When the Hg level in each sample is ≥100 ng, the instrument operates in autocalibration mode automatically; if not, the DMA-1 can choose to do autocalibration after every 10 samples. Activated carbon treated with sulfur was used to create blanks for use in the lab and in the field. To create the laboratory blanks, about 0.011 g of AC were weighed and placed into the quartz sample cells from the bulk AC supplied by the supplier. Field blanks were PASs that were returned to the laboratory after being correctly sealed and exposed to air for about a minute while the samplers were being deployed in the field.

The mean Hg concentration (ng Hg g-1 AC) was found to be comparable in four field studies (0.72±0.16; 0.62-0.95) and five laboratory blanks (1.01±0.35; 0.58-1.4). Their average (0.88±0.30) ranks within the lower range of blank levels (0.38±0.08 to 36±17) that have been documented for earlier studies using this sampler (Hoang *et al.,* 2023). Samples were blank corrected by deducting the quantity measured in the sorbent from that sampler (in ng Hg) from the average concentration in blanks (in ng Hg g-1 AC) multiplied by the mass of the sorbent in a sampler (in g AC). The instrument detection limit (IDL) was set at 50 % of the calibration curve's lowest level (0.001 ng). By taking three times the standard deviation (SD) of the level in the blank and converting it to ng m^{-3} using the average of the modified SR (0.154 $m^3 day^{-1}$) and an average deployment length of 100 days, the method detection limit (MDL) (0.041 ng m^{-3}) was determined. Before being analyzed, quartz sample cells were cleaned by immersing them in 5 % nitric acid for overnight. Afterward, they were rinsed with deionized water and heated to 550 °C for a few hours to remove any traces of Hg. Prior to sample analysis, the Hg residue on empty quartz cells was measured using the same technique as sample analysis, with the cells placed in the DMA-1 apparatus. If the average Hg residue level of the triple analysis was greater than 50 % of the average level identified in the blanks (0.0045 ng), the procedure was repeated three times, and the cells were washed in 5 % nitric acid overnight.

3.4.2 HMs

All laboratory equipment was either high quality polypropylene or Teflon. All chemicals were analytical grade. Field blanks were brought to the laboratory in closed boxes/bags after being exposed to ambient air for 1-2 minutes. A mixture of acids which were used for sample digestion was used in preparation of laboratory blank samples. A total of 12 blank samples for PUFs and a total of 14 blank samples for soils were prepared and they were handled in the equal manner as the samples. The reproducibility of the obtained results was checked by analyzing CRM 540. Relative standard deviation of results between certified value and analysis ranged between 1.38 % (Mn) and 14.4 % (Pb) with an average RSD of 6.31±4.41 %. Further details on RSD values detected for target contaminants are given in Appendix-8.

For digestion, method spike samples (n=10) were prepared by adding known quantity of target elements (100 ppb each) into acid mixture and process was carried out similar manner as done for samples. The average recovery ratio was 96.4±4.89 % ranging between 89.7 % (Co) and 103 % (As and Pb). The Instrument Detection Limit (IDL) was based on half the concentration value of the lowest calibration level that the instrument was able to determine in the set of calibration solutions. Samples were not blank corrected. Therefore, method detection limit (MDL) was calculated based on average blank concentration + 3 x Standard deviation (SD) of the concentration detected in the blank samples.

3.4.3 BFRs

In soil all glassware and metals were soaked in Alconox® overnight after use. All glassware was baked at 450 °C for at least for 4 hours (except volumetric ones) and rinsed with acetone before use. A total of 18 blank samples using baked Na_2SO_4 were analyzed. In the current study, none of the blanks contained concentrations of any target compounds, hence no blank correction was done for samples.

Table 3.2: IDLs and MDLs values of target metals in dry deposition particles and soil samples

	Dry Deposition Particles (PM)						**Soil**	
	Flux [a] (µg/m^2.day)		**mass per unit volume[b] (µg/m^3)**		**mass per weight unit of PM (µg/g)**		**µg/g [c]**	
Element	**IDL**	**MDL**	**IDL**	**MDL**	**IDL**	**MDL**	**IDL**	**MDL**
Cr	1.27	1.68	5.56x10^{-5}	9.26x10^{-5}	2.7	4.6	0.26	0.71
Mn	1.27	3.90	5.56x10^{-5}	1.49x10^{-4}	2.7	7.3	0.26	0.63
Ni	1.27	3.73	5.56x10^{-5}	8.95x10^{-5}	2.7	4.4	0.26	1.00
Cu	1.27	2.67	5.56x10^{-5}	1.15x10^{-4}	2.7	5.7	0.26	5.27
Zn	2.55	19.31	1.11x10^{-4}	7.59x10^{-4}	5.5	37.5	0.51	11.05
Cd	0.06	0.09	2.78x10^{-6}	6.46x10^{-6}	0.1	0.3	0.01	0.10
Pb	2.55	5.72	1.11x10^{-4}	2.47x10^{-4}	5.5	12.2	0.51	2.75

[a] based on an average 100 days of deployment and the area of 0.01819 cm^2 of acid digested cores; [b] based on a daily sampling rate of 9 m^3/day (Gaga *et al.*, 2019) and an average 100 days of deployment; [c] based on an average digested amount (dw basis) of 0.196 g of soil sample.

Matrix spike recoveries of target compounds (20 ng each) from the spiked samples baked Na$_2$SO$_4$ (n=5)) were tested. The % recovery of targeted chemicals ranged between 76.8±6.7 % (BDE-203) and 112.3 ± 15.2 (BDE-207). The average recoveries of BDE-77, 13C$_{12}$-BDE-209 and 13C$_6$-HxBBz were 84.3 ± 11.4 % (57.5 - 115.6 %), 95.8 ± 14.2 % (66.2 -128.3 %) and 78.5 ± 10.5 % (53.2-110.2 %), respectively.

Standard reference material SRM 2583 (NIST element in indoor dust) was used to validate the methods used. The concentrations recorded were within acceptable values. SRM 2583 was certified for elements, however, concentration levels of PBDEs present in this SRM were reported by Stapleton *et al.* (2006). Average % RSD between detected concentrations and reported concentrations of 16 BDE congeners was 13.3 ± 9.5 % ranged between 1.0 % (BDE-49) and 28.5 % (BDE-206). The quantifiable amounts of PBDEs for 1 µl injection ranged between 0.02 pg (BDE-138) and 0.15 pg (BDE-209) while it was 0.01 pg for HxBBz, 0.2 pg for γ-HBCDD, 0.1 pg PBB-156 and 2.48 pg for PBB-153. The Instrument Detection Limit (IDL) was the lowest signal producing level that is distinguishable from a reagent blank at a signal to noise ratio of 3:1. MDLs were calculated based on the average+3xStandard deviation of the concentration detected in the blank samples. IDL and MDL values of each targeted element I air, and soil are given in Table 3.2 As none of the target chemicals was present in blank samples, it is accepted that IDLs=MDLs. IDLs and MDLs were calculated for an extracted soil dry weight of 4.6 g (Appendix- 9).

In air, glass and metal materials used during the experiments were cleaned with dichloromethane or hexane. Where possible, all glassware (except volumetric measuring materials such as flasks, measuring tapes, pipettes) was baked at 450 ºC for at least 4 hours. PBDE-77, $13C_{12}$-PBDE-209 and $13C_6$-HBB were used as method recovery performance compound (recovery efficiency chemical). By adding 20 ng of these chemicals to each analyzed sample prior to analysis, recovery performance was evaluated from the beginning to the end of the analysis. Field and laboratory blank samples were prepared to test whether there was any contamination interference during the analyses. Recovery efficiency performance compounds were added to the witness samples, and they were passed through all the stages of the samples. Basically, 2 types of blank samples were used. All concentration values reported were corrected for the average analyte concentration determined in the blank samples.

The method determination limit (MDL) was calculated by adding 3 times the standard deviation (Mean+3xSD) to the mean concentration of the control samples if the target chemical was determined in the control samples. In the absence of target chemicals in the control samples, the instrument detection limit (IDL) was accepted as MDL. The IDL is calculated based on half of the concentration value of the lowest calibration level that the instrument can detect in the set of calibration solutions.

3.5 Geo-accumulation Index (Igeo) of HMs

The contamination level of heavy HMs in soils were determined by calculating the values of the geo-accumulation index (I_{geo}) (also known as Muller index) (Han *et al.,* 2018; Muller, 1981). This indicator is used to calculate the scale of contamination by assessing the relation between calculated concentration level and background level of the contaminant (Muller, 1969). Eq. 3.4 is used to calculate I_{geo}:

$$I_{geo} = \mathrm{Log2} \times \frac{C}{1.5BG} \qquad \text{(Eq. 3.4)}$$

Here C represents the heavy metal concentrations in the soil samples analyzed while BG is the geo-chemical background concentration of the element in the earth's crust and 1.5 is background matrix correction factor as consequence of lithogenic effects. This coefficient depicts any anthropogenic effect in the computation as well as the influence of geological and depositional features.

3.6 Enrichment Factor (EF) of HMs

Assessing the contamination level of heavy metals from human activities involves comparing the concentrations of heavy metals in soil and particulate samples with those of reference elements found in the Earth's crust. For this purpose, enrichment factor (EF) is calculated as shown in the Eq. 3.5 below (Al-Khashman, 2013; Abdulaziz *et al.,* 2022; Tepe *et al.,* 2022) for soil and particulate matter, separately.

$$EF = \frac{(\frac{C_i}{C_{ref}})sample}{(\frac{C_i}{C_{ref}})earth\ crust} \qquad \text{(Eq. 3.5)}$$

Where Ci is the concentrations of target heavy metals (µg/g) in particulate matter or soil and Earth crust. C_{ref} represents reference elements concentration in particulate matter/soil and Earth crust. As Mn is one of the reference elements used in previous studies (Rahman *et al.,* 2021; Pasha *et al.,* 2015; Zajusk-Zubek *et al.,* 2015; Fabretti *et al.,* 2009; Sakata & Asakura, 2011; Abdulaziz *et al.,* 2022), it is used as reference element in the current study. Tayler (1964) provides Heavy metals concentrations in Earth's crust. An EF level of ≤10 indicates the cause of the metal from the natural source of Earth's crust while EF value of >10 suggests anthropogenically enriched (Duan *et al.,* 2021; Kodat *et al.,* 2023)

Table 3.3: Parameters used for exposure assessment

Parameter	Definition	Unit	Values for Adults	Reference
EXPOSURE THROUGH SOIL				
C_{soil}	The mean concentrations of heavy metal in soil	mg/kg	From the present study	This study
IngRsoil	Soil Ingestion Rate	mg/day	100	Ahmed *et al.*, 2020; Singh *et al.*, 2018
InhR	Inhalation Rate	M^3/day	20	Singh *et al.*, 2018
EF	Exposure Frequency	Days/year	300	Ahmed *et al.*, 2020; Singh *et al.*, 2018
ED	Exposure Duration	Years	24	Wu *et al.*, 2022
ET	Exposure Time	Hours/day	10	Wu *et al.*, 2022
AT	Average lifetime	Days	EDx365 (non-carcinogens) 70x365 (carcinogens)	USEPA, 2004
BW	Body weight	Kg	70	USEPA, 2004
SA	Skin surface area	cm^2	5700	USEPA, 2004
EF	Adherence Factor	mg/cm^2	0.07	USEPA, 2004
ABF	Absorption factor	-	0.1 (Pb), 0.03 (As), 0.001 (Cd), 0.01 (others)	Zhang *et al.*, 2021
PEF	Particulate Emission Factor	m^3/kg	1.3x10^9	Ahmed *et al.*, 2020; Singh *et al.*, 2018
FE	fraction of the dermal exposure ratio to soil	-	0.61	USEPA, 2004
AF	adherence factor	mg/cm2	0.07	Ajani *et al.*, 2022
ABS	fraction of the applied dose absorbed across the skin	0.1		Ajani *et al.*, 2022
EXPOSURE THROUGH PARTICULATE MATTER				
C_{PM}	The mean concentration of heavy metal in particulate matter	(µg/m^3) for EC calculation, (mg/kg) for ADI calculation	From the present study	This study
IngR$_{PM}$	Particulate matter Ingestion Rate	mg/day	100	USEPA, 2002
EF	Exposure Frequency	Days/year	300	Ahmed *et al.*, 2020; Singh *et al.*, 2018
ED	Exposure Duration	Years	24	Wu *et al.*, 2022
BW	Body weight	Kg	70	USEPA, 2004
AT	Average lifetime	Days	EDx365 (non-carcinogens) 70x365 (carcinogens)	USEPA, 2004
ET	Exposure Time	Hours/day	10	Wu *et al.*, 2022
AF	Adherence Factor	mg/cm^2	0.07	USEPA, 2004
AT$_n$	Average Lifetime	Hours	EDx365x24 (non-carcinogens) 70x365x24 (carcinogens)	USEPA, 2004
SA	Skin surface area	cm^2	5700	USEPA, 2004
AF	adherence factor	mg/cm^2	0.07	Ajani *et al.*, 2022
ABF	Absorption factor	-	0.1 (Pb), 0.03 (As), 0.001 (Cd), 0.01 (others)	Zhang *et al.*, 2021; EPA, 2024

3.7 Human health risk assessment

HMs Exposure of HMs to the human body can occur through ingestion via mouth, inhalation via mouth and nose, and dermal exposures via skin when in proximity of informal e-waste recycling. The present study calculates the non-carcinogenic health and lifetime cancer risk based on inhalation, ingestion, and dermal exposure routes of HMs. In addition, overall data used for the calculation of average daily intake is given in Table 3.3.

Estimation of HMs daily intake through contaminated soil are calculated based on recommendations proposed by United States Environmental Protection Agency (USEPA 1989; 1997; 2000 and 2001). The average daily intake (ADI) (mg/kg-day) of each heavy metal through soil ingestion, inhalation and dermal contact pathways was calculated using the following equations (Eq. 3.6 to Eq. 3.8) (Ajani *et al.,* 2022):

$$ADI_{Soil-Ing} = \frac{C_{soil}\ x\ IngR_{soil}\ x\ EF\ x\ ED}{BW\ x\ AT\ x\ 10^6} \quad \text{(Eq. 3.6)}$$

$$ADI_{Soil-Inh} = \frac{C_{soil}\ x\ InhR\ x\ EF\ x\ ED}{BW\ x\ AT\ x\ PEF} \quad \text{(Eq. 3.7)}$$

$$ADI_{Soil-Dermal} = \frac{C_{soil}\ x\ SA\ x\ FE\ x\ AF\ x\ ABS\ x\ EF\ x\ ED}{BW\ x\ AT\ x\ 10^6} \quad \text{(Eq. 3.8)}$$

Where $ADI_{Soil-Ing}$, $ADI_{Soil-Inh}$ and $ADI_{Soil-Dermal}$ are the average daily intake doses through soil ingestion, inhalation, and dermal absorption, respectively (mg/kg/day) and C_{soil} is the concentration of heavy metal in soil.

Estimation of daily Intake through air particulate matter is also measured in terms of average daily intake (ADI) via ingestion (Eq. 3.9) and exposure concentration via inhalation (EC) of air particulate matter (Eq. 3.10) and dermal absorption (Eq. 3.11) (mg/kg/day) of air particulate matter (Abdulaziz *et al.,* 2022)

$$ADI_{PM-Ing} = \frac{C_{PM}\ x\ IngR_{PM}\ x\ EF\ x\ ED}{BW\ x\ AT\ x\ 10^6} \quad \text{(Eq. 3.9)}$$

$$EC_{PM-Inh} = \frac{C_{PM}\ x\ ET\ x\ EF\ x\ ED}{AT_n} \quad \text{(Eq. 3.10)}$$

$$ADI_{PM-Dermal} = \frac{C_{PM}\ x\ SA\ x\ AF\ x\ ABF\ x\ EF\ x\ ED}{BW\ x\ AT\ x\ 10^6} \quad \text{(Eq. 3.11)}$$

Where $ADI_{PM\text{-}Ing}$, and $ADI_{PM\text{-}Dermal}$ are the average daily intake doses through particulate matter ingestion and dermal absorption, respectively (mg/kg/day) and $EC_{PM\text{-}Inh}$ is the exposure concentration via inhalation (µg/m^3) of air particulate matter. C_{PM} is the concentration of heavy metal (mg/kg for $ADI_{PM\text{-}Ing}$, and $ADI_{PM\text{-}Dermal}$; mass per unit volume (µg/m^3) for $EC_{PM\text{-}Inh}$).

3.7.1 Non-Carcinogenic Health Risk

Non-carcinogenic adverse health effects assessment is carried out for both carcinogenic and non-carcinogenic heavy metals. The IARC has classified As, Cr, Cd and Ni as Group 1 carcinogens, whereas Pb and Co were classified as Group 2A carcinogens (IARC, 2024). USEPA (1989; 1997; 2000 and 2001) proposed that target hazard quotients (HQ) and hazard index (HI) characterize the potential health risk. HQ is a ratio of determined average daily intake (ADI, (mg/kg/day)) to reference dose (RfD, (mg/kg/day)) of an individual element. HQ values ≤1 indicate no significant or acceptable risk, while HQ values >1 indicate the potential for adverse health effects (USEPA, 2001). For a given heavy metal, HQ values for exposure through soil ingestion, inhalation, and dermal contact in addition to particulate matter ingestion and dermal contact is calculated using the equations given below (Ajani *et al.,* 2022; Abdulaziz *et al.,* 2022).

$$HQ_{Soil-Ing}=\frac{ADI_{Soil-Ing}}{RFD} \quad \text{(Eq. 3.12)}$$

$$HQ_{Soil-Inh}=\frac{ADI_{Soil-Inh}}{RFD} \quad \text{(Eq. 3.13)}$$

$$HQ_{Soil-Dermal}=\frac{ADI_{Soil-Dermal}}{RFD} \quad \text{(Eq. 3.14)}$$

$$HQ_{PM-Ing}=\frac{ADI_{PM-Ing}}{RFD} \quad \text{(Eq. 3.15)}$$

$$HQ_{PM-Dermal}=\frac{ADI_{PM-Dermal}}{RFD} \quad \text{(Eq. 3.16)}$$

Whereas RfD is the reference dose (mg/kg/day) (Table 3.4).

HQ value for exposure through particulate matter inhalation can be calculated based on the equation given below (Abdulaziz *et al.,* 2022)

$$HQ_{PM-Inh}=\frac{ADI_{PM-Inh}}{RfCx1000} \quad \text{(Eq. 3.17)}$$

Whereas RfC is the reference concentration of the heavy metal (mg/m^3) (Table 3.4)

Health risks associated with exposure to multiple metals is estimated by using Hazard index (HI) (the summation of hazard quotients (HQ_k) of individual metal "k") which can be calculated using the following equation (USEPA 2001; Khan *et al.,* 2020)

$$HI = \sum HQ_k \qquad \text{(Eq. 3.18)}$$

For non-carcinogenic or carcinogenic heavy metals, a value of HI > 1 represents that there is a chance of occurrence of non-carcinogenic effects, while the exposed individual is unlikely to experience obvious adverse health effects when HI < 1.

3.7.2 Lifetime Cancer Risk

The probability of developing cancer because of human exposure to carcinogenic heavy metals (As, Cr, Cd and Ni as Group 1 carcinogens and Pb and Co as Group 2A carcinogens (IARC, 2024)). Cancer risk over the lifetime (ILCR) can be estimated using equations below for ingestion, inhalation, and dermal contact respectively.

$$ILCR_{\sum ing} = (ADI_{Soil-Ing} + ADI_{PM-Ing})\ x\ SF \qquad \text{(Eq. 3.19)}$$

$$ILCR_{\sum inh} = (ADI_{Soil-Inh}\ x\ SF) + (EC_{PM-Inh}\ x\ IUR) \qquad \text{(Eq. 3.20)}$$

$$ILCR_{\sum dermal} = (ADI_{soil-dermal} + ADI_{PM-dermal}) x\ SF \qquad \text{(Eq. 3.21)}$$

Where $ILCR_{\Sigma ing}$, $ILCR_{\Sigma inh}$, $ILCR_{\Sigma dermal}$ represent incremental lifetime cancer risks via soil+particulate matter ingestion, inhalation, and dermal contact, respectively. Values of Slope factor (SF, mg/kg.day) and inhalation unit risk (IUR, $\mu g/m^3$) for carcinogenic metals are given in Table 3.4. Classification of ILCR is as follows: $ILCR \leq 1x10^{-6}$ (very low); $10^{-6} \leq ILCR \leq 10^{-4}$ (low); $10^{-4} \leq ILCR \leq 10^{-3}$ (moderate); $10^{-3} \leq ILCR < 10^{-1}$ (high) and $ILCR \geq 10^{-1}$ (very high) (Zhang *et al.,* 2021). The Cumulative ILCR for a given carcinogenic metal can be calculated as the sum of ILCR values occurred due to ingestion, inhalation, and dermal contact (Sun *et al.,* 2021) and this value should be maintained below 10^{-4} (Chalvatzaki *et al.,* 2019).

$$Cumulative\ ILCR = ILCR_{\Sigma ing} + ILCR_{\Sigma inh} + ILCR_{\Sigma dermal} \qquad \text{(Eq. 3.22)}$$

Table 3.4: Reference dose for metals through different routes

	Unit	Cr	Mn	Ni	Cu	Zn	Cd	Pb	Ref
RfD_{ing}	mg/kg.day	$3x10^{-3}$	$4.6x10^{-2}$	$2x10^{-2}$	$4x10^{-2}$	$3x10^{-1}$	$1x10^{-3}$	$3.5x10^{-3}$	EPA, 2024; Izhar *et al.*, 2016
RfD_{der}	mg/kg.day	$2.86x10^{-5}$	$1.43x10^{-5}$	$2.06x10^{-2}$	$1.2x10^{-2}$	$6x10^{-2}$	$1x10^{-5}$	$5.25x10^{-4}$	Ajani *et al.*, 2022; Izhar *et al.*, 2016
RfD_{inh}	mg/kg.day	$1x10^{-4}$	$5.0x10^{-5}$	$1.4x10^{-5}$	$1.2x10^{-2}$	$3x10^{-1}$	$1x10^{-5}$	$3.5x10^{-3}$	Izhar *et al.*, 2016
RfC	mg/m^3	$1x10^{-4}$	$5x10^{-5}$	$1.4x10^{-5}$	$4.02x10^{-2}$	$3x10^{-1}$	$1x10^{-5}$	$1.5x10^{-4}$	EPA, 2024; Liu *et al.*, 2023; Zhou *et al.*, 2023; Izhar *et al.*, 2016
IUR	$\mu g/m^3$	$8.4x10^{-2}$	-	$2.4x10^{-4}$	-	-	$1.8x10^{-3}$	$1.2x10^{-5}$	EPA, 2024, Izhar *et al.*, 2016
SF_{oral}	Unitless	0.5		0.84			15	$8.5x10^{-3}$	EPA, 2024; Liu *et al.*, 2023; Oni *et al.*, 2022
SF_{der}	Unitless	20		**0.84**			**6.1**	1.5	**Mohammadi *et al.*, 2019**
SF_{inh}	Unitless	**41**		0.84			6.3	**8.5**	**Aliyu *et al.*, 2022;** Liu *et al.*, 2023; **Mohammadi *et al.*, 2019**

3.7.3 Human health exposure of FRs to contaminated air and soil

Inhalation of contaminated air and ingestion of soil was assumed as possible routes of BFRs exposure among workers at informal e-waste recycling facilities. Several research have highlighted the possible adverse health impacts of e-waste recycling (Zhao *et al.*, 2023; Nyeko *et al.*, 2023; Tzoraki & Lasithiotakis, 2018). Furthermore, levels of various FRs evaluated in human serum or breast milk have previously been observed to correlate with concentrations measured in hair and/or nails, indicating that inhalation and/or ingestion may be important exposure mechanisms (Wemken *et al.*, 2020; Müller *et al.*, 2016). Average doses were calculated based on the assumption that laborers are directly exposed to contaminated air and soil. Human exposure to environmental pollutants from inhalation of outdoor air and ingestion of soil was estimated using average concentrations found in air and soil samples collected and the EPA-recommended inhalation and ingestion factors (USEPA, 1992).

Human exposure to environmental contaminants through the inhalation of outdoor air, and the ingestion of soil was estimated using average concentrations that we found in air (gaseous phase) and soil samples across all sites through the application of inhalation and ingestion factors recommended by the EPA. Average daily doses for gaseous phase (ADDgas) and soil ingestion (ADDsoil) were calculated using eq. 3.23 & 3.24 for BFRs analyzed through the application of the exposure factors provided by EPA (USEPA, 2004; Wayne & Lance, 2006, Syed *et al.*, 2020).

$$\text{ADDgas} = \text{Cgas} \times \text{InhR} \times \text{ET/BW} \qquad \text{(Eq. 3.23)}$$

$$\text{ADDing} = \text{Csoil} \times \text{IngR} \times \text{ET/BW} \qquad \text{(Eq. 3.24)}$$

Where, Cgas (pg/m^3) and Csoil (ng/kg) is the average concentration of BFR in Gaseous phase and soil, InhR is the inhalation rate (m^3/h), IngR is ingestion rate of soil (g/day), ET is the exposure time of an adult and BW is body weight of an adult (kg). A mean daily inhalation rate of 0.833 m^3/h (Kelepertzis, 2014) was used with the assumption that on average a person spends 6 h/day (i.e., 1/4 of the day) in an outdoor environment. Ingestion Rate of 0.057 soil (g/day) (Jones-Otazo *et al.,* 2005) based on the assumption that laborers are directly exposed to contaminated soil. Average body weight was assumed to be 70 kg (Ali *et al.,* 2012). Factors needed for the calculations were obtained from similar studies and US EPA recommended settings. Details are given in Tables 3.5 and Appendix- 9.

Table 3.5: Details of parameters and exposure doses for estimation of human exposures

Parameters	**Abbreviations**	**Exposure doses**	**References**
Exposure frequency (days/year) EF 3504	EF	350	Umair *et al*. (2013)
Exposure duration (years)	ED	30	Umair *et al.* (2013)
Body weight (kg)	BW	70	Ali *et al.* (2012)
Averaging time (days; ED x 365 days/year)	AT	10950	WHO (2015)
Lifetime (years)	LT	65	WHO (2015)
Ingestion Rate of soil (g/day)	IngR	0.05	Jones-Otazo *et al*. (2005)

Oral reference dose (ng/kg bw/day), some BDEs data were suggested by the United States Environmental Protection Agency Integrated Risk Information System (www.epa.gov/ncea/iris/index.html) and other BDEs congeners date were assumed BDEs congeners with the same bromine atoms numbers were equivalent reference dose.

3.8 Statistical Analysis

SPSS Statistics version 22 was employed to carry out the statistical analysis. We employed analysis of variance (ANOVA) to explore differences in the average levels of target chemicals across all study locations and seasonal variation at single site. Additionally, linear regression models were employed to interpret the data for correlations between levels, reference site concentrations, and meteorological data. Moreover, we utilize analysis of variance with repeated measurements (RMANOVA) as one approach to ascertain the significance of variations in concentration through a four-season period in every city. Arc-GIS software (version 10.2.2) was used to identify sampling sites, to construct sample maps and other relevant work.

Chapter 4

Results and Discussion

Part 1: Gaseous Elemental Mercury Emissions from Informal E-Waste Recycling Facilities in Pakistan

Part 2: Informal E -Waste Recycling in Nine Cities of Pakistan Reveals Significant Impacts on Local Air and Soil Quality and Associated Health Risks

Part 3: Characterization and Distribution of Brominated Flame Retardants in Soils from Informal E-Waste Recycling Facilities: Insights from Pakistan

Part 4: Investigating Brominated Flame Retardants (BFRs) in Informal E-Waste Recycling Facilities: An Assessment of Source, Distribution, and Human Exposure in Pakistan

4.1 Part-I

"Gaseous Elemental Mercury Emissions from Informal E-Waste Recycling Facilities in Pakistan"

The results presented in part 1 are published and complete reference is:

Kazim, M., Syed, J. H., Kurt-Karakus, P. B., Akcetin, M. O., Akram, S., Birgul, A., ... & Wania, F. (**2023**). Gaseous elemental mercury emissions from informal E-Waste recycling facilities in Pakistan. Waste Management, 170, 261-269.

4.1.1 Methodology

Detailed description of field sampling and laboratory analysis, statistical analysis and QC/QA of GEM in air are given in Chapter 3 (Section 3.2).

4.1.2 Results and Discussion

4.1.2.1 Average GEM Concentrations at Background and E-Waste Sites

Table 4.1 presents the GEM concentration levels that were determined at each of the four deployment times at the sampling sites. As of right now, there is inadequate national environmental monitoring data to evaluate the normal background GEM concentrations in Pakistan. The concentration at background site in Rawalpindi ranged seasonally from 1.9 to 3.8 ng m^{-3} and was recorded in the (3.1± 0.81 ng m^{-3}) as average level. According to Venter et al. (2015) and Sprovieri et al. (2016), this is around twice and three times the global background concentration in the Northern (1.5–1.7 ng m^{-3}) and Southern (1.1–1.3 ng m^{-3}) hemispheres, respectively. For example, in a distant mountain peak station in Kodaikanal, India, GEM levels of 1.5 ng m^{-3} have been determined (Karthik *et al.,* 2017; Karuppasamy *et al.,* 2020). According to Fu et al. (2010), the concentration level in Rawalpindi (3.1± 0.81 ng m^{-3}) is higher or equivalent to background locations in Southern China (2.8 ng m^{-3}).

Such elevated GEM concentrations at background (reference site) in Pakistan presumably caused by a number of factors, such as the burning of coal (Joy and Qureshi, 2023), chlor-alkali facilities (Jamil *et al.*, 2015), production of coal (Ali *et al.*, 2017, and gold mining operations (Riaz *et al.*, 2018). Other probable sources might include air transport from other regions, especially from neighboring countries with significant Hg emissions like India (Lin *et al.,* 2019), and traffic-related emissions in metropolitan areas (Yue *et al.,* 2021; Cabassi *et al.,* 2022).

Table 4.1: Descriptive statistics of spatio-temporal GEM (ng m^{-3}) levels at nine major cities of Pakistan

Sampling cities	Site code	Autumn	Winter	Spring	Summer	Site Mean	Site S.D	Site Range	City's Mean±S.D (Range)
Peshawar	**J1**	14.0	13.4	6.57	79.9	28.4	34.5	6.57-79.9	15.2±17.5 (4.86-79.9)
	J2	15.4	13.1	10.9	10.7	12.5	2.20	10.7-15.4	
	J3	13.2	13.8	9.7	6.93	10.9	3.21	6.93-13.8	
	J4	7.58	11.1	12.8	4.86	9.08	3.56	4.86-12.8	
Faisalabad	**J5**	11.3	7.99	5.77	7.74	8.2	2.29	5.77-11.3	9.08±2.92 (5.69-13.9)
	J6	7.7	9.1	6.07	5.69	7.14	1.57	5.69-9.10	
	J7	12.8	14	12.7	8.05	11.9	2.63	8.05-14.0	
Rawalpindi	**Background Site**	3.36	2.83	1.94	3.84	2.99	0.81	1.94-3.84	10.4±8.85 (1.78-34.7)
	J8	9.25	6.45	3.67	1.78	5.29	3.26	1.78-9.25	
	J9	7.79	10.7	4.08	6.31	7.21	2.78	4.08-10.7	
	J10	34.7	18.3	12.9	9.01	18.7	11.3	9.01-34.7	
Lahore	**J11**	18.1	19.2	21.6	20.3	19.8	1.50	18.1-21.6	16.4±4.16 (8.21-21.6)
	J12	15	17.5	8.21	13.5	13.6	3.93	8.21-17.5	
	J13	20.3	13.6	10.9	18.7	15.9	4.38	10.9-20.3	
Karachi	**J14**	92.1	49.5	39.2	42.6	55.9	24.5	39.2-92.1	16.9±22.2 (4.20-92.1)
	J15	8.99	8.39	5.73	5.9	7.25	1.68	5.73-8.99	
	J16	9.08	5.32	4.2	6.27	6.22	2.09	4.20-9.08	
	J17	6.4	8.17	9.13	8.88	8.15	1.23	6.40-9.13	
	J18	7.7	5.96	6.63	8.02	7.08	0.95	5.96-8.02	
Gujranwala	**J19**	5.09	5.49	5.87	5.16	5.4	0.36	5.09-5.87	12.7±8.01 (3.61-28.1)
	J20	12.2	3.61	19.5	17.3	13.2	7.06	3.61-19.5	
	J21	28.1	20.6	10.4	18.8	19.5	7.27	10.4-28.1	
Multan	**J22**	12	12.9	2.78	6.06	8.42	4.84	2.78-12.9	11±8.11 (2.78-34.5)
	J23	12.7	10.5	5.2	5.62	8.38	3.69	5.20-12.3	
	J24	34.5	11.9	7.99	10.9	16.3	12.2	7.99-34.5	
Quetta	**J25**	4.47	13.2	-	32.6	16.7	14.40	4.47-32.6	9.32±6.67 (2.78-32.6)
	J26	6.07	6.51	11.5	4.95	7.24	2.90	4.95-11.5	
	J27	4.33	2.78	10.3	3.82	5.31	3.39	2.78-10.3	
	J28	7.24	9.19	4.79	12.6	8.46	3.3	4.79-12.6	
	J29	12.8	11.1	3.94	7.65	8.86	3.92	3.94-12.8	
Hyderabad	**J30**	3.27	2.51	3.09	8.52	4.35	2.80	2.51-8.52	6.92±6.17 (3.13-25.2)
	J31	6.04	5.15	5.75	4.98	5.48	0.50	4.98-6.04	
	J32	25.2	9.95	3.13	5.51	10.9	9.9	3.13-25.2	
Seasonal mean±S.D		**15.1±16.5**	**11.6±8.45**	**9.19±7.28**	**12.8±8.66**				
Range		**3.27 - 91.7**	**2.51 - 49.5**	**3.09 - 39.2**	**1.78 – 80**				

Countrywide annual Mean±S.D (range) 12.2 ±12.3 (1.78-91.7)

The GEM concentration was four times higher than the levels seen at the reference background location, averaging 12 ng m^{-3} across all 32 e-waste recycling sites in all seasons. It is also around twice as high as what has been recorded for the Pearl River Delta in China (Chen *et al.,* 2013), urban/coastal air in Mexico City (Morton-Bermea *et al.,* 2021; Schiavo *et al.,* 2022) and coastal/urban air in Chennai, India (4.7 ng m^{-3}) (Table 2.1). In addition, the reported levels are similar or slightly above the reported concentration level in Guiyang, China (Feng *et al.,* 2003). High industrialization processes in certain areas have usually been linked to GEM pollution, with coal-fired power stations and cement manufacturing facilities being the main sources of Hg emissions. Even if there are other potential sources of mercury emissions, these significantly high GEM levels seen in Pakistani urban areas imply that recycling of e-waste has the potential to be a significant contributor. They are supporting previous research from Pakistan (Iqbal *et al.,* 2015, 2017; Umair *et al.,* 2016; Imran *et al.,* 2017; Sajid *et al.,* 2019) that suggested informal e-waste recycling facilities as a potential source of GEM emission.

4.1.2.2 Spatial Trends

Spatial trends of GEM emission into the atmosphere from each sampling city is given in Table 2. Average GEM concentration recorded were ((mean ± standard deviation) (Range) in ng m^{-3} as: 16.4±9.3 (3.9-92.1), 14.3±1.4 (5.5-21.6), 13.7±14.7 (4.9-79.9), 12.7±3.9 (3.61-28.06), 11.6±3.6 (3.6-28.1), 10.0±4.2 (2.8-34.5), 8.6±4.6 (1.8-34.7), 8.5±4.1 (2.8-32.6), 6.2±4.1 (1.6-25.2) for cities in decreasing order of Karachi > Lahore > Peshawar > Gujranwala > Multan > Rawalpindi > Quetta > Faisalabad > Hyderabad, respectively. There was a serious contamination of GEM in all informal e-waste recycling facilities in all cities. Presumably, the extent of higher emission levels are directed towards quantity and magnitude of the recycling processes responsible for emission.

Among all cities, higher GEM levels were reported from Karachi.

The spatial extent of average GEM emission at individual recycling site is given in Table 4.1 and Figure 4.1. Site (J19: Shershah) is hub of recycling industry (Hasan, 2002) reported highest level of GEM concentration (56.0 ± 24.5 ng m^{-3}). These levels are higher than the values reported at e-waste recycling facilities in Taizhou, China, with an average of 30.7 ng/m^{3} (Tang *et al.,* 2015). This site is in center of Karachi and is the biggest junkyard of Pakistan where all kind of used electronic and locomotive parts are dismantled, re-paired / recycled and then transported to entire country. Average GEM levels the studied sites of Karachi showed the following trend: J19 > J22

> J20 >J23 > J21 > J18. Site J19 along with J21 are major e-waste recycling sites (Rafeeq, 2020) where most of the waste dumped into the Lyari River, which eventually makes its way through the mangroves and into the Arabian Sea. These wastes are a serious threat for Karachi coastal areas which become polluted for marine environment, marine life as well as human health (Tahir, 2017).

Lahore city reported the 2nd largest average GEM concentration with site J15 top ranked (19.8 ± 1.52 ng m^{-3}) among other sites i.e J17, J16 and J14 a contributing (15.9 ± 4.4 ng m^{-3}), (13.6 ± 3.9 ng m^{-3}) and (7.9 ± 2.2 ng m^{-3}), respectively.

The reported level in Lahore city is slightly higher than the Valais city of Switzerland contaminated with 33 tons of Hg at the Gamsenried landfill area monitor by McLagan et al. (2021). Lahore stands among the largest business center of e-waste which imports an average of 5807 tons (6.09 % of total) per year (Imran *et al.,* 2017). Site J15 is the biggest electronic market in Lahore, where tonnes of second-hand equipment are offered for cheap prices by local vendors (Mehmood, 2022). The recycling processes are carried out by various factories and warehouses with non-ventilated rooms spread across site J17 and J16.

Peshawar city ranked among the highest average GEM concentration city with site J2 among other sites observed 25.9±36.0 ng m^{-3}. The reported level in this site is comparable with earlier study by Decharat, (2018) investigated GEM emissions by e-waste recycling site at Thammarat Province, Thailand i.e., (29 ng/m^3). The elevated trends of GEM on other sampling sites i.e., J3 > J4> J1 > J5. Mostly, recycling activities at Peshawar city are carried out by teen-aged and women without any safety or protective measures. At Gujranwala city high level were reported from densely populated residential J27 site, already highlighted for e-waste recycling and metal smelting factories (Crossing)). GEM concentration level followed the trend as J27 > J26 > J24 > J25. The observed results at site J25 suggested that Chandala village near Kamoke, is well-known for dismantling and open burning of printed circuit boards are responsible for local atmospheric-Hg pollution in the area.

The concentrations levels reported in Rawalpindi city are (18.7 ± 11.3, 7.2 ± 2.8, 5.3 ± 3.3 and 3.0 ± 0.8 ng m^{-3}) for sites J13, J12, J11 and J10, respectively. Rawalpindi is located near the capital city (Islamabad), where e-waste recycling and disposal is far lower/small-scale compared to Lahore and Karachi (Iqbal *et al.,* 2015; Imran *et al.,* 2017). Similar patterns of GEM emissions were also observed while comparing them with both cities. Concentration levels of GEM at

Faisalabad sites are ranked as J9> J7 > J8 > J6. The average levels are comparable the study by Feng et al. (2003) reported (7.39 ng m^{-3}) at the Guiyang Coal Fired Power Plant and the Guizhou Cement Production Plant, the two largest single mercury emission point sources in China. Sites J9 (Motor market) and J8 (Sargodha Road (Bilal Gunj)) are famous for used electronic and electrical equipment repairing, refurbishment and recycling for secondary use. Site J7 (Rex City) marked as city's massive repairing and disassembling center for second-hand computers, laptops, and LCDs. Most of the e-waste is dismantled here, and individual components are sold to recyclers.

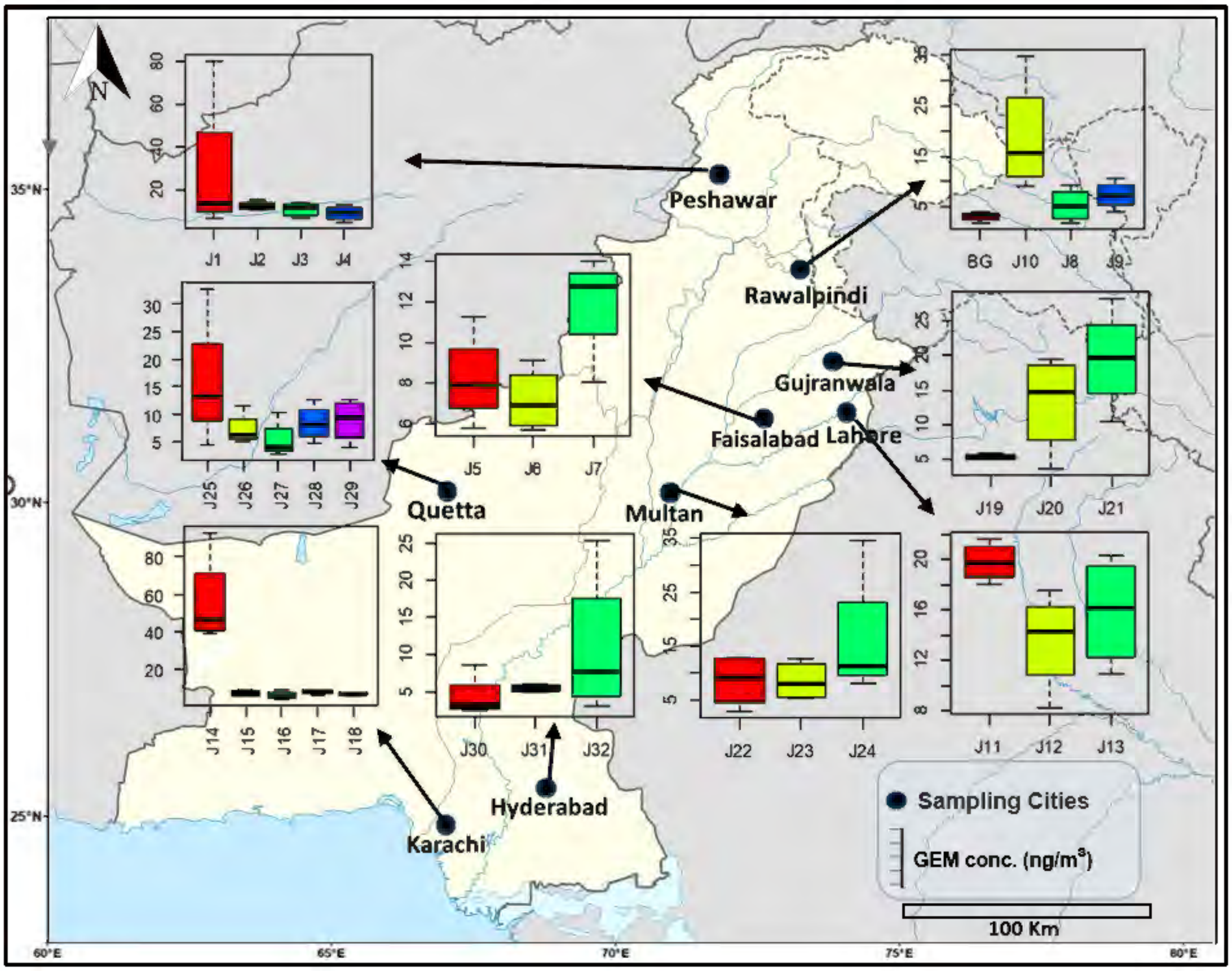


Figure 4.1: Yearly mean concentrations of GEM (ng m^{-3}) at individual e-waste recycling sites in Pakistan

The highest concentration observed in Multan city was at site J31 (16.3 ± 12.2 ng m^{-3}). This site is famous for repairing, dismantling, and recycling for recovery of precious metal from laptops, mobile phones, printers, monitors, and other electronic gadgets. While highest levels were recorded at site J33 i.e., (16.7 ± 14.4 ng m^{-3}) in Quetta City. Among all cities, lower average concentration was reported in Hyderabad. The average concentration level in Hyderabad sites were (10.9 ± 9.9, 5.48 ± 0.5 and 4.4 ± 2.8 and 4.0 ± 2.3 ng m^{-3}) for J41, J40, J39 and J38, respectively. The results are comparable with coal-fired power plant emitting an average of 2.8 ng/m^3 of GEM annually at Mexico's Pacific coast (Garca *et al.,* 2017).

Among the studied cities, GEM concentrations in Gujranwala, Rawalpindi, Faisalabad, Multan, Quetta and Hyderabad were lower, but still well above background. This may be due to less and smaller-scale recycling activities in those cities when compared to Karachi, Lahore and Peshawar (Imran *et al.*, 2017), consistent with what has been reported by Shaikh et al. (2020) and Hameed et al. (2020). According to Ilyas et al. (2017), small and medium-sized steel and metal extraction industries operate in Gujranwala, suggesting that industrial emissions from chrome-plating facilities, metal smelters and informal melting of e-waste for the extraction of precious metals (Faiz *et al.*, 2015) could be active source of emissions in this city.

4.1.2.3 Seasonal Trends

The actual GEM concentration levels at each season are presented in Figure 4.2. Pakistan has four well defined seasons, the warm and rainy Summer (June to August), dry Autumn (September to November), cold and dry Winter (December to February) and Spring (March to May). The seasonal variation in the coastal area (i.e Karachi) is slightly different from rest of the country: winter (January to March), pre-monsoon (April to June), monsoon (July to September), and post-monsoon (October to December) (Khan, 1991).

Average seasonal concentration (13.8 ± 4.9, 11.2 ±5.1, 10.2 ± 2.6 and 8.1 ± 3.2 ng m^{-3}) were recorded with a slight decreasing trend as; autumn > summer > winter > spring, respectively. The variations among seasonal level could be due to the magnitude of yearly e-waste recycling activities in monitoring sites (Wan *et al.,* 2009). While the variations may also be due to the photochemical oxidation processes among different species of Hg which have various trend among different seasons (Zhang *et al.*, 2013). However, the slight difference in the mean seasonal levels showed a negligible impact of meteorological parameters on GEM distribution.

Similar seasonal variations were also extensively reported in coastal/rural sites (Mao *et al.*, 2008; Kellerhals *et al.,* 2003). Several natural and anthropogenic factors contribute to this seasonal variation. Naturally, seasonal difference of meteorological conditions, reduced mixing height that can enhance GEM levels cold seasons. While greater GEM oxidation and subsequent high removal rate can reduce GEM levels in warm seasons (Mao *et al.,* 2008).

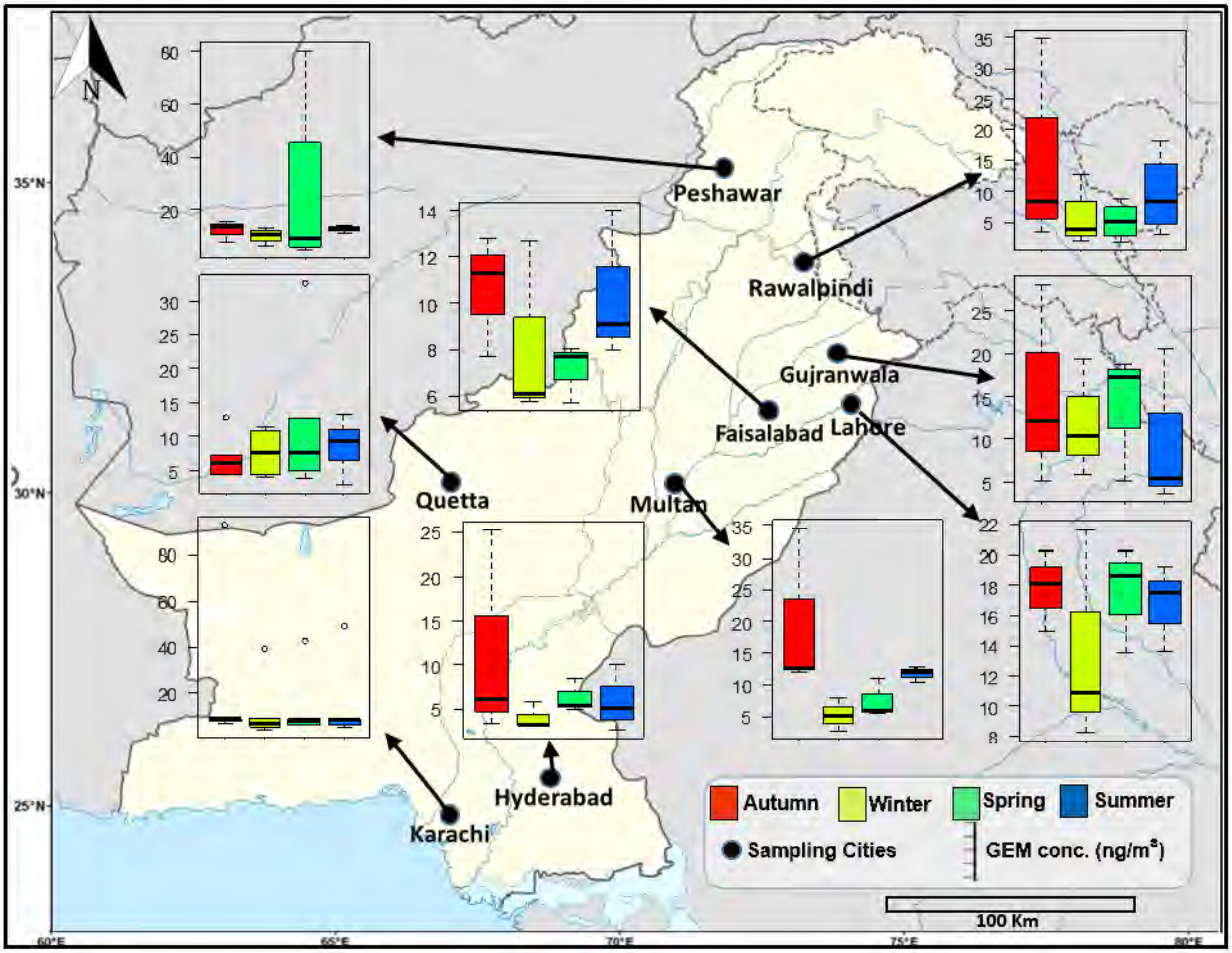


Figure 4.2: Temporal level of GEM (ng m^{-3}) at study sites

4.1.2.4 Comparing measurements from global e-waste recycling sites

The annual mean GEM concentration investigated in current study are compared to those earlier reported for several e-waste recycling sites globally in Table 2.1 (Chapter 2: review of literature). The current study illustrated a yearly average GEM concentration of 12 ng m^{-3} at studied e-waste recycling locations, which is minimal while comparing to the values reported in Norway (Snow *et al.*, 2021) and Taizhou, China (Tang *et al.*, 2015). Conversely, the elevated GEM concentrations we noticed at site J1 in Peshawar and J14 in Karachi which are similar with the mean levels reported in earlier research studies. The closeness of PASs to e-waste recycling operations (5-20 m) in previous research may have led to higher levels, while in our study samplers were installed approximately (~200 m) of distance presumably reason for the lower levels. According to Snow et al. (2021), GEM levels ranged between 2.8 and 3.8 ng m^{-3} in their study conducted outside an e-waste recycling factory in Norway. The researcher justified that the quantities of GEM within the enclosed facility were much higher, ranging from 30 to over 1000 ng m^{-3} compared to what is detected outside. The other possible reason for such high levels in Norway was the type of e-waste as Snow et al. (2021) discovered elevated GEM levels around particular types of mercury-containing e-waste, such as fluorescent tubes and broken compact fluorescent light (CFL) bulbs. Similar to the values in this study (e.g., Hyderabad: 6.2 ng m^{-3}), Nipen et al. (2022) monitored GEM levels at Dar-e-Salaam, Tanzania (5.3 ng m^{-3}) as the sites were near to an e-waste recycling center.

4.1.2.5 Implications for Human Inhalation Exposure to GEM

The U.S. Agency for Toxic Substances and Disease Registry (USATSDR, 2015) expresses the Minimal Risk Level (MRL) for chronic inhalation exposure to GEM on a on a daily basis as 200 ng m^{-3}. While USEPA recommended reference value of 300 ng m^{-3} for GEM inhalation on daily basis (Palma *et al.,* 1999). Additionally, the World Health Organization (WHO, 2000) and the International Programme on Chemical Safety (Fisher & WHO, 2003) sets value in-between 100 to 200 ng m^{-3}. Japanese suggested occupational GEM inhalation limits of 40 ng m^{-3} (MOE, 2003). Aside from a few temporal samplings at J14 at Karachi and J1 at Peshawar, which surpassed the Japanese Ministry of the Environment recommended limits, the levels measured here have continuously been lower than above mentioned agencies. Nonetheless, we feel that our results raise major concerns about human inhalation exposure to GEM.

Reason one, we may anticipate that potentially higher levels of GEM prevailed during smaller time periods since our study demonstrated a three-months interval for the calculation of average GEM concentration. Secondly, more prominently, given that our sample installation sites were typically ~200 m away from the actual recycling operations, we assume that the GEM levels in inhaled air might be significantly elevated than the provided value in our study as average yearly values (12 ng m^{-3}). Specifically, we should expect extremely elevated gradients in spatial level among the location of the actual recycling processes and sampling locations (~200m). A solid reason behind our arguments is the previous study conducted by Snow et al. (2021). The researchers in this study found that GEM levels inside a Norwegian e-waste recycling factory falls in between 31 - 1140 ng m^{-3}, which is too high than levels ranged from 2.8 to 3.8 ng m^{-3} at a distance of 100 m from the actual recycling site. In another study conducted by Monaci et al. (2022) reported average GEM levels spanning more than two orders of magnitude (between 17 to 4,200 ng m^{-3}) with a difference of a few 100 m alongside the abandoned Hg- mine processing factories. Furthermore, Snow et al. (2021) employed a different samplers like stationary samplers and personal wearable samplers at two locations i.e., Norwegian e-waste recycling facility and artisanal gold mining communities in Ghana, the latter had constantly higher GEM levels, more commonly by an order of magnitude.

To summarize above discussion, it is projected that inhalation exposures to the human against GEM will persistently and routinely exceed MRLs levels for chronic inhalation exposure by calculating annual mean levels as higher as 56 ng m^{-3} at a rational distance from actual e-waste recycling processes. Such exposures can take place in the community, especially children, who live and play near to such recycling factories in addition to those ones who are actively involved in such operations (laborer).

4.2 Part-II

"Informal E -Waste Recycling in Nine Cities of Pakistan Reveals Significant Impacts on Local Air and Soil Quality and Associated Health Risks"

The results presented in part 2 are published. Here is the complete reference:

Kazim, M., Syed, J. H., Saqib, Z., Kurt-Karakus, P. B., Iqbal, M., Nasir, J., ... & Odabasi, M. (2024). Informal E-Waste Recycling in Nine Cities of Pakistan Reveals Significant Impacts on Local Air and Soil Quality and Associated Health Risks. Environmental Pollution, 124259.

4.2.1 Methodology

Details of field sampling, sample preparation, laboratory analysis, statistical analysis and QC/QA of HMs are provided in Chapter-3 (Section 3.2).

4.2.2 Results and Discussion

4.2.2.1 Concentrations levels of Heavy metals at e-waste sites

Mean level of HMs in air and soil as well as background site in four seasons are detailed in Table 4.2. At background site in Islamabad, the average deposition flux of HMs in air during four deployment seasons was noted as 41.8 ± 33.8 µg/m^2.day. Whereas the average deposition flux was found to be 161 ± 111 µg/m^2.day ranging from 56.0 µg/m^2.day (Rawalpindi) to 331 µg/m^2.day (Karachi). Substantially, higher deposition flux at study sites (> 3 times the background site, Table 4.2) presumably due to the presence of active sources of HMs at studied sites. Deposition flux of HMs in air was found in following sequence Zn > Mn > Pb > Cu > Ni > Cr > Cd. Since, the present study is first of its kind from Pakistan in which passive samplers were deployed to study HMs and report concentration in the units of flux (µg/m^2.day), therefore the comparison of deposition flux of HMs in air was not viable with regional or global studies using different methodologies. The compositional trend of HMs in present study were accorded well with those of other e-waste recycling sites in previous studies with higher concentrations of Pb, Zn and Mn than Cr, Ni, Cu and Cd (Table 2.2). The elevated levels of HMs at study sites compared to the background site indicate the contribution of emissions from e-waste recycling sites to the local atmosphere.

Table 4.2: Descriptive statistics of heavy metals at (all e-waste studied sites) refernce site (Islamabad)

	Concentration level in air (Flux, µg/m^2.day)				**Concentration level in soils (µg/g dw)**			
	E-waste Recycling sites		**Background site**		**E-waste Recycling sites**		**Background site**	
HMs	Mean+S.D	Range	Mean+S.D	Range	Mean+S.D	Range	Mean+S.D	Range
Cr	18.9±13.8	2.3-131	5.34±2.58	2.23-7.66	49.4±35.5	3.6-716	19.5±3.10	16.5-23.8
Mn	116±95.8	10.5-1520	33.47±13.3	15.8-45.8	372±152	25.1-1599	210±59.9	161-296
Ni	42.2±61.8	1.1-1057	10.0±7.33	3.08-20.2	37.3±26.1	2.9-542	12.2±4.60	8.3-18.8
Cu	97±52.4	7.5-1000	24.7±17.0	5.67-40.8	155±85.3	5.4-2784	11.9±2.06	8.9-13.63
Zn	733±273	23.6-8105	169±110	67.1-323	220±96.9	15.8-2301	45.5±3.81	41.6-49.3
Cd	1.8±0.3	0.1-23.4	0.18±0.09	0.03-0.24	0.6±0.3	0.03-6.3	0.11±0.02	0.10-0.14
Pb	112±74.5	5.9-2992	49.9±86.1	2.35-179	63.1±46.3	2.2-2786	7.97±2.07	4.87-9.16
Avg.	161±111	0.1-8105	41.8 + 33.8	0.03-179	128±63.2	0.03-2786	43.8±10.8	0.10-296

For soil samples, the mean concentrations from recycling facilities were much greater (~1.5 to 13 times) than the background concentration suggesting the influence of extensive e-waste recycling operations (Table 4.2). The mean concentrations of HMs in soils were found in the following sequence Mn>Zn>Cu>Pb>Cr>Ni>Cd which is almost identical to those reported for previous studies at e-waste recycling, dumping and/or dismantling sites (Table 2.3 Chapter-2). This shows that e-waste dismantling and recycling activities substantially contribute towards the contamination of soil. The mean concentration and their ranges for Mn, Cr and Ni were comparable to those noted in Nigeria (Isimekhai *et al.,* 2017), Ghana (Teye *et al.,* 2023), and China (Han *et al.,* 2019), whereas for Cu, Zn, Cd and Pb, the concentrations were much lower than reported by those studies (Table 2.3 in Chapter-2). Soil pollution is often assessed either by comparing total metal concentrations with standard guideline values or by classifying using pollution indices (Wu *et al.,* 2018). In this study, it is apparent that the mean concentrations of Zn and Cd in soils from e-waste facilities exceeded the safe regulatory limits of WHO i.e., 50 µg/g

(Osobamiro *et al.,* 2019) and 0.003 µg/g (Ahmad *et al.,* 2021), respectively. Out of nine selected cities, mean concentrations of Ni, Cu and Pb in four major industrial cities *i.e.,* Karachi, Lahore, Faisalabad and Gujranwala were higher than WHO standard limits of 35 µg/g (El-Naggar *et al.,* 2021), 100 µg/g and 50 µg/g (Teye and Tetteh, 2023), respectively. The soil concentration of Cr in all cities was found under the standard limit of WHO *i.e.,* 100 µg/g (Teye and Tetteh, 2023) except for Gujranwala city where the concentration (112 µg/g) just exceeded the standard limit. For Mn, except in Lahore and Faisalabad, its mean levels were within the recommended limits of WHO (437 µg/g) (Bawwab *et al.,* 2022).

Heavy metal's deposition fluxes reported in the current study were generally align with the patterns observed in the earlier research conducted from various parts of the world, reinforcing the global nature of the issue (Table 2.2 in Chapter-2). For instance, similar to findings in India (Ha *et al.,* 2009), Nigeria (Isimekhai *et al.,* 2017), China (Han *et al.,* 2019 and Ghana (Teye *et al.,* 2023), Pakistani cities exhibit elevated levels of Zn, Mn, Pb, Cu, Ni and Cr as these metals are often associated with electronic waste (Purchase *et al.,* 2020). Zn is used in die-castings, batteries fluorescent lights and X-ray screens in EEE while Mn as an alloy with Pb, Al or Cu is a major constituent of batteries, sensors, and super capacitors. Similarly, Al, Pb Cr, and Cu are major components of printed circuit boards, smart card chips, electrical wiring, and various other EEE. During recycling process (mostly informal) including dismantling, repairing, burning and acids treatment to recover precious metals may possibly initiate heavy metal contamination at the e-waste recycling facilities (Li *et al.,* 2011). In addition to the overall concentration of the metals, the extent of contamination is determined by the fraction of their movable and bioavailable forms, which in general controlled by the organic matter, pH and other properties in soil (Tang *et al.,* 2010).

4.2.2.2 Spatial trends

An intra-city relationship of HMs in the air samples near e-waste facilities is illustrated in Figure 4.3 and Figure 4.4 while descriptive statistics are given in Table 4.3. Karachi, Gujranwala, Lahore, and Faisalabad were found to be the leading cities with high level of HMs. Out of studied HMs, four metals were found higher in Karachi (µg/m^2.day) i.e., Cr (with annual mean 38.4), Mn (231), Zn (1410) and Pb (410) whereas higher fluxes of Ni (157) and Cu (255) were noted for Gujranwala. In Karachi, the maximum fluxes (µg/m^2.day) of Cr (131), Mn (1520), Ni (276), Cu (931), Zn (8105), Cd (23.4), and Pb (2993) were observed at Sher shah (J18) or its adjacent Lyari area (J20). Sher Shah market is the biggest junkyard of Pakistan for used electronic and locomotive parts storage, dismantling, and recycling reported in earlier studies (Hameed *et al.*, 2020; Rafeeq *et al.*, 2021). Recently, Kazim et al. (2023) also reported the higher levels of gaseous elemental mercury at this site which they had associated with e-waste dismantling and recycling processes in Pakistan.

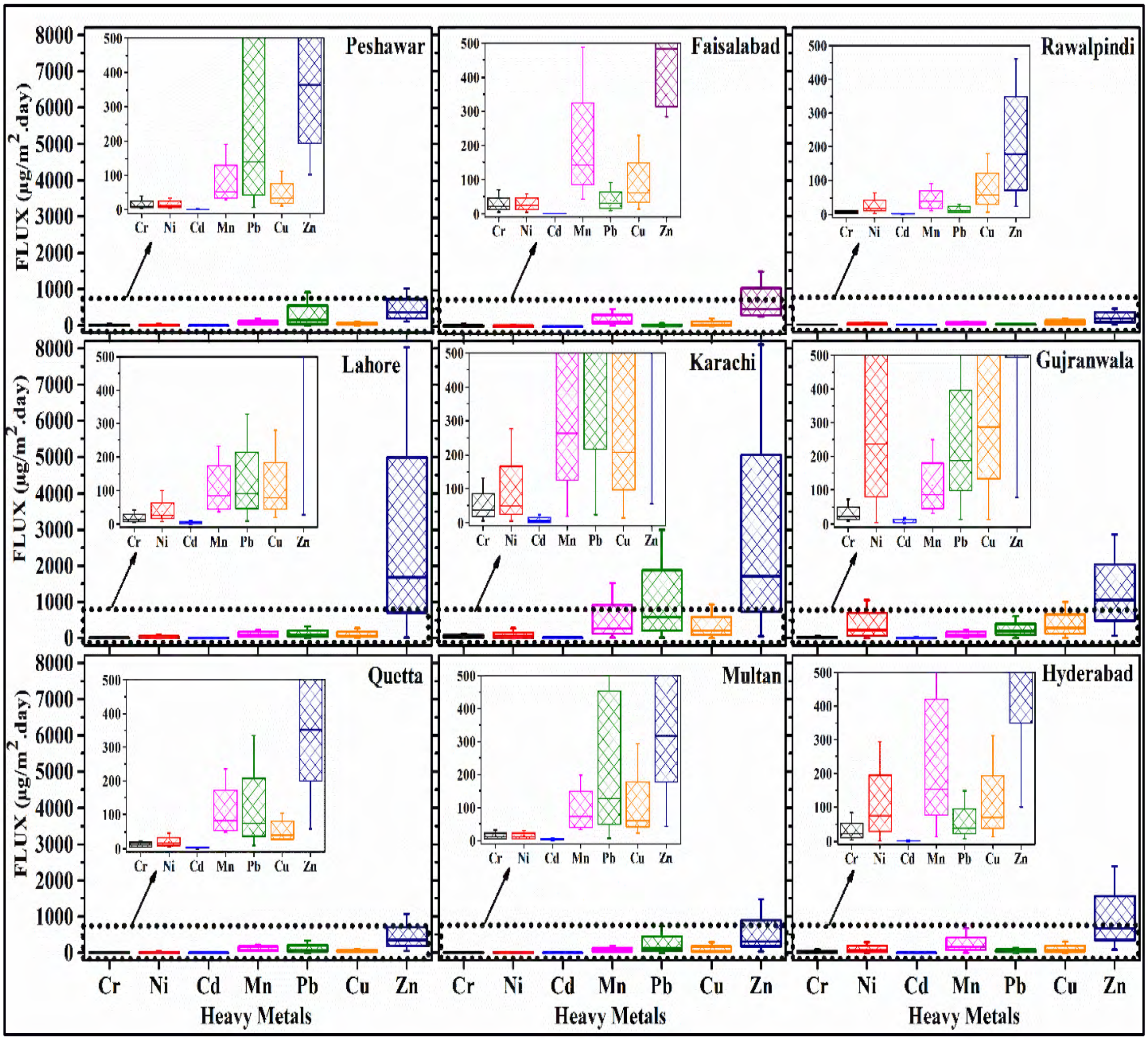


Figure 4.3: An intra-city comparison of heavy metals (flux (µg/m^2.day) in air

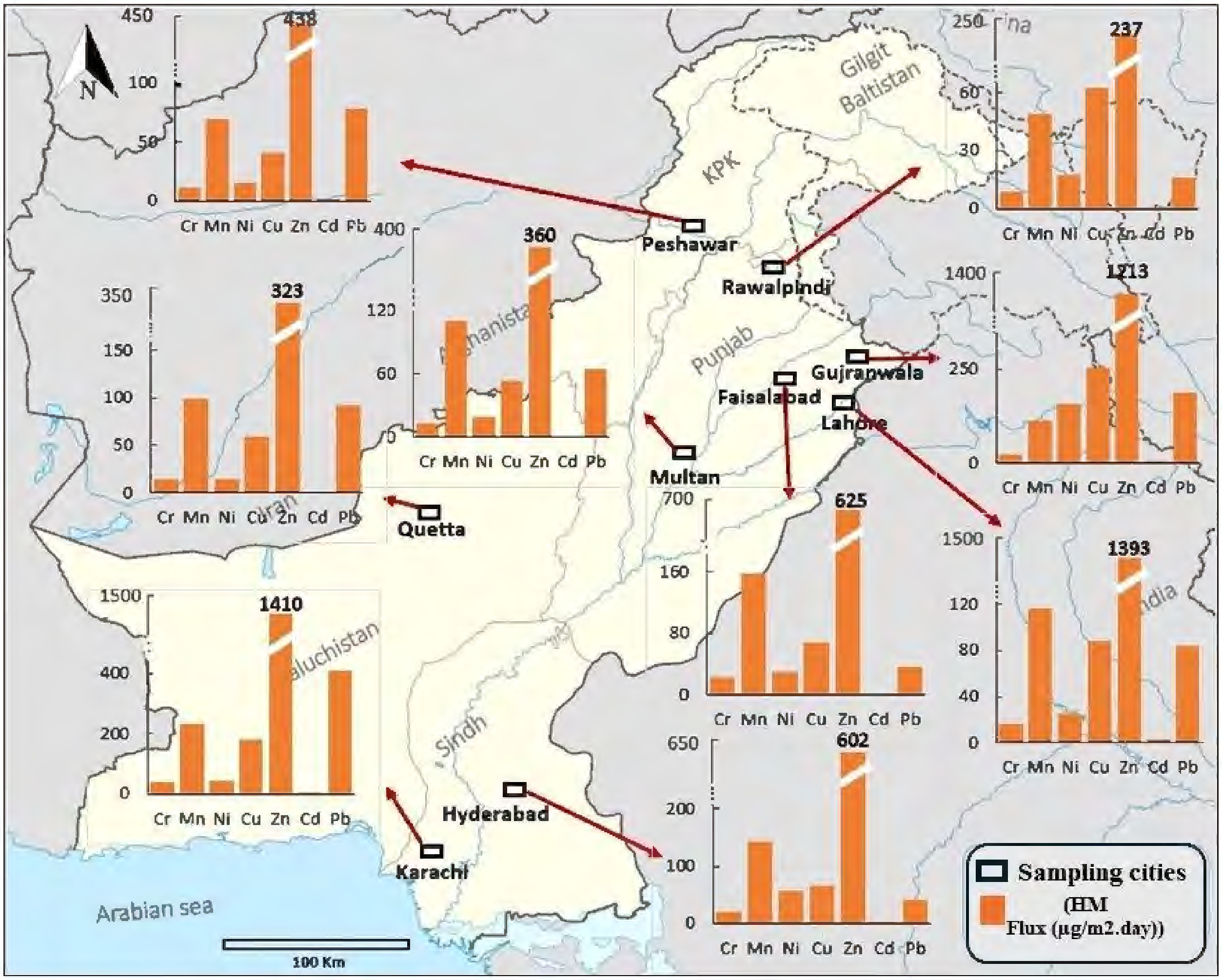


Figure 4.4: Spatial distribution of HMs fluxes (µg/m^2.day) in air from 9 cities of Pakistan

Among the sampling cities, HMs concentrations in Rawalpindi, Multan, Quetta, and Peshawar were lower but still well above background HM levels. High variability of Zn, Cu, Pb, Mn and Ni in major cities in comparison to background concentrations (Table 4.2) may also be due to different sources in addition to contribution from e-waste recycling sites. These sources could also be attributed to the industrial emissions and vehicular traffic (Zhou *et al.,* 2014) as most of the studied sites are densely populated and industrial hubs of some scale. Vehicles emit HMs into the atmosphere mainly via exhaust (fossil fuel emissions) and non-exhaust emissions which include wearing and tearing of different vehicular sections like tires, brake pads, and corrosion of metallic parts. Therefore, USEPA highlights 21 hazardous elements that can mostly be appointed to road traffic (Gupta, 2020); and the five dominant HMs (Zn, Cu, Pb, Mn and Ni) as observed in our study are among them.

Table 4.3: Basic statistics of studied heavy metals fluxes (μg/m^2.day) in air from 9 cities of Pakistan

HMs		Peshawar	Faisalabad	Rawalpindi	Lahore	Karachi	Gujranwala	Multan	Quetta	Hyderabad
Cr	Mean	11.5	23.3	8.7	16.8	38.4	24.5	13.1	13.8	19.7
	S.D	8.62	17.5	3.52	9.33	32.2	20.3	5.12	6.37	21.6
	Min	4.08	5.12	3.42	4.22	3.87	8.07	5.84	4.81	2.26
	Max	41.2	69.5	12.8	41.6	131	73.6	24.0	31.7	83.5
Mn	Mean	69.4	159	49.3	116	231	112	110	99.1	143
	S.D	36.6	128	26.2	53.7	296	59.9	49.5	46.2	166
	Min	29.4	43.7	10.5	35.7	18.6	30.5	54.9	32.8	12.0
	Max	191	489	90.7	232	1520	250	235	198	676
Ni	Mean	15.9	30.5	17.5	25.0	44.0	157	18.8	14.8	56.3
	S.D	9.18	17.9	18.8	24.6	55.1	319	11.4	6.30	94.5
	Min	4.51	5.30	2.70	7.16	3.91	3.39	4.96	5.56	1.08
	Max	34.4	57.5	64.6	100	276	1057	44.6	30.6	295
Cu	Mean	41.0	68.9	62.4	88.5	179	255	54.0	58.9	65.5
	S.D	27.7	53.9	55.2	67.6	235	321	26.6	61.0	73.9
	Min	11.4	13.7	7.51	20.1	13.6	13.5	27.4	22.4	11.7
	Max	113	230	180	280	931	1000	105	295	313
Zn	Mean	438	625	237	1393	1410	1213	360	323	602
	S.D	289	285	119	1948	1997	911	343	310	753
	Min	102	343	23.6	27.3	56.8	78.6	59.0	43.0	100
	Max	1014	1515	461	8028	8105	2860	1072	1475	2394
Cd	Mean	0.95	0.51	0.46	3.23	3.69	5.21	0.67	0.91	0.70
	S.D	0.72	0.29	0.41	3.53	6.39	6.10	0.98	1.65	0.71
	Min	0.17	0.11	0.12	0.11	0.09	0.18	0.11	0.11	0.10
	Max	2.51	1.17	1.37	11.3	23.4	17.9	3.80	7.54	2.21
Pb	Mean	77.9	37.0	16.1	84.0	410	189	65.0	92.0	40.6

S.D	203	24.1	7.78	96.8	768	186	83.2	165	36.1
Min	7.42	8.29	5.91	8.22	23.1	11.3	8.97	6.97	6.87
Max	918	91.1	30.8	328	2993	604	335	741	149

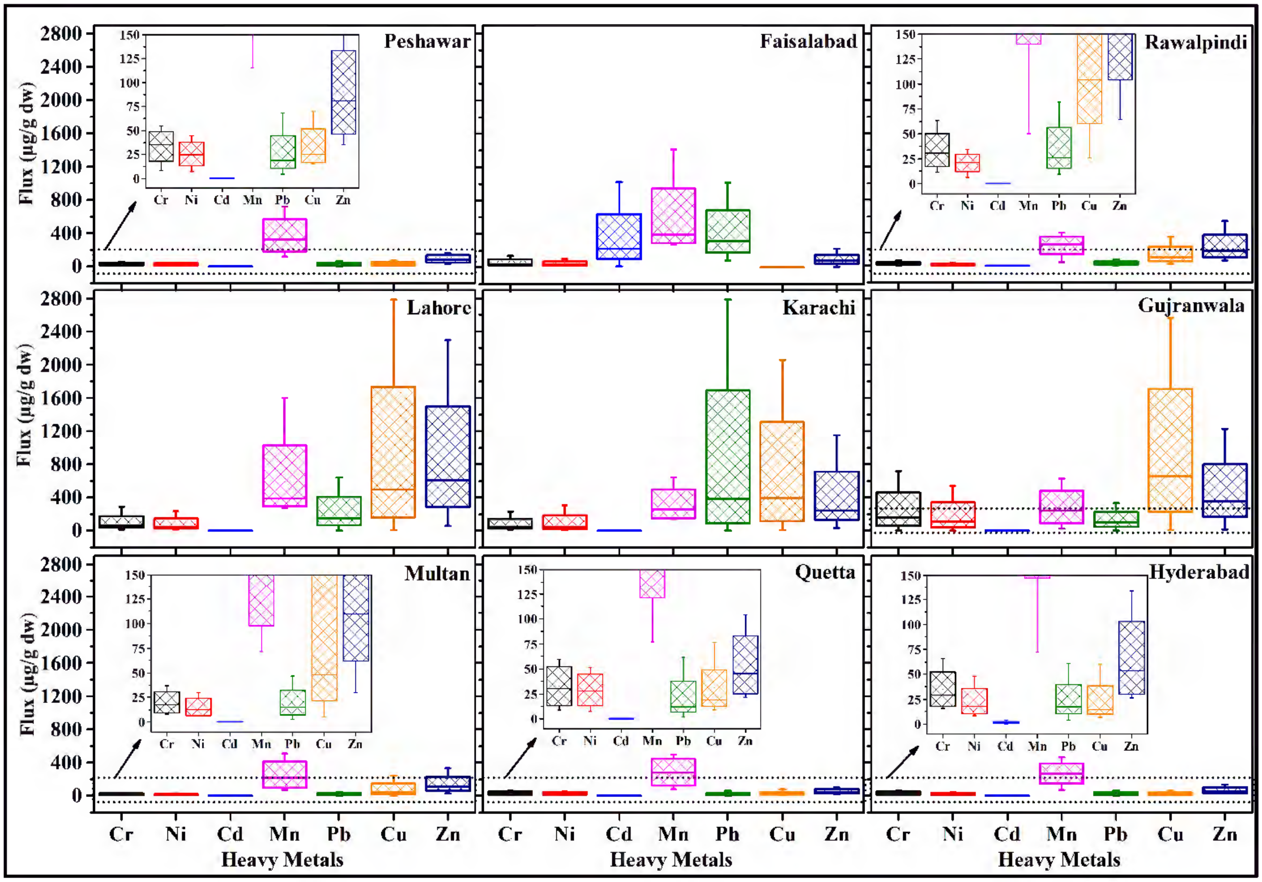


Figure 4.5: An intra-city comparison of targeted metals in soils (µg/g dw)

Descriptive statistics for the HMs concentrations found in samples collected from soil at contaminated sites in nine cities are summarized in Table 4.4 and their variations are shown in Figure 4.5, while spatial distribution maps are given at Figure 4.6. Higher mean concentrations (µg/g dw) of Cr (112), Ni (79), Cu (457) and Cd (1.32) were found in Gujranwala. Among four selected study sites in Gujranwala, the industrial zone site (J26 Site) made major contribution in elevating the mean concentration of HMs.

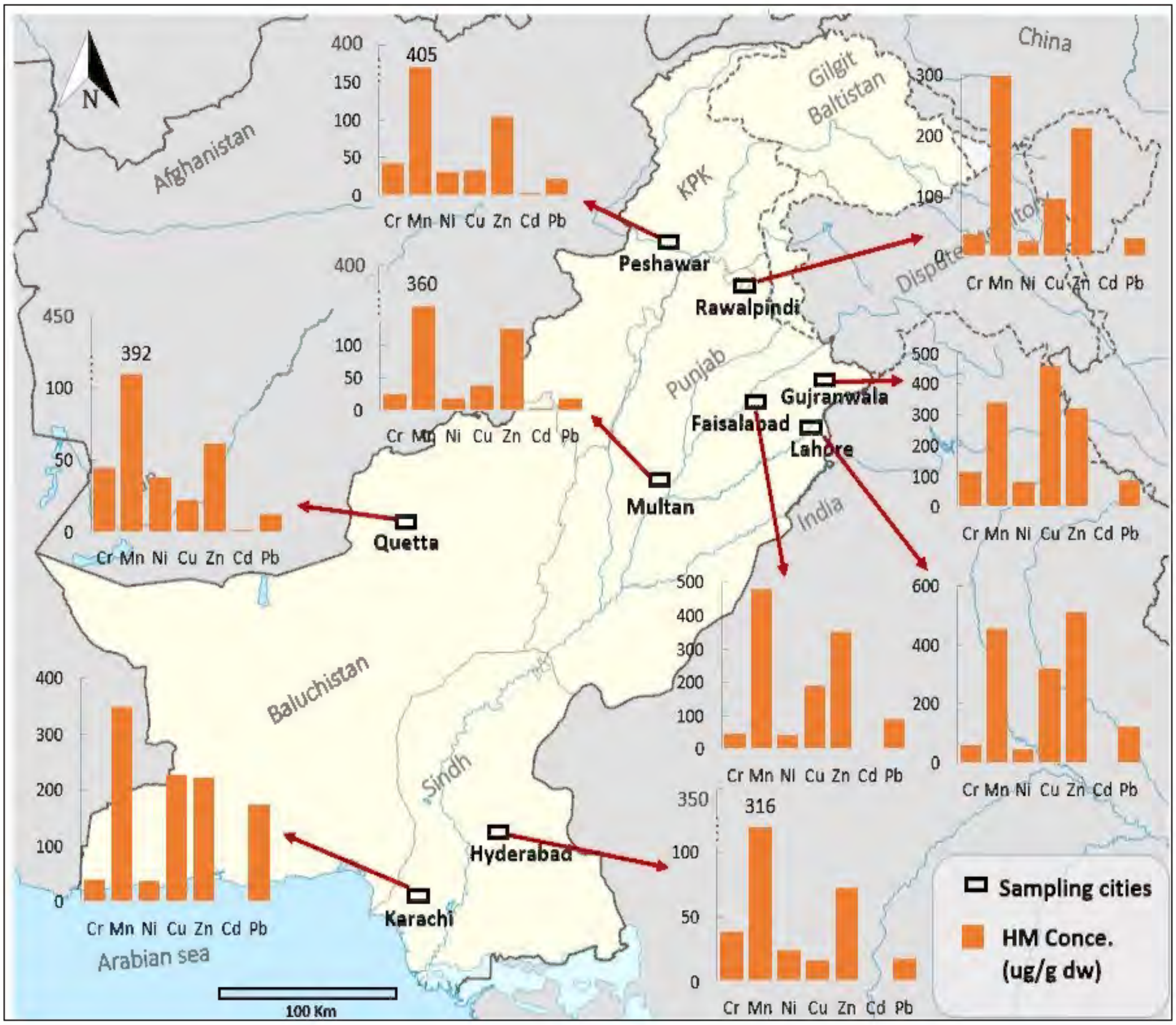


Figure 4. 6: Spatial distribution of heavy metals (µg/g) in soils from 9 cities of Pakistan

Maximum concentrations of Cr, Ni, Cu, and Cd at this site were observed up to 716, 542, 2565 and 4.53 (in µg/g dw) respectively in different seasons which were nearly 1 ~ 2 orders of magnitude higher than the background site (Table 4.2). The Gujranwala’s industrial zone is a center for buying/selling of e-waste with informal recycling of printed circuit boards (PCBs) by using include acid baths, open burning etc.

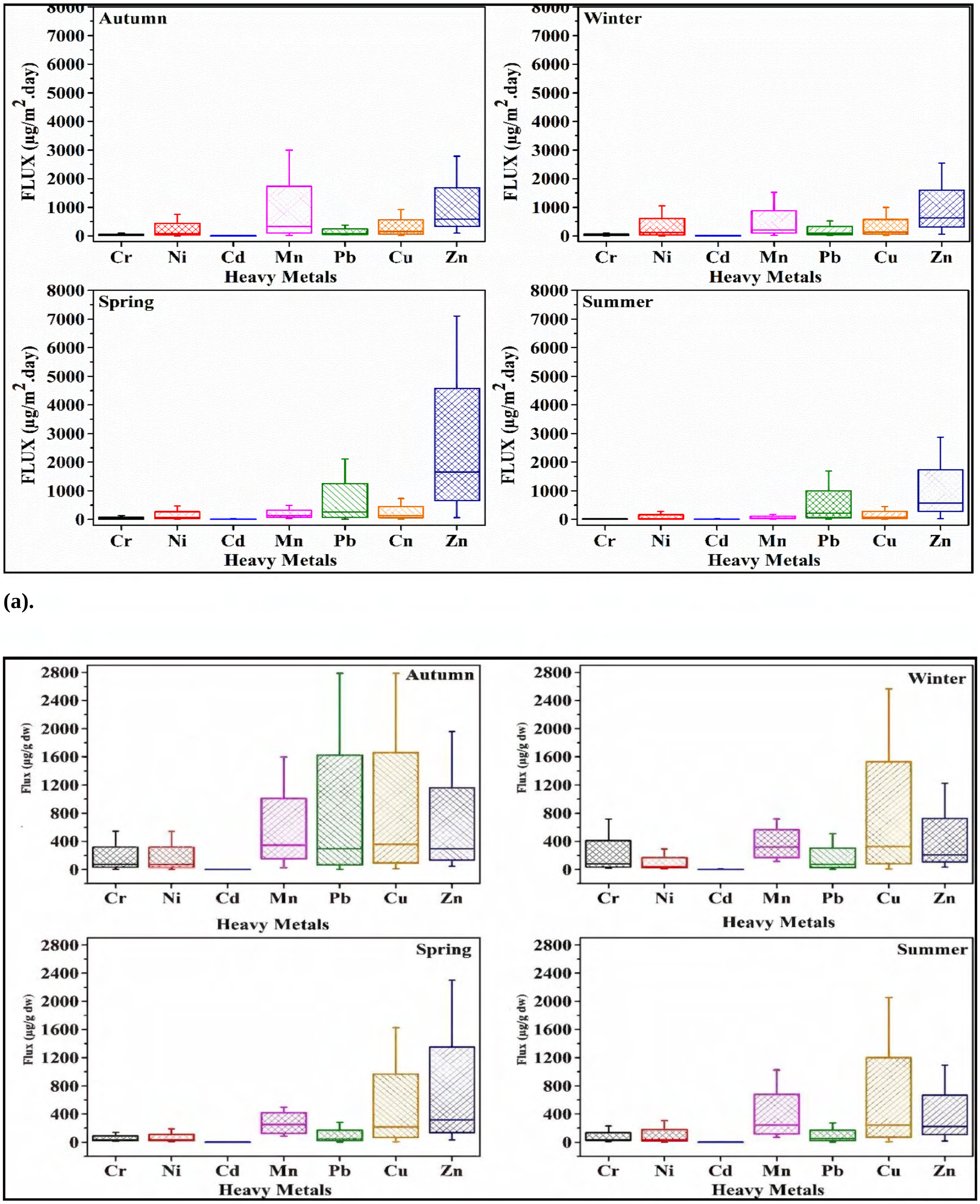
Table 4.4: Basic statistics of studied heavy metals (µg/g) in soils from 9 cities of Pakistan

HMs		Peshawar	Faisalabad	Rawalpindi	Lahore	Karachi	Gujranwala	Multan	Quetta	Hyderabad
Cr	Mean	42.4	46.2	37.1	60.4	39.5	112	24.6	44.3	38.4
	S.D	8.06	32.2	11.5	67.3	50.2	208	8.11	8.89	15.7
	Min	27.5	18.6	23.8	18.0	14.4	3.6	10.7	17.1	19.8
	Max	54.8	142	63.4	286	229	716	36.8	59.7	66.3
Mn	Mean	405	477	299	456	348	337	316	392	316
	S.D	116	307	50.2	322	142	156	123	76.9	72.4
	Min	250	272	229	273	161	25.1	71.7	165	223
	Max	720	1415	405	1599	645	630	513	497	466
Ni	Mean	31.0	40.6	24.8	44.8	37.3	79.3	18.8	37.2	23.8
	S.D	7.30	25.6	6.20	53.9	63.2	146	6.80	7.34	8.61
	Min	18.4	17.6	17.7	15.8	8.45	2.89	6.62	18.5	12.5
	Max	44.4	105	34.3	238	304	542	29.8	51.8	47.9
Cu	Mean	32.8	190	94.4	319	228	457	37.7	21.6	16.6
	S.D	15.1	254	114	680	562	856	58.4	16.3	12.9
	Min	17.6	11.7	26.0	8.36	6.39	6.52	5.41	8.78	7.02
	Max	69.9	1024	350	2784	2054	2565	244	76.6	60.2
Zn	Mean	104	350	213	514	221	319	124	61.5	72.4
	S.D	34.9	277	143	694	273	380	94.1	21.7	34.0
	Min	57.8	84.1	64.6	56.8	32.9	15.8	30.2	29.3	26.7
	Max	164	1013	539	2301	1150	1225	335	104	134
Cd	Mean	0.25	1.10	0.34	0.73	0.87	1.32	0.32	0.15	0.70
	S.D	0.17	1.70	0.15	0.95	1.58	1.57	0.22	0.08	1.33
	Min	0.12	0.10	0.20	0.03	0.10	0.12	0.11	0.03	0.08
	Max	0.71	6.05	0.69	4.05	6.25	4.53	0.80	0.40	4.22
Pb	Mean	20.6	89.3	30.8	121.9	172.4	86.2	17.4	11.6	18.0
	S.D	16.4	80.9	20.7	169.4	594	122.5	12.8	12.9	16.9
	Min	4.11	7.32	9.73	5.03	4.98	3.02	2.84	2.24	4.02
	Max	67.9	221	81.9	643	2786	331	46.4	61.7	60.9

Highest mean concentrations of Mn (477 µg/g), Cu (514 µg/g) and Pb (172 µg/g) in soil were detected in Faisalabad, Lahore, and Karachi. The dominant site in Faisalabad, which had particularly contributed to mean concentrations of HMs was Motor Market (J9) where the concentration of Mn (1415 µg/g dw), Cr (142 µg/g dw), Zn (1014 µg/g dw) and Pb (221 µg/g dw) were higher than other three selected sites within the city. In Lahore and Karachi, the elevated inter-city concentrations of mostly HMs were observed in soil samples collected from Misri Shah (J15) and Sher Shah (J18) respectively. The description of all these sites is summarized in Table 3.3.

4.2.2.3 Seasonal trends

Previous studies have reported substantial influence of meteorological conditions (temperature, wind speed, rainfall) on levels of air pollutants (Nasir *et al.,* 2019) and physicochemical characteristics of soils (Aydın *et al.,* 2023; Isimekhai *et al.,* 2017). Pakistan enjoys four seasons i.e., dry autumn between September and November, dry and cold winter during December and February, spring from March to May, warm and rainy summer which generally lasts from June to August. Since the present study was carried out for one year covering all four seasons, seasonal comparisons of concentrations of studied HMs (Cr, Mn, Ni, Cu, Zn, Cd, Pb) in air and soil were undertaken for each city. Seasonal mean deposition fluxes of HMs in air are presented in Table 4.5 and their seasonal variations are illustrated in Figure 4.7a. On average, higher mean fluxes of all HMs in air were recorded either in Winter or Autumn whereas lowest fluxes were observed during the summer except for Zn, Mean deposition fluxes (µg/m^2.day) of Cu (122), Cd (2.4), and Pb (159) were observed in Autumn whereas those for Cr (25.3), Mn (167) and Ni (67.8) were found during winter. For Zn, higher mean deposition fluxes were inversely found during the spring season. As presented in Table 4.5, this rise in fluxes was only contributed by elevated levels of Zn in Karachi and Lahore. This might be due to the contribution by some additional sources at sites and/or extraordinary dismantling / recycling.



(a).

(b).

Figure 4.7: Seasonal variations of studied heavy metals in (a). air & (b). soil

Table 4.5: Seasonal fluxes (Mean; µg/m^2.day) of heavy metals in air

	Autumn							Winter						
Cities	Cr	Mn	Ni	Cu	Zn	Cd	Pb	Cr	Mn	Ni	Cu	Zn	Cd	Pb
Peshawar	11.5	60.1	25.6	27.2	445	1.3	34.6	16.3	90.0	16.7	67.7	689	1.4	69.9
Faisalabad	19.0	114	43.0	56.6	484	0.6	33.9	41.0	206	42.3	113	857	0.8	47.6
Rawalpindi	11.8	72.6	44.9	79.0	352	0.6	22.0	10.9	68.1	13.5	101	254	0.7	18.8
Lahore	21.5	132	54.1	143	1145	2.8	137	16.5	109	15.5	95.3	879	7.3	132
Karachi	36.5	200	45.6	220	828	4.9	635	43.1	383	30.4	77.7	411	0.7	123
Gujranwala	31.3	123	216	386	1253	9.1	315	28.2	102	274	326	1319	6.4	222
Multan	14.8	114	32.7	84.1	311	0.6	140	13.1	120	15.0	49.8	398	0.4	47.2
Quetta	12.4	85.2	17.8	57.0	266	0.7	51.3	18.3	132	16.3	92.4	462	1.8	91.9
Hyderabad	9.9	66.3	13.3	41.7	142	1.1	59.5	40.3	296	187	141	862	0.3	24.0
	Spring							Summer						
cities	Cr	Mn	Ni	Cu	Zn	Cd	Pb	Cr	Mn	Ni	Cu	Zn	Cd	Pb
Peshawar	12.0	81.1	13.9	49.9	214	0.6	194	6.4	46.4	7.1	19.3	405	0.5	13.1
Faisalabad	20.7	220	23.8	60.2	537	0.3	25.8	12.5	93.6	12.9	45.8	622	0.3	40.5
Rawalpindi	6.5	35.9	6.8	27.7	189	0.2	11.4	4.3	20.5	4.8	42.1	153	0.2	10.0
Lahore	20.3	154	18.2	77.5	3122	1.9	31.0	6.4	55.3	7.8	21.4	104	0.2	19.2
Karachi	58.8	260	42.6	233	3878	3.9	459	18.7	86.0	57.4	193	934	5.3	429
Gujranwala	29.4	165	132	280	1255	3.7	177	9.0	58.4	6.1	28.3	1023	0.4	41.3
Multan	13.6	131	16.2	39.9	399	0.2	19.5	11.0	81.1	10.7	38.8	343	2.0	42.2
Quetta	17.2	133	17.5	41.1	285	0.4	42.4	8.5	56.9	8.6	39.1	267	0.4	181
Hyderabad	19.2	138	17.8	45.7	654	0.3	29.8	9.5	70.6	7.5	34.0	750	1.0	36.7

Average seasonal concentrations of selected HMs in soil at sampling sites are given in Table 4.6. Similarly, higher concentrations of HMs in soil were associated with the dry season i.e., autumn followed by winter, spring, and summer. Mean concentrations (in µg/g dw) of Cr, Mn, Ni, Cu, Cd, Pb were recorded as 59.6, 415.2, 47.8, 188.2, 0.8, 118.5 respectively except for Zn for which the mean elevated levels were observed in spring likewise levels in air.

Table 4.6: Seasonal concentrations (Mean; µg/g) of heavy metals in soils

	Autumn							Winter						
Cities	Cr	Mn	Ni	Cu	Zn	Cd	Pb	Cr	Mn	Ni	Cu	Zn	Cd	Pb
Peshawar	47.3	410	35.7	25.1	74.9	0.1	21.6	44.2	528	35.7	34.5	102.4	0.3	26.3
Faisalabad	40.1	600	32.8	98.9	184	0.6	117	46.9	443	36.0	89.3	281.7	1.7	66.3
Rawalpindi	30.7	257	19.4	49.8	139	0.4	35.3	36.1	358	27.5	56.5	255.2	0.3	49.8
Lahore	91.3	649	75.1	729	607	1.2	186	32.3	341	25.1	40.2	130	0.4	45.2
Karachi	45.1	334	33.1	129	276	1.0	479	24.7	384	30.6	387	266	0.8	108.
Gujranwala	174	367	153	601	504	1.4	168	198	409	87.7	661	357	1.7	90.0
Multan	27.9	382	21.5	23.2	146	0.3	23.8	28.4	389	21.4	25.9	130	0.3	20.1
Quetta	45.5	423	39.2	19.8	72.3	0.2	17.7	48.3	449	40.9	25.2	66.9	0.1	14.3
Hyderabad	33.6	313	20.3	17.0	83.3	2.1	17.6	36.4	384	27.5	25.7	91.7	0.2	34.5

	Spring							Summer						
Cities	Cr	Mn	Ni	Cu	Zn	Cd	Pb	Cr	Mn	Ni	Cu	Zn	Cd	Pb
Peshawar	42.0	374	28.1	28.9	110	0.2	14.6	36.2	307	24.5	42.7	129	0.3	21.1
Faisalabad	57.4	343	56.5	436	575	1.4	107	40.3	520	37.2	134	360	0.5	73.7
Rawalpindi	37.8	274	24.4	135	200	0.4	23.4	43.7	306	27.8	136	258	0.3	20.9
Lahore	51.1	407	37.5	184	768	0.7	95.9	66.9	427	41.5	323	552	0.6	141
Karachi	22.7	275	15.8	25.7	88.4	0.4	7.8	65.5	399	69.6	369	253	1.2	45.9
Gujranwala	51.8	320	61.9	432	287	1.3	56.6	21.4	251	14.4	26.9	128	0.7	10.8
Multan	26.9	330	22.2	28.3	154	0.3	15.5	15.2	163	10.1	85.4	49.8	0.9	7.6
Quetta	43.3	377	37.0	17.9	60.3	0.2	7.8	40.1	319	31.6	23.6	46.5	0.2	7.6
Hyderabad	27.0	293	19.7	11.7	75.7	0.1	11.6	56.6	274	27.5	12.2	38.9	0.2	5.2

In contrast to variability pattern as observed for air levels, high seasonal variability was observed for most of the HMs (Figure 4.7b). The spatial spread of HMs could be attributed to magnitude of e-waste dismantling / recycling activities in addition to variable rainfall patterns in different cities, surface runoffs, human activities across the sites and soil characteristics (Isimekhai *et al.,* 2017). The range of HMs concentrations at e-waste processing sites depends on nature of activities. Isimekhai et al. 2017 had associated clustering of Cd, Cu, Cr, Pb and Zn with recycling activities, whereas the presence of Ni and Mn indicates dismantling activities. Nevertheless, no significant difference ($p > 0.05$) in HMs concentrations were found in different seasons despite different meteorological conditions which shows that sampling sites are hot spots of HMs throughout the year. While positive correlation ($p<0.05$) of most of the heavy metals in soil and in Particulate matter suggest common source of contamination (Table 4.7).

Table 4.7: Correlation analysis of heavy metals in soil (A) and in Particulate matter (B)

HMs	Cr	Mn	Ni	Cu	Zn	Cd	Pb
Cr	1						
Mn	0.096	1					
Ni	0.971	0.221	1				(A)
Cu	0.845	0.216	0.882	1			
Zn	0.482	0.542	0.527	0.797	1		
Cd	0.680	0.193	0.723	0.815	0.612	1	
Pb	0.304	0.317	0.444	0.716	0.684	0.651	1
Cr	1						
Mn	0.932	1					
Ni	0.424	0.160	1				(B)
Cu	0.684	0.412	0.874	1			
Zn	0.741	0.617	0.491	0.729	1		
Cd	0.607	0.362	0.748	0.921	0.878	1	
Pb	0.851	0.723	0.331	0.702	0.694	0.693	1

Spearman Rank's correlation analysis plots for heavy metals in soil (A) and in Particulate matter (B) where blue represents positive correlation ($p<0.05$), red negative ($p<0.05$) and a blank space denotes no existing correlation ($p>0.05$)

4.2.2.4 Geo-accumulation index (Igeo)

Geo-accumulation index (I_{geo}) was determined based on the comparison between concentration level of heavy metals at e-waste recycling facilities with the background site (Islamabad). The calculated I_{geo} values for given recycling sites at sampling cities have been presented in supplementary information (Table 4.8) and assessed with the given criteria for determining the scale of contamination. The I_{geo} values for each heavy metal was interpreted as follows: ≤ 0 (uncontaminated); $0 - \leq 1$ (uncontaminated – moderately contaminated); $1 - \leq 2$ (moderately contaminated); 2 – ≤ 3 (moderately – heavily contaminated); 3 – ≤ 4 (heavily contaminated); 4 – ≤ 5 (heavily to extremely contaminated) and 5 < (extremely contaminated).

Table 4.8: Calculated I_{geo} values at informal e-waste recycling facilities in sampling cities

HMs	Peshawar	Faisalabad	Rawalpindi	Lahore	Karachi	Gujranwala	Multan	Quetta	Hyderabad
Cr	0.54 +	0.66 +	0.34 +	1.05 ++	0.43 +	1.93 ++	-0.25 --	0.60 +	0.39 +
Mn	0.36 +	0.60 +	-0.08 --	0.53 +	0.14 +	0.10 +	0.00 +	0.32 +	0.01 +
Ni	0.76 +	1.15 ++	0.44 +	1.29 ++	1.03 ++	2.12 ++	0.04 +	1.02 ++	0.38 +
Cu	0.88 +	3.41 ++++	2.40 +++	4.16 +++++	3.68 ++++	4.68 +++++	1.08 ++	0.28 +	-0.10 --
Zn	0.60 +	2.36 +++	1.64 ++	2.91 +++	1.69 ++	2.22 +++	0.87 +	-0.15 --	0.08 +
Cd	0.71 +	2.87 +++	1.17 ++	2.29 +++	2.53 +++	3.14 ++++	1.11 ++	-0.03 --	2.22 +++
Pb	0.78 +	2.90 +++	1.36 ++	3.34 ++++	3.84 ++++	2.84 +++	0.53 +	-0.04 --	0.59 +

(Uncontaminated: --; moderately contaminated: +; moderately to heavily contaminated: ++; heavily contaminated: +++; heavily to extremely contaminated: ++++; extremely contaminated: +++++)

Among sampling cities, Lahore, Gujranwala, Karachi, and Faisalabad were the most contaminated ones based on soil residues of the heavy metals. More specifically, Lahore and Gujranwala were extremely contaminated by Cu, while heavily to extremely contaminated by Pb and Cd, respectively. Similarly, Karachi and Faisalabad were marked for moderately to extremely contaminated for all target heavy metals especially Cu, Pb, Ni and Zn. Rawalpindi and Multan have high Cu contamination levels, whereas these sites were moderately to heavily contaminated with Zn, Cd, and Pb. Interestingly, Peshawar and Hyderabad showed moderate contamination of all metals except Cd in Hyderabad. However, the I_{geo} levels for studied sites are elevated while comparing I_{geo} levels of some other regional e-waste recycling locations of the world, e.g., informal e-waste recycling shops in Dhaka, Bangladesh (Mowla *et al.,* 2021) and inside the dumping area of e-waste recycling facility at Korle Lagoon, Ghana for Ni, Pb and Cu (Fosu-Mensah *et al.,* 2017).

The present study found moderate to extreme levels of contamination of soil around e-waste recycling locations (primarily in Pakistan's megacities) by most e-waste oriented heavy metals, raising concerns about their possible exposure to workers and the surrounding environment.

4.2.2.5 Enrichment Factor (EF)

Table 4.9 presents the contamination factor results of HMs in soil and particulate samples of 40 e-waste recycling facilities throughout the country. The mean EF value of Pb>Zn>Cd>Cu>Ni>Cr>Mn was 12.7>8.27>7.83>7.16>1.29>1.28>1.00 in soil, while Zn>Cd>Pb>Cu>Ni>Cr>Mn was 78.9>78.5>64.6>15.2>4.89>1.49>1.00 for particulate samples respectively. Among cities, higher EF values were calculated for Gujranwala, Lahore, Karachi, Peshawar, and Quetta, being the most populated and industrialized cities depicting higher contamination levels. In both sampling matrices, EF values indicate elevated contamination between e-waste recycling facilities for most of the metals studied except for Cr whereas Ni shows a considerable contamination level. Pb, Cd, Zn and Cu levels were found to be elevated in comparison with levels reported from e-waste recycling sites in India (Pradhan & Kumar, 2014). Similarly, higher levels of Cu, Pb, Cd and Zn and low levels of Mn and Ni were calculated from another study conducted in India (Arya *et al.,* 2021). The contamination levels at e-waste recycling sites ranged from substantial or moderate contamination to extremely high contamination in Pakistan’s megacities.

4.2.2.6 Human health risk assessment

In soil $ADI_{soil\text{-}ing}$ was the main exposure pathway to the workers in proximity of e-waste recycling sites in all sampling cities (Table 4.10). Higher $ADI_{soil\text{-}ing}$ was calculated for Zn, Mn, Pb and Cu, while $ADI_{soil\text{-}inh}$ was the least exposure pathway in all sampling cities. Non-CRs exposure of HQ through different exposure routes suggests that $HQ_{soil\text{-}der}$ was the major route followed by $HQ_{soil\text{-}ing}$ and $HQ_{soil\text{-}inh}$ in all sampling cities (Table 4.11).

Table 4.9: Enrichment Factor (EF) of studied metals in soil and particulate matter

Samp. cities	CF	Cr	Mn	Ni	Cu	Zn	Cd	Pb
Peshawar	EF soil	1.00	1.00	0.97	1.40	3.48	2.88	3.86
	EF particulate	1.51	1.00	3.85	10.5	90.4	71.2	61.7
Faisalabad	EF soil	0.92	1.00	1.08	6.87	10.0	11.0	14.2
	EF particulate	1.51	1.00	3.24	7.26	67.9	17.3	19.2
Rawalpindi	EF soil	1.18	1.00	1.05	5.45	9.67	5.36	7.82
	EF particulate	1.51	1.00	4.74	19.5	58.5	35.4	22.6
Lahore	EF soil	1.26	1.00	1.24	12.1	15.3	7.6	20.3
	EF particulate	1.39	1.00	3.01	13.9	146	129	53.3
Karachi	EF soil	1.08	1.00	1.36	11.3	8.6	11.8	37.6
	EF particulate	1.50	1.00	2.36	10.8	57.9	56.4	97.2
Gujranwala	EF soil	3.14	1.00	2.98	23.4	12.8	18.6	19.4
	EF particulate	2.16	1.00	17.4	43.2	153	302	198
Multan	EF soil	0.74	1.00	0.75	2.06	5.35	4.89	4.18
	EF particulate	1.16	1.00	2.68	11.5	38.4	25.4	45.6
Quetta	EF soil	1.07	1.00	1.20	0.95	2.13	1.78	2.26
	EF particulate	1.32	1.00	1.97	11.5	47.2	48.1	59.4
Hyderabad	EF soil	1.16	1.00	0.95	0.91	3.11	10.5	4.3
	EF particulate	1.35	1.00	4.81	8.50	50.2	22.3	24.2
Mean	**EF soil**	**1.28**	**1.00**	**1.29**	**7.16**	**7.83**	**8.27**	**12.7**
	EF particulate	**1.49**	**1.00**	**4.89**	**15.2**	**78.9**	**78.5**	**64.6**

All elements did not pose any threat with value of (HI < 1) for workers residing near e-waste recycling sites. Our results trends were similar to the previous studies on non-CRs health risk assessment (Dutta *et al.,* 2022; Han *et al.,* 2018; Singh *et al.,* 2018). $HQ_{soil\text{-}der}$ was observed to be the main exposure route of heavy metals with high values of HI were calculated for Gujranwala, Lahore, Karachi, and Faisalabad with a value of 3.27×10^{-1}, 2.63×10^{-1}, 2.43×10^{-1} and 2.22×10^{-1}, respectively.

Table 4.10: ADIsoil-$_{ing,}$ ADIsoil-$_{inh}$ and ADIsoil-$_{der}$ due to exposure to heavy metals through soils (mg/kg-day)

Sampling cities	Exposure Pathways	Cr	Mn	Ni	Cu	Zn	Cd	Pb
Peshawer	ADIsoil-ing	4.98×10^{-5}	4.75×10^{-4}	3.64×10^{-5}	3.85×10^{-5}	1.22×10^{-4}	2.88×10^{-7}	2.41×10^{-5}
	ADIsoil-inh	7.32×10^{-9}	6.99×10^{-8}	5.35×10^{-9}	5.67×10^{-9}	1.79×10^{-8}	4.23×10^{-1}	3.55×10^{-9}
	ADIsoil-der	1.21×10^{-5}	1.16×10^{-4}	8.86×10^{-6}	9.38×10^{-6}	2.96×10^{-5}	7.00×10^{-8}	5.88×10^{-6}
Faislabad	ADIsoil-ing	5.42×10^{-5}	5.60×10^{-4}	4.76×10^{-5}	2.23×10^{-4}	4.11×10^{-4}	1.29×10^{-6}	1.05×10^{-4}
	ADIsoil-inh	7.98×10^{-9}	8.23×10^{-8}	7.01×10^{-9}	3.27×10^{-8}	6.05×10^{-8}	1.90×10^{-0}	1.54×10^{-8}
	ADIsoil-der	1.32×10^{-5}	1.36×10^{-4}	1.16×10^{-5}	5.42×10^{-5}	1.00×10^{-4}	3.14×10^{-7}	2.55×10^{-5}
Rawalpindi	ADIsoil-ing	4.35×10^{-5}	3.51×10^{-4}	2.91×10^{-5}	1.11×10^{-4}	2.50×10^{-4}	3.96×10^{-7}	3.61×10^{-5}
	ADIsoil-inh	6.40×10^{-9}	5.16×10^{-8}	4.28×10^{-9}	1.63×10^{-8}	3.68×10^{-8}	5.83×10^{-1}	5.31×10^{-9}
	ADIsoil-der	1.06×10^{-5}	8.54×10^{-5}	7.08×10^{-6}	2.70×10^{-5}	6.09×10^{-5}	9.65×10^{-8}	8.79×10^{-6}
Lahore	ADIsoil-ing	7.09×10^{-5}	5.35×10^{-4}	5.26×10^{-5}	3.75×10^{-4}	6.04×10^{-4}	8.59×10^{-7}	1.43×10^{-4}
	ADIsoil-inh	1.04×10^{-8}	7.87×10^{-8}	7.74×10^{-9}	5.51×10^{-8}	8.88×10^{-8}	1.26×10^{-0}	2.10×10^{-8}
	ADIsoil-der	1.73×10^{-5}	1.30×10^{-4}	1.28×10^{-5}	9.12×10^{-5}	1.47×10^{-4}	2.09×10^{-7}	3.48×10^{-5}
Karachi	ADIsoil-ing	4.64×10^{-5}	4.09×10^{-4}	4.38×10^{-5}	2.68×10^{-4}	2.59×10^{-4}	1.02×10^{-6}	2.02×10^{-4}
	ADIsoil-inh	6.82×10^{-9}	6.01×10^{-8}	6.44×10^{-9}	3.94×10^{-8}	3.81×10^{-8}	1.50×10^{-0}	2.98×10^{-8}
	ADIsoil-der	1.13×10^{-5}	9.95×10^{-5}	1.07×10^{-5}	6.52×10^{-5}	6.31×10^{-5}	2.47×10^{-7}	4.93×10^{-5}
Gujranwala	ADIsoil-ing	1.31×10^{-4}	3.96×10^{-4}	9.31×10^{-5}	5.37×10^{-4}	3.74×10^{-4}	1.55×10^{-6}	1.01×10^{-4}
	ADIsoil-inh	1.93×10^{-8}	5.82×10^{-8}	1.37×10^{-8}	7.90×10^{-8}	5.51×10^{-8}	2.28×10^{-10}	1.49×10^{-8}
	ADIsoil-der	3.19×10^{-5}	9.64×10^{-5}	2.27×10^{5}	1.31×10^{-4}	9.11×10^{-5}	3.77×10^{-7}	2.46×10^{-5}
Multan	ADIsoil-ing	2.89×10^{-5}	$3.71\times10\text{-}^{4}$	2.21×10^{-5}	4.43×10^{-5}	1.46×10^{-4}	3.81×10^{-7}	2.04×10^{-5}
	ADIsoil-inh	4.25×10^{-9}	5.45×10^{-8}	3.24×10^{9}	6.51×10^{-9}	2.15×10^{-8}	5.61×10^{-10}	3.00×10^{-9}
	ADIsoil-der	7.03×10^{-6}	9.03×10^{-5}	5.37×10^{-6}	1.08×10^{-5}	3.56×10^{-5}	9.28×10^{-8}	4.96×10^{-6}
Quetta	ADIsoil-ing	5.20×10^{-5}	4.60×10^{-4}	4.37×10^{-5}	2.54×10^{-5}	7.22×10^{-5}	1.72×10^{-7}	1.37×10^{-5}
	ADIsoil-inh	7.65×10^{-9}	6.77×10^{-8}	6.42×10^{-9}	3.74×10^{-9}	1.06×10^{-8}	2.53×10^{-10}	2.01×10^{-9}
	ADIsoil-der	1.27×10^{-5}	1.12×10^{-4}	1.06×10^{-5}	6.18×10^{-6}	1.76×10^{-5}	4.19×10^{-8}	3.33×10^{-6}
Hyderabad	ADIsoil-ing	4.51×10^{-5}	3.71×10^{-4}	2.79×10^{-5}	1.95×10^{-5}	8.50×10^{-5}	8.23×10^{-7}	2.12×10^{-5}
	ADIsoil-inh	6.64×10^{-9}	5.46×10^{-8}	4.10×10^{-9}	2.87×10^{-9}	1.25×10^{-8}	1.21×10^{-10}	3.11×10^{-9}
	ADIsoil-der	1.10×10^{-5}	9.03×10^{-5}	6.79×10^{-6}	4.76×10^{-6}	2.07×10^{-5}	2.00×10^{-7}	5.16×10^{-6}

Table 4.11: Non-CRs assessment of HMs in soils via ingestion, inhalation, and dermal exposure

Sampling cities	Exposure Pathways	Cr	Mn	Ni	Cu	Zn	Cd	Pb	HI
Peshawar	$\mathrm{HQ}_{\text{soi-Ing}}$	9.96×10^{-3}	3.39×10^{-3}	1.82×10^{-3}	1.04×10^{-3}	4.06×10^{-3}	2.88×10^{-4}	6.90×10^{-3}	2.75×10^{-2}
	$\mathrm{HQ}_{\text{soil-Inh}}$	2.56×10^{-4}	4.99×10^{-3}	2.60×10^{-7}	1.42×10^{-7}	5.97×10^{-8}	4.23×10^{-6}	$1.01\times10\text{-}^{6}$	$5.25\times10\text{-}^{3}$
	$\mathrm{HQ}_{\text{soil-der}}$	4.85×10^{-2}	4.82×10^{-2}	1.64×10^{-3}	4.94×10^{-3}	4.94×10^{-4}	7.00×10^{-3}	1.12×10^{-2}	1.22×10^{-1}
Faisalabad	$\mathrm{HQ}_{\text{soi-Ing}}$	1.08×10^{-2}	4.00×10^{-3}	2.38×10^{-3}	6.02×10^{-3}	1.37×10^{-2}	1.29×10^{-3}	2.99×10^{-2}	6.82×10^{-2}
	$\mathrm{HQ}_{\text{soil-Inh}}$	2.79×10^{-4}	5.88×10^{-3}	3.41×10^{-7}	8.18×10^{-7}	2.02×10^{-7}	1.90×10^{-5}	4.40×10^{-6}	6.18×10^{-3}
	$\mathrm{HQ}_{\text{soil-der}}$	5.28×10^{-2}	5.67×10^{-2}	2.15×10^{-3}	2.85×10^{-2}	1.67×10^{3}	3.14×10^{-2}	4.86×10^{-2}	2.22×10^{-1}
Rawalpindi	$\mathrm{HQ}_{\text{soi-Ing}}$	8.71×10^{-3}	2.51×10^{-3}	1.45×10^{-3}	3.00×10^{3}	8.34×10^{-3}	3.96×10^{-4}	1.03×10^{-2}	3.47×10^{-2}
	$\mathrm{HQ}_{\text{soil-Inh}}$	2.24×10^{-4}	3.69×10^{-3}	2.08×10^{-7}	4.07×10^{-7}	1.23×10^{-7}	5.83×10^{-6}	1.52×10^{-6}	3.92×10^{-3}
	$\mathrm{HQ}_{\text{soil-der}}$	4.24×10^{-2}	3.56×10^{-2}	1.31×10^{-3}	1.42×10^{-2}	1.01×10^{-3}	9.65×10^{-3}	1.67×10^{-2}	1.21×10^{-1}
Lahore	$\mathrm{HQ}_{\text{soi-Ing}}$	1.42×10^{-2}	3.82×10^{-3}	2.63×10^{-3}	1.01×10^{-2}	2.01×10^{-2}	8.59×10^{-4}	4.09×10^{-2}	9.26×10^{2}
	$\mathrm{HQ}_{\text{soil-Inh}}$	3.65×10^{-4}	5.62×10^{-3}	3.76×10^{-7}	1.38×10^{-6}	2.96×10^{-7}	1.26×10^{-5}	6.01×10^{-6}	6.01×10^{-3}
	$\mathrm{HQ}_{\text{soil-der}}$	6.91×10^{-2}	5.43×10^{-2}	2.37×10^{-3}	4.80×10^{-2}	2.45×10^{-3}	2.09×10^{-2}	6.63×10^{-2}	2.63×10^{-1}
Karachi	$\mathrm{HQ}_{\text{soi-Ing}}$	9.28×10^{-3}	2.92×10^{-3}	2.19×10^{-3}	7.24×10^{-3}	8.65×10^{-3}	1.02×10^{-3}	5.78×10^{-2}	8.91×10^{-2}
	$\mathrm{HQ}_{\text{soil-Inh}}$	2.39×10^{-4}	4.29×10^{-3}	3.12×10^{-7}	9.84×10^{-7}	1.27×10^{-7}	1.50×10^{-5}	8.51×10^{-6}	4.56×10^{-3}
	$\mathrm{HQ}_{\text{soil-der}}$	4.52×10^{-2}	4.15×10^{-2}	1.97×10^{-3}	3.43×10^{-2}	1.05×10^{-3}	2.47×10^{-2}	9.38×10^{-2}	2.43×10^{-1}
Gujranwala	$\mathrm{HQ}_{\text{soi-Ing}}$	2.62×10^{-2}	2.83×10^{-3}	4.65×10^{-3}	1.45×10^{-2}	1.25×10^{-2}	1.55×10^{-3}	2.89×10^{-2}	9.11×10^{-2}
	$\mathrm{HQ}_{\text{soil-Inh}}$	6.73×10^{-4}	4.16×10^{-3}	6.65×10^{-7}	1.97×10^{-6}	1.84×10^{-7}	2.28×10^{-5}	4.25×10^{-6}	4.86×10^{-3}
	$\mathrm{HQ}_{\text{soil-der}}$	1.27×10^{-1}	4.02×10^{-2}	4.20×10^{-3}	6.88×10^{-2}	1.52×10^{-3}	3.77×10^{-2}	4.69×10^{-2}	3.27×10^{-1}
Multan	$\mathrm{HQ}_{\text{soi-Ing}}$	5.78×10^{-3}	2.65×10^{-3}	1.10×10^{-3}	1.20×10^{-3}	4.87×10^{-3}	3.81×10^{-4}	5.82×10^{-3}	2.18×10^{-2}
	$\mathrm{HQ}_{\text{soil-Inh}}$	1.49×10^{-4}	3.90×10^{-3}	1.58×10^{-7}	1.63×10^{-7}	7.16×10^{-8}	5.61×10^{-6}	8.56×10^{-7}	4.05×10^{-3}
	$\mathrm{HQ}_{\text{soil-der}}$	2.81×10^{-2}	3.76×10^{-2}	9.95×0^{-4}	5.67×10^{-3}	5.93×10^{-4}	9.28×10^{-3}	9.45×10^{-3}	9.17×10^{-2}
Quetta	$\mathrm{HQ}_{\text{soi-Ing}}$	1.04×10^{-2}	3.29×10^{-3}	2.18×10^{-3}	6.87×10^{-4}	2.41×10^{-3}	1.72×10^{-4}	3.91×10^{-3}	2.30×10^{-2}
	$\mathrm{HQ}_{\text{soil-Inh}}$	2.68×10^{-4}	4.83×10^{-3}	3.12×10^{-7}	9.34×10^{-8}	3.54×10^{-8}	2.53×10^{-6}	5.74×10^{-7}	5.11×10^{-3}
	$\mathrm{HQ}_{\text{soil-der}}$	5.07×10^{-2}	4.67×10^{-2}	1.97×10^{-3}	3.25×10^{-3}	2.93×10^{-4}	4.19×10^{-3}	6.34×10^{-3}	1.13×10^{-1}
Hyderabad	$\mathrm{HQ}_{\text{soi-Ing}}$	9.03×10^{-3}	2.65×10^{-3}	1.40×10^{-3}	5.28×10^{-4}	2.83×10^{-3}	8.23×10^{-4}	6.05×10^{-3}	2.33×10^{-2}
	$\mathrm{HQ}_{\text{soil-Inh}}$	2.32×10^{-4}	3.90×10^{-3}	1.99×10^{-7}	7.19×10^{-8}	4.17×10^{-8}	1.21×10^{-5}	8.90×10^{-7}	4.14×10^{-3}
	$\mathrm{HQ}_{\text{soil-der}}$	4.39×10^{-2}	3.76×10^{-2}	1.26×10^{-3}	2.50×10^{-3}	3.45×10^{-4}	2.00×10^{-2}	9.82×10^{-3}	1.16×10^{-1}

Estimation model of daily intake of particulate matter through different route suggest that inhalation exposure (ECPM-inh) was the major pathway for all studied metals in all sampling cities followed by ingestion, while dermal exposure have least observed values (Table 4.12). High inhalation exposure (µg/m^3) was observed for Zn, Pb and Cu for Karachi (4.21×10^{-1}, 1.22×10^{-1}, 5.34×10^{-2}), Lahore (4.16×10^{-1}, 2.51×10^{-2}, 2.64×10^{-2}) and Gujranwala (3.62×10^{-1}, 5.64×10^{-2}, 7.62×10^{-2}), respectively. Non-CRs model provide evidence that the value of $HQ_{PM\text{-}inh}$ was >1 for Ni at Gujranwala (3.35) and Hyderabad (1.20), Mn at Karachi (1.38) and Faisalabad (~1) (Table 4.13) indicate the potential for adverse health effects (USEPA, 2001). While HI values of $HQ_{PM\text{-}inh}$ was >1 for Gujranwala (4.63), Karachi (3.37), Hyderabad (2.21), Faisalabad (1.76), Lahore (1.54) Multan (1.25) and Quetta (1.17) suggest the chance of occurrence of non-CRs effects to the workers and public living near e-waste recycling facilities in these cities. Previously, Aziz et al. (2022) also reported high level heavy metal (particulate) exposure via inhalation route among ingestion and dermal at Makkah city in Saudia Arabia. To summarize, non-CRs assessments indicate that dermal exposure is the major route of exposure to the contaminated soil, while inhalation for particulate matter. Karachi, Gujranwala, Lahore, Faisalabad were the most contaminated cities while Pb, Zn, Cu, Cd are key elements (exposure and contamination) in soil and particulate matter to the workers and general population residing near e-waste recycling sites in Pakistan.

Table 4.12: $ADI_{PM-ing,}$ EC_{PM-inh} and ADI_{PM-der} due to exposure to heavy metals through particulate phase (mg/kg-day)

Sampling Cities	**Exposure Pathways**	**Cr**	**Mn**	**Ni**	**Cu**	**Zn**	**Cd**	**Pb**
Peshawar	ADI_{PM-ing}	7.10×10^{-8}	4.26×10^{-7}	9.75×10^{-8}	2.52×10^{-7}	2.69×10^{-6}	5.84×10^{-9}	4.79×10^{-7}
	$EC_{PM-inh*}$	3.45×10^{-3}	2.07×10^{-2}	4.74×10^{-3}	1.23×10^{-2}	$1.31\times10_{-1}$	2.84×10^{-4}	2.33×10^{-2}
	ADI_{PM-der}	4.72×10^{-9}	2.84×10^{-8}	6.48×10^{-9}	1.68×10^{-8}	1.79×10^{-7}	3.89×10^{-11}	3.18×10^{-7}
Faisalabad	ADI_{PM-ing}	1.43×10^{-7}	9.74×10^{-7}	1.87×10^{-7}	4.23×10^{-7}	3.84×10^{-6}	3.15×10^{-9}	2.27×10^{-7}
	$EC_{PM-inh*}$	6.97×10^{-3}	4.74×10^{-2}	9.10×10^{-3}	2.06×10^{-2}	1.87×10^{-1}	1.53×10^{-4}	1.10×10^{-2}
	ADI_{PM-der}	9.53×10^{-9}	6.48×10^{-8}	1.25×10^{-8}	2.82×10^{-8}	2.55×10^{-7}	2.09×10^{-11}	1.51×10^{-7}
Rawalpindi	ADI_{PM-ing}	5.01×10^{-8}	3.03×10^{-7}	1.07×10^{-7}	3.83×10^{-7}	1.46×10^{-6}	$2.42\times10_{-9}$	9.26×10^{-8}
	$EC_{PM-inh*}$	2.43×10^{-3}	1.47×10^{-2}	5.22×10^{-3}	1.86×10^{-2}	7.08×10^{-2}	1.18×10^{-4}	4.50×10^{-3}
	ADI_{PM-der}	3.33×10^{-9}	2.01×10^{-8}	7.15×10^{-9}	2.55×10^{-8}	9.69×10^{-8}	1.61×10^{-11}	6.16×10^{-8}
Lahore	ADI_{PM-ing}	1.03×10^{-7}	7.16×10^{-7}	1.53×10^{-7}	5.44×10^{-7}	8.56×10^{-6}	1.99×10^{-8}	5.16×10^{-7}
	$EC_{PM-inh*}$	5.02×10^{-3}	3.48×10^{-2}	7.46×10^{-3}	2.64×10^{-2}	$4.16\times10_{-1}$	9.65×10^{-4}	2.51×10^{-2}
	ADI_{PM-der}	6.87×10^{-9}	4.76×10^{-8}	1.02×10^{-8}	3.61×10^{-8}	$5.69\times10_{-7}$	1.32×10^{-10}	3.43×10^{-7}
Karachi	ADI_{PM-ing}	2.36×10^{-7}	1.42×10^{-6}	2.71×10^{-7}	1.10×10^{-6}	8.66×10^{-6}	2.27×10^{-8}	2.52×10^{-6}
	$EC_{PM-inh*}$	1.15×10^{-2}	6.91×10^{-2}	1.32×10^{-2}	5.34×10^{-2}	4.21×10^{-1}	1.10×10^{-3}	1.22×10^{-1}
	ADI_{PM-der}	1.57×10^{-8}	9.45×10^{-8}	1.80×10^{-8}	7.31×10^{-8}	5.76×10^{-7}	1.51×10^{-10}	1.67×10^{-6}
Gujranwala	ADI_{PM-ing}	1.50×10^{-7}	6.87×10^{-7}	9.65×10^{-7}	1.57×10^{-6}	7.45×10^{-6}	3.20×10^{-8}	1.16×10^{-6}
	$EC_{PM-inh*}$	7.31×10^{-3}	3.34×10^{-2}	4.69×10^{-2}	7.62×10^{-2}	3.62×10^{-1}	1.56×10^{-3}	5.64×10^{-2}
	ADI_{PM-der}	9.99×10^{-9}	4.57×10^{-8}	6.42×10^{-8}	1.04×10^{-7}	4.96×10^{-7}	2.13×10^{-10}	7.72×10^{-7}
Multan	ADI_{PM-ing}	8.06×10^{-8}	6.77×10^{-7}	1.16×10^{-7}	3.32×10^{-7}	2.21×10^{-6}	3.62×10^{-9}	4.00×10^{-7}
	$EC_{PM-inh*}$	3.92×10^{-3}	3.29×10^{-2}	5.62×10^{-3}	1.61×10^{-2}	1.08×10^{-1}	1.76×10^{-4}	1.94×10^{-2}
	ADI_{PM-der}	5.36×10^{-9}	4.50×10^{-8}	7.69×10^{-9}	2.21×10^{-8}	1.47×10^{-7}	2.41×10^{-11}	2.66×10^{-7}
Quetta	ADI_{PM-ing}	8.68×10^{-8}	6.29×10^{-7}	9.33×10^{-8}	3.65×10^{-7}	1.99×10^{-6}	5.36×10^{-9}	5.21×10^{-7}
	$EC_{PM-inh*}$	4.22×10^{-3}	3.06×10^{-2}	4.54×10^{-3}	1.78×10^{-2}	9.67×10^{-2}	2.60×10^{-4}	2.53×10^{-2}
	ADI_{PM-der}	5.77×10^{-9}	4.19×10^{-8}	6.20×10^{-9}	2.43×10^{-8}	1.32×10^{-7}	3.56×10^{-11}	3.46×10^{-7}
Hyderabad	ADI_{PM-ing}	1.21×10^{-7}	8.77×10^{-7}	3.46×10^{-7}	4.03×10^{-7}	3.70×10^{-6}	4.02×10^{-9}	2.49×10^{-7}
	$EC_{PM-inh*}$	5.90×10^{-3}	4.26×10^{-2}	1.68×10^{-2}	1.96×10^{-2}	1.80×10^{-1}	1.96×10^{-4}	1.21×10^{-2}
	ADI_{PM-der}	8.06×10^{-9}	5.83×10^{-8}	2.30×10^{-8}	2.68×10^{-8}	2.46×10^{-7}	2.67×10^{-11}	1.66×10^{-7}

$* = \mu g/m^3$

Table 4.13: Non-CRs assessment of HMs in particulate phase via ingestion, inhalation, and dermal exposure

Sampling Cities	**Risk Assessment**	**Cr**	**Mn**	**Ni**	**Cu**	**Zn**	**Cd**	**Pb**	**HI**
Peshawer	$HQ_{PM\text{-}ing}$	1.42×10^{-5}	3.05×10^{-6}	4.87×10^{-6}	6.82×10^{-6}	8.98×10^{-5}	5.84×10^{-6}	1.37×10^{-4}	2.61×10^{-4}
	$HQ_{PM\text{-}inh}$	3.45×10^{-2}	4.15×10^{-1}	3.38×10^{-1}	3.06×10^{-4}	4.36×10^{-4}	2.84×10^{-2}	1.55×10^{-1}	9.72×10^{-1}
	$HQ_{PM\text{-}der}$	1.89×10^{-5}	1.18×10^{-5}	1.20×10^{-6}	8.83×10^{-6}	2.98×10^{-6}	3.89×10^{-6}	6.06×10^{-4}	6.54×10^{-4}
Faislabad	$HQ_{PM\text{-}ing}$	2.87×10^{-5}	6.96×10^{-6}	9.36×10^{-6}	1.14×10^{-5}	1.28×10^{-4}	3.15×10^{-6}	6.49×10^{-5}	2.52×10^{-4}
	$HQ_{PM\text{-}inh}$	6.97×10^{-2}	9.47×10^{-1}	6.50×10^{-1}	5.14×10^{-4}	6.22×10^{-4}	1.53×10^{-2}	7.36×10^{-2}	1.76
	$HQ_{PM\text{-}der}$	3.81×10^{-5}	2.70×10^{-5}	2.31×10^{-6}	1.48×10^{-5}	4.26×10^{-6}	2.09×10^{-6}	2.88×10^{-4}	3.76×10^{-4}
Rawalpindi	$HQ_{PM\text{-}ing}$	1.00×10^{-5}	2.16×10^{-6}	5.37×10^{-6}	1.04×10^{-5}	4.86×10^{-5}	2.42×10^{-6}	2.65×10^{-5}	1.05×10^{-4}
	$HQ_{PM\text{-}inh}$	2.43×10^{-2}	2.94×10^{-1}	3.73×10^{-1}	4.66×10^{-4}	2.36×10^{-4}	1.18×10^{-2}	3.00×10^{-2}	7.34×10^{-1}
	$HQ_{PM\text{-}der}$	1.33×10^{-5}	8.39×10^{-6}	1.32×10^{-6}	1.34×10^{-5}	1.61×10^{-6}	1.61×10^{-6}	1.17×10^{-4}	1.57×10^{-4}
Lahore	$HQ_{PM\text{-}ing}$	2.07×10^{-5}	5.11×10^{-6}	7.67×10^{-6}	1.47×10^{-5}	2.85×10^{-4}	1.99×10^{-5}	1.48×10^{-4}	5.01×10^{-4}
	$HQ_{PM\text{-}inh}$	5.02×10^{-2}	6.96×10^{-1}	5.33×10^{-1}	6.61×10^{-4}	1.39×10^{-3}	9.65×10^{-2}	1.67×10^{-1}	1.54
	$HQ_{PM\text{-}der}$	2.75×10^{-5}	1.98×10^{-5}	1.89×10^{-6}	1.90×10^{-5}	9.49×10^{-6}	1.32×10^{-5}	6.54×10^{-4}	7.45×10^{-4}
Karachi	$HQ_{PM\text{-}ing}$	4.72×10^{-5}	1.02×10^{-5}	1.35×10^{-5}	2.97×10^{-5}	2.89×10^{-4}	2.27×10^{-5}	7.19×10^{-4}	1.13×10^{-3}
	$HQ_{PM\text{-}inh}$	1.15×10^{-1}	1.38	9.40×10^{-1}	1.33×10^{-3}	1.40×10^{-3}	1.10×10^{-1}	8.16×10^{-1}	3.37
	$HQ_{PM\text{-}der}$	6.28×10^{-5}	3.94×10^{-5}	3.33×10^{-6}	3.84×10^{-5}	9.60×10^{-6}	1.51×10^{-5}	3.19×10^{-3}	3.36×10^{-3}
Gujranwala	$HQ_{PM\text{-}ing}$	3.01×10^{-5}	4.91×10^{-6}	4.83×10^{-5}	4.23×10^{-5}	2.48×10^{-4}	3.20×10^{-5}	3.32×10^{-4}	7.38×10^{-4}
	$HQ_{PM\text{-}inh}$	7.31×10^{-2}	6.68×10^{-1}	3.35	1.90×10^{-3}	1.21×10^{-3}	1.56×10^{-1}	3.76×10^{-1}	4.63
	$HQ_{PM\text{-}der}$	4.00×10^{-5}	1.90×10^{-5}	1.19×10^{-5}	5.48×10^{-5}	8.26×10^{-6}	2.13×10^{-5}	1.47×10^{-3}	1.63×10^{-3}
Multan	$HQ_{PM\text{-}ing}$	1.61×10^{-5}	4.84×10^{-6}	5.78×10^{-6}	8.97×10^{-6}	7.38×10^{-5}	3.62×10^{-6}	1.14×10^{-4}	2.27×10^{-4}
	$HQ_{PM\text{-}inh}$	3.92×10^{-2}	6.58×10^{-1}	4.02×10^{-1}	4.03×10^{-4}	3.59×10^{-4}	1.76×10^{-2}	1.30×10^{-1}	1.25
	$HQ_{PM\text{-}der}$	2.14×10^{-5}	1.88×10^{-5}	1.42×10^{-6}	1.16×10^{-5}	2.45×10^{-6}	2.41×10^{-6}	5.06×10^{-4}	5.64×10^{-4}
Quetta	$HQ_{PM\text{-}ing}$	1.74×10^{-5}	4.50×10^{-6}	4.67×10^{-6}	9.88×10^{-6}	6.63×10^{-5}	5.36×10^{-6}	1.49×10^{-4}	2.57×10^{-4}
	$HQ_{PM\text{-}inh}$	4.22×10^{-2}	6.12×10^{-1}	3.24×10^{-1}	4.44×10^{-4}	3.22×10^{-4}	2.60×10^{-2}	1.69×10^{-1}	1.17
	$HQ_{PM\text{-}der}$	2.31×10^{-5}	1.74×10^{-5}	1.15×10^{-6}	1.28×10^{-5}	2.21×10^{-6}	3.56×10^{-6}	6.60×10^{-4}	7.20×10^{-4}
Hyderabad	$HQ_{PM\text{-}ing}$	2.43×10^{-5}	6.27×10^{-6}	1.73×10^{-5}	1.09×10^{-5}	1.23×10^{-4}	4.02×10^{-6}	7.12×10^{-5}	2.57×10^{-4}
	$HQ_{PM\text{-}inh}$	5.90×10^{-2}	8.53×10^{-1}	1.20	4.90×10^{-4}	5.99×10^{-4}	1.96×10^{-2}	8.08×10^{-2}	2.21
	$HQ_{PM\text{-}der}$	3.23×10^{-5}	2.43×10^{-5}	4.26×10^{-6}	1.41×10^{-5}	4.10×10^{-6}	2.67×10^{-6}	3.16×10^{-4}	3.98×10^{-4}

Table 4.14: ILCRing, ILCRinh, ILCRdermal and Cumulative ILCR for Cd, Cr, Ni and Pb (carcinogenic heavy metals)

Sampling cities	Exposure Risk	Cr	Ni	Cd	Pb	ΣILCR
Peshawar	$\mathrm{ILCR}_{\Sigma\mathrm{ing}}$	8.55×10^{-6}	1.05×10^{-5}	1.51×10^{-6}	7.18×10^{-8}	2.06×10^{-5}
	$\mathrm{ILCR}_{\Sigma\mathrm{inh}}$	9.47×10^{-5}	3.91×10^{-7}	1.75×10^{-7}	9.76×10^{-8}	9.53×10^{-5}
	$\mathrm{ILCR}_{\Sigma\mathrm{Der}}$	1.70×10^{-4}	2.55×10^{-6}	1.51×10^{-7}	1.81×10^{-5}	1.91×10^{-4}
Faisalabad	$\mathrm{ILCR}_{\Sigma\mathrm{ing}}$	9.32×10^{-6}	1.38×10^{-5}	6.66×10^{-6}	3.06×10^{-7}	3.01×10^{-5}
	$\mathrm{ILCR}_{\Sigma\mathrm{inh}}$	1.91×10^{-4}	7.51×10^{-7}	9.49×10^{-8}	5.33×10^{-8}	1.92×10^{-4}
	$\mathrm{ILCR}_{\Sigma\mathrm{Der}}$	1.86×10^{-4}	3.35×10^{-6}	6.79×10^{-7}	7.48×10^{-5}	2.64×10^{-4}
Rawalpindi	$\mathrm{ILCR}_{\Sigma\mathrm{ing}}$	7.47×10^{-6}	8.41×10^{-6}	2.05×10^{-6}	1.06×10^{-7}	1.80×10^{-5}
	$\mathrm{ILCR}_{\Sigma\mathrm{inh}}$	6.68×10^{-5}	4.31×10^{-7}	7.27×10^{-8}	2.13×10^{-8}	6.73×10^{-5}
	$\mathrm{ILCR}_{\Sigma\mathrm{Der}}$	1.49×10^{-4}	2.04×10^{-6}	2.08×10^{-7}	2.58×10^{-5}	1.77×10^{-4}
Lahore	$\mathrm{ILCR}_{\Sigma\mathrm{ing}}$	1.22×10^{-5}	1.52×10^{-5}	4.52×10^{-6}	4.18×10^{-7}	3.23×10^{-5}
	$\mathrm{ILCR}_{\Sigma\mathrm{inh}}$	1.38×10^{-4}	6.16×10^{-7}	5.96×10^{-7}	1.14×10^{-7}	1.39×10^{-4}
	$\mathrm{ILCR}_{\Sigma\mathrm{Der}}$	2.43×10^{-4}	3.69×10^{-6}	4.52×10^{-7}	1.02×10^{-4}	3.49×10^{-4}
Karachi	$\mathrm{ILCR}_{\Sigma\mathrm{ing}}$	8.00×10^{-6}	1.27×10^{-5}	5.35×10^{-6}	5.97×10^{-7}	2.66×10^{-5}
	$\mathrm{ILCR}_{\Sigma\mathrm{inh}}$	3.15×10^{-4}	1.08×10^{-6}	6.80×10^{-7}	5.19×10^{-7}	3.17×10^{-4}
	$\mathrm{ILCR}_{\Sigma\mathrm{Der}}$	1.59×10^{-4}	3.07×10^{-6}	5.35×10^{-7}	1.48×10^{-4}	3.11×10^{-4}
Gujranwala	$\mathrm{ILCR}_{\Sigma\mathrm{ing}}$	2.25×10^{-5}	2.71×10^{-5}	8.13×10^{-6}	2.98×10^{-7}	5.80×10^{-5}
	$\mathrm{ILCR}_{\Sigma\mathrm{inh}}$	2.01×10^{-4}	3.86×10^{-6}	9.61×10^{-7}	2.40×10^{-7}	2.06×10^{-4}
	$\mathrm{ILCR}_{\Sigma\mathrm{Der}}$	$4.48\times10-^{4}$	6.54×10^{-6}	8.15×10^{-7}	7.40×10^{-5}	5.30×10^{-4}
Multan	$\mathrm{ILCR}_{\Sigma\mathrm{ing}}$	4.97×10^{-6}	6.39×10^{-6}	1.98×10^{-6}	6.06×10^{-8}	1.34×10^{-5}
	$\mathrm{ILCR}_{\Sigma\mathrm{inh}}$	1.07×10^{-4}	4.64×10^{-7}	1.09×10^{-7}	8.15×10^{-8}	1.08×10^{-4}
	$\mathrm{ILCR}_{\Sigma\mathrm{Der}}$	9.89×10^{-5}	1.55×10^{-6}	2.01×10^{-7}	1.52×10^{-5}	1.16×10^{-4}
Quetta	$\mathrm{ILCR}_{\Sigma\mathrm{ing}}$	8.94×10^{-6}	1.26×10^{-5}	9.13×10^{-7}	4.14×10^{-8}	2.25×10^{-5}
	$\mathrm{ILCR}_{\Sigma\mathrm{inh}}$	1.16×10^{-4}	3.75×10^{-7}	1.61×10^{-7}	1.05×10^{-7}	1.16×10^{-4}
	$\mathrm{ILCR}_{\Sigma\mathrm{Der}}$	1.78×10^{-4}	3.06×10^{-6}	9.05×10^{-8}	1.07×10^{-5}	1.92×10^{-4}
Hyderabad	$\mathrm{ILCR}_{\Sigma\mathrm{ing}}$	7.76×10^{-6}	8.14×10^{-6}	4.25×10^{-6}	6.25×10^{-8}	2.02×10^{-5}
	$\mathrm{ILCR}_{\Sigma\mathrm{inh}}$	1.62×10^{-4}	1.39×10^{-6}	1.21×10^{-7}	5.15×10^{-8}	1.63×10^{-4}
	$\mathrm{ILCR}_{\Sigma\mathrm{Der}}$	1.55×10^{-4}	1.96×10^{-6}	4.33×10^{-7}	1.55×10^{-5}	1.72×10^{-4}

4.2.2.7 Lifetime Cancer Risk

Among all investigated heavy metals, IARC-2024 (The International Agency for Research on Cancer) has categorized Ni Cr, and Cd as group-1 carcinogens while Pb lies in group-2A carcinogens. Cancer risk over lifetime (ILCR) of Cr, Ni, Cd and Pb via ingestion, inhalation and dermal contact were determined and shown in Table 4.14. Moderate to very low ILCR was observed for metals through different exposure routes in all cities ($ILCR_{\Sigma inh}$: 9.76×10^{-8} at Peshawar to $ILCR_{\Sigma der}$:1.02×10^{-4} at Lahore for Pb).

$ILCR_{\Sigma inh}$ and $ILCR_{\Sigma Der}$ were most common exposure pathways for Cr being the major contributor of ΣILCR in all e-waste recycling sites. The accumulative ILCR ranged: high from Multan (1.08×10^{-4}) and low at Peshawar (9.53×10^{-5}) for inhalation pathways. Overall, cumulative ILCR model suggest that inhalation and dermal contact are main exposure route depicting moderate to low CRs for workers at e-waste recycling facilities in Pakistan. The children living near and adults working in the proximity of these e-waste recycling sites may encounter acute as well as chronic health effects due to continuous exposures to HMs (Wu *et al.,* 2019). Moreover, local population living nearby these uncontrolled informal e-waste recycling practices (through secondary exposure) in the studied cities especially Karachi, Lahore and Faisalabad could potentially suffer health related problems by e.g., liver, and vascular system disorders, chronic kidney damage, irritation of upper respiratory tract due to chronic HMs exposure (Grant *et al.,* 2013). In conclusion, soil and particulate matter contamination from e-waste recycling operations poses a potentially alarming risk of cancer and other health issues in Pakistan.

4.3 Part-III

Characterization and Distribution of Brominated Flame Retardants in Soils from Informal E-Waste Recycling Facilities: Insights from Pakistan

The results presented in part 3 are submitted to the journal "Environmental Science and Pollution Research" and are currently in the process of under review.

4.3.1 Methodology

Details about methodology sections including sampling scheme, sample collection, sample preparation, GC-MS analysis and QC/QA are given in Chapter-3 (section 3.2).

4.3.2 Results and Discussion

4.3.2.1 Occurrence and Concentrations

Table 4.15 presents a descriptive overview of the concentrations of all target compounds (PBDEs, PBBs, HBB, and ∑HBCDD) in the soils under investigation. PBDEs demonstrate an average detection frequency exceeding 76 %, ranging from 40 % to 100 % for BDE-17 (minimum) and BDE-209 (maximum), respectively. This detection frequency notably surpasses that of the background sites, which stand at 56 %. The total mean concentrations of $\sum_{27}$PBDEs detected ranged from 0.76 to 11141 ng/g dw, with a mean of 176 ng/g dw and a median of 12.6 ng/g dw. The concentration levels of PBDEs were notably high, with BDE-209, BDE-47, and BDE-99 emerging as the most prevalent congeners, with yearly levels of mean, median (range) ng/g dw: 45.5, 6.55 (0.13 - 1152), 22, 0.44 (0.03-2206), and 19.9, 0.53 (0.03-1823) across all sites, respectively. The concentrations of Σ_{27}PBDEs detected in this study were significantly higher than those found in e-waste contaminated soils of South Korea (9.0 ± 11 (1.3-17) ng/g dw) and Vietnam (68 ng/g dw), but lower than those in China (3900 ± 5100 (60-14000) ng/g dw) (Li *et al.,* 2016). Similarly, the concentrations observed in this study were lower compared to soil concentrations at e-waste recycling sites in Guiyu (1440 ± 1260 (893-2890) ng/g dw), which is recognized as a major informal e-waste recycling area globally (Leung *et al.,* 2007).

Table 4.15: Descriptive statistics of BRs in soils at all e-waste and background sites (ng/g dw)

FRs	**E-waste sample (n=127)**			**Background sites (n=36)**		
	D.F (%)	**Mean (Median)**	**Range**	**D.F (%)**	**Mean (Median)**	**Range**
BDE-17	40	5.28 (0.06)	0.02 – 260	04	0.11 (0.11)	0.03-0.18
BDE-28	51	18.1 (0.12)	0.02 – 1143	09	0.23 (0.07)	0.05-0.94
BDE-49	85	13.7 (0.3)	0.05 – 1404	24	0.25 (0.17)	0.05-1.49
BDE-71	83	0.4 (0.09)	0.02 - 29.0	20	0.60 (0.50)	0.02-0.19
BDE-47	93	22.0 (0.44)	0.03 – 2206	28	0.44 (0.23)	0.05-4.24
BDE-66	59	13.4 (0.13)	0.02 – 971	08	0.22 (0.90)	0.04-1.07
BDE-100	76	3.7 (0.18)	0.03 – 257	13	0.13 (0.11)	0.03-0.40
BDE-99	97	19.9 (0.53)	0.03 – 1823	35	0.38 (0.19)	0.03-3.82
BDE-85	61	4.25 (0.10)	0.04 – 283	15	0.13 (0.12)	0.04-0.26
BDE-126	33	0.78 (0.17)	0.03 - 17.2	03	0.10 (0.08)	0.04-0.19
BDE-154	86	1.91 (0.09)	0.01 – 151	30	0.05 (0.04)	0.01-0.16
BDE-153	89	8.11 (0.29)	0.02 – 760	28	0.17 (0.10)	0.02-0.95
BDE-138	43	3.12 (0.18)	0.04 – 144	05	0.14 (0.14)	0.08-0.20
BDE-184	55	0.33 (0.11)	0.02 - 3.81	08	0.04 (0.05)	0.02-0.07
BDE-183	91	2.89 (0.61)	0.03 - 76.5	27	0.24 (0.12)	0.03-0.89
BDE-191	94	0.45, (0.22)	0.02 - 6.18	30	0.12 (0.12)	0.02-0.30
BDE-180	55	0.49 (0.19)	0.03 - 5.7	05	0.12 (0.12)	0.11-0.14
BDE-171/190	49	0.48 (0.21)	0.03 - 3.82	04	0.12 (0.14)	0.08-0.15
BDE-201	89	0.62, (0.11)	0.01 - 31.2	25	0.04 (0.04)	0.01-0.11
BDE-197	91	0.93 (0.21)	0.01 - 24.9	26	0.08 (0.06)	0.01-0.25
BDE-203	85	0.62 (0.15)	0.01 - 26.2	20	0.08 (0.06)	0.02-0.20
BDE-196	81	1.35 (0.34)	0.03 - 44.7	20	0.15 (0.12)	0.03-0.38
BDE-208	94	1.38 (0.24)	0.02 - 59.5	31	0.10 (0.05)	0.02-0.29
BDE-207	96	2.56 (0.43)	0.02 – 103	32	0.17 (0.09)	0.02-0.60
BDE-206	99	3.63 (0.58)	0.04 – 155	34	0.28 (0.15)	0.04-1.18
BDE-209	100	45.5 (6.55)	0.13 – 1152	36	4.83 (0.90)	0.06-52.8
ΣPBDEs	**Avg=76%**	**176 (12.6)**	**0.76 – 11141**	**Avg=56 %**	**8.80 (3.48)**	**0.92-71.4**
PBB-153	2	1.99 (1.99)	0.65 - 3.32	N.D.*		
PBB-156	46	29.0 (29.0)	1.0 - 58.0	05	0.06 (0.05)	0.06-0.12
ΣPBBs	**-**	**31.0 (31.0)**	**0.65-58.0**	**-**	**0.06 (0.05)**	**0.06-0.12**
HxBBz	**53**	**1.39 (0.06)**	**0.01 - 42.8**	**09**	**0.11 (0.02)**	**0.01-0.49**
HBCDDs	75	**12.0 (3.12)**	**0.22 – 461**	**17**	**2.07 (1.22)**	**0.22-7.40**

D.F*= Detection Frequency, N.D.*= Not detected

This distribution of PBDEs may originate from the historical use of commercial products, as soil remains a significant reservoir for PBDEs. For instance, the consumption of a commercial mixture (BDE-209) in Asian countries amounted to 23000 tons in 2001 (Hites, 2004), with China (10000 t in 2000), South Korea (12324 tons in 2002), and Japan (2800 tons in 2000) representing the largest consumers (Watanabe & Sakai, 2003).

In the case of PBBs and ∑HBCDD, the total annual average concentration ranged from 1.66-104 and 0.22-461 with mean and median values of 32.4, 31.0 ng/g dw and (12.0, 3.12) ng/g dw, respectively (Table 4.15). No prior research has focused on non-PBDEs in Pakistani soils, except for the study conducted by Iqbal et al. (2017), which reported HBB concentrations of 23 (N.D-461) ng/g dw in soils near informal e-waste recycling facilities in Karachi, Pakistan. This level of HBB was significantly higher compared to the levels reported in this study (1.39 ng/g dw) but higher/comparable to the overall PBBs level (32.4 ng/g dw) in this study. PBBs and HBB are two types of historically used flame retardants. Decabromobiphenyl and possibly some other PBB mixtures are still commercially produced (de Boer *et al.,* 2000), and HBB is being reintroduced into the market (Salamova and Hites, 2011). HBCDDs are the most widely used brominated flame retardants, accounting for 8.2 % of the total market demand for such chemicals in 2001 (Morose, 2006)

Table 4.16: Correlation of BFRs in soil

	BDE-17	BDE-28	BDE-49	BDE-71	BDE-47	BDE-66	BDE-100	BDE-99	BDE-85	BDE-126	BDE-154	BDE-153	BDE-138	BDE-184	BDE-183	BDE-191	BDE-180	BDE-171.190	BDE-201	BDE-197	BDE-203	BDE-196	BDE-208	BDE-207	BDE-206	BDE-209	PBB-153	PBB-156	HBB	γ-HBCDD
BDE-17	1.00																													
BDE-28	1.00	1.00																												
BDE-49	1.00	1.00	1.00																											
BDE-71	1.00	1.00	1.00	1.00																										
BDE-47	1.00	1.00	1.00	1.00	1.00																									
BDE-66	1.00	1.00	1.00	1.00	1.00	1.00																								
BDE-100	0.99	0.99	0.99	0.99	1.00	0.99	1.00																							
BDE-99	0.99	0.99	0.99	0.99	1.00	0.99	1.00	1.00																						
BDE-85	1.00	1.00	1.00	1.00	1.00	1.00	0.99	0.99	1.00																					
BDE-126	0.09	0.08	0.08	0.15	0.08	0.09	0.10	0.08	0.08	1.00																				
BDE-154	0.99	0.99	0.99	1.00	1.00	0.99	1.00	1.00	1.00	0.11	1.00																			
BDE-153	1.00	1.00	1.00	1.00	1.00	1.00	0.99	1.00	1.00	0.09	1.00	1.00																		
BDE-138	1.00	1.00	1.00	1.00	1.00	1.00	0.99	0.99	1.00	0.10	1.00	1.00	1.00																	
BDE-184	0.74	0.73	0.74	0.77	0.74	0.74	0.74	0.73	0.74	0.62	0.75	0.74	0.75	1.00																
BDE-183	0.97	0.97	0.97	0.98	0.98	0.97	0.98	0.98	0.97	0.21	0.98	0.98	0.98	0.83	1.00															
BDE-191	0.66	0.65	0.65	0.70	0.66	0.66	0.67	0.66	0.66	0.67	0.68	0.66	0.67	0.88	0.77	1.00														
BDE-180	0.65	0.64	0.64	0.69	0.65	0.65	0.67	0.65	0.65	0.69	0.67	0.65	0.66	0.97	0.77	0.90	1.00													
BDE-171.190	0.83	0.83	0.83	0.86	0.84	0.83	0.85	0.84	0.83	0.56	0.85	0.84	0.84	0.95	0.91	0.90	0.92	1.00												
BDE-201	0.10	0.10	0.10	0.13	0.10	0.10	0.11	0.11	0.11	0.35	0.12	0.11	0.12	0.59	0.25	0.40	0.66	0.37	1.00											
BDE-197	0.67	0.67	0.67	0.69	0.68	0.67	0.69	0.68	0.67	0.37	0.70	0.68	0.68	0.91	0.80	0.77	0.91	0.82	0.78	1.00										
BDE-203	0.32	0.32	0.32	0.34	0.33	0.32	0.34	0.33	0.33	0.28	0.34	0.33	0.34	0.69	0.46	0.51	0.74	0.51	0.97	0.89	1.00									
BDE-196	0.47	0.47	0.47	0.50	0.48	0.47	0.49	0.48	0.48	0.40	0.50	0.48	0.49	0.83	0.61	0.66	0.87	0.68	0.91	0.96	0.97	1.00								
BDE-208	0.31	0.31	0.31	0.34	0.31	0.31	0.32	0.32	0.31	0.45	0.33	0.32	0.33	0.76	0.46	0.59	0.82	0.57	0.97	0.89	0.98	0.98	1.00							
BDE-207	0.39	0.39	0.39	0.42	0.40	0.39	0.41	0.40	0.40	0.49	0.42	0.40	0.41	0.82	0.54	0.66	0.87	0.65	0.94	0.93	0.97	0.99	0.99	1.00						
BDE-206	0.39	0.39	0.39	0.41	0.39	0.39	0.40	0.39	0.39	0.37	0.41	0.40	0.41	0.75	0.52	0.59	0.81	0.59	0.94	0.91	0.98	0.98	0.99	0.98	1.00					
BDE-209	0.51	0.50	0.51	0.55	0.51	0.51	0.53	0.52	0.51	0.75	0.54	0.52	0.52	0.89	0.64	0.87	0.94	0.83	0.64	0.82	0.69	0.80	0.79	0.84	0.79	1.00				
PBB-153	-0.04	-0.04	-0.04	-0.02	-0.02	-0.04	-0.02	-0.02	-0.03	-0.04	-0.01	-0.03	-0.04	0.01	0.07	0.03	0.02	0.03	0.00	0.11	0.02	0.07	0.00	0.01	-0.01	-0.04	1.00			
PBB-156	0.15	0.15	0.15	0.18	0.17	0.15	0.19	0.18	0.16	0.12	0.19	0.17	0.17	0.30	0.28	0.43	0.32	0.33	0.20	0.35	0.24	0.29	0.23	0.25	0.23	0.28	0.25	1.00		
HxBBz	0.79	0.79	0.79	0.83	0.79	0.79	0.81	0.79	0.79	0.65	0.81	0.80	0.80	0.89	0.84	0.87	0.87	0.95	0.22	0.69	0.35	0.54	0.45	0.53	0.45	0.81	-0.03	0.19	1.00	
HBCDDs	0.07	0.07	0.07	0.13	0.07	0.07	0.10	0.07	0.07	0.99	0.10	0.07	0.08	0.57	0.19	0.63	0.63	0.53	0.25	0.30	0.18	0.31	0.36	0.40	0.27	0.71	0.00	0.12	0.66	1.00

■ Correlation is significant at the 0.01 level (2-tailed).

□ Correlation is significant at the 0.05 level (2-tailed).

Additionally, levels of all target compounds were significantly higher compared to their respective reference background site values (Table 4.15), suggesting that informal e-waste recycling facilities are major emission sources. The high concentration of BDE-209 is consistent with the fact that the deca-BDE mixture is one of the most frequently used flame retardants in electronic/electric products (McGrath *et al.*, 2018; Iqbal *et al.*, 2017). Similarly, lower PBDEs, including BDE-47, BDE-99, and BDE-28, were also abundant, possibly due to past recycling operations of e-waste, which were more extensively produced and used (Bruce-Vanderpuije *et al.*, 2019). Most of the recycling facilities in the study area were observed to be involved in recycling operations such as open burning, smelting, and acid bathing of printed circuit boards containing relatively high proportions of tetra- and penta-BDEs (Hoang *et al.*, 2022; Zhou *et al.*, 2013). During these processes, lighter BDEs are deposited at the soil surface, potentially serving as a source of high levels near sampling sites. Additionally, BDE-209 may undergo debromination to lower and more toxic lower PBDEs during this process. Table 4.16 illustrates the correlations among BFRs in the soil. Most of the BFRs exhibit positive and significant correlations, suggesting one or more common emission sources.

4.3.2.2 Spatial Distribution

Table 4.17 illustrates the concentration variability of studied BFRs in the Punjab province, encompassing cities such as Faisalabad, Rawalpindi, Lahore, Gujranwala, and Multan. Meanwhile, Table 4.18 delineates the levels in KPK (Peshawar city), Sindh (Karachi and Hyderabad city), and Baluchistan (Quetta city) Provinces. Significant spatial variability in FRs concentrations was noted among the sampling cities. Karachi exhibits higher levels of PBDEs, PBBs, and ∑HBCDD, with a total annual concentration mean, median (range) ng/g: 727, 17.7 (1.84 – 10231), 10.2, 5.2 (1.66 - 51.5), and 8.96, 2.33 (0.94 - 45.6), respectively.

Table 4.17: Descriptive statistics of BFRs at sampling cities of Punjab Province (ng/g dw)

BFRs	**Faisalabad (n=11)**			**Rawalpindi (n=12)**			**Lahore (n=12)**			**Gujranwala (n=12)**			**Multan (n=12)**		
	Det*	**Mean (median)**	**Range**	**Det***	**Mean (median)**	**range**	**Det***	**Mean (median)**	**Range**	**Det***	**Mean (median)**	**range**	**Det***	**Mean (median)**	**range**
BDE_17	7	0.4, 0.24	0.04 - 1.55	5	0.06, 0.06	0.03 - 0.08	8	0.18, 0.08	0.03 - 0.59	8	0.14, 0.14	0.02 - 0.29	4	0.08, 0.05	0.03 - 0.19
BDE_28	9	0.92, 0.3	0.09 - 3.99	7	0.1, 0.07	0.04 - 0.17	10	0.36, 0.17	0.03 - 1.84	8	0.26, 0.2	0.02 - 0.78	6	0.09, 0.07	0.04 - 0.19
BDE_49	10	1.82, 1.05	0.11 - 6.71	12	0.35, 0.34	0.14 - 0.56	12	0.86, 0.45	0.11 - 5.52	10	0.7, 0.45	0.1 - 2.08	11	0.49, 0.34	0.05 - 2.65
BDE_71	10	0.31, 0.19	0.04 - 1.03	12	0.09, 0.09	0.02 - 0.15	12	0.17, 0.11	0.04 - 0.53	10	0.13, 0.11	0.03 - 0.31	10	0.1, 0.08	0.02 - 0.26
BDE_47	11	7.95, 6.5	0.08 - 22.4	12	0.57, 0.64	0.12 - 1.08	12	14.8, 0.99	0.34 - 154.	11	1.39, 0.93	0.03 - 7.36	11	1.05, 0.23	0.09 - 7.55
BDE_66	8	1.17, 0.6	0.14 - 5.33	9	0.12, 0.1	0.04 - 0.21	9	0.47, 0.19	0.06 - 2.37	7	0.37, 0.28	0.08 - 1.02	5	0.3, 0.15	0.04 - 1.08
BDE_100	9	2.32, 1.99	0.26 - 5.62	11	0.25, 0.24	0.04 - 0.73	12	4.93, 0.32	0.07 - 51.6	9	0.53, 0.31	0.03 - 2.49	7	0.43, 0.13	0.03 - 1.91
BDE_99	11	11.3, 7.01	0.09 - 41.3	12	1.13, 1	0.14 - 3.41	12	30.0, 1.7	0.43 – 326	11	2.22, 1.03	0.03 - 15.0	11	2.32, 0.19	0.04 - 19.7
BDE_85	10	0.78, 0.55	0.12 - 2.18	7	0.12, 0.1	0.07 - 0.24	11	2.21, 0.18	0.05 - 21.2	8	0.42, 0.19	0.05 - 1.67	5	0.38, 0.2	0.04 - 1.36
BDE_126	8	2.48, 0.17	0.07 - 17.2	2	0.08, 0.08	0.06 - 0.1	9	0.51, 0.31	0.03 - 1.64	6	0.62, 0.36	0.28 - 1.72	3	0.11, 0.06	0.05 - 0.23
BDE_154	11	1.67, 1.02	0.03 - 6.29	12	0.12, 0.12	0.03 - 0.28	12	1.94, 0.22	0.08 - 18.7	10	0.61, 0.23	0.02 - 2.72	10	0.25, 0.04	0.02 - 1.02
BDE_153	11	3.55, 1.67	0.05 - 12.5	12	0.39, 0.41	0.08 - 0.71	12	4.96, 0.68	0.15 - 46.2	11	1.09, 0.43	0.02 - 7.78	10	0.61, 0.08	0.04 - 4.01
BDE_138	9	0.73, 0.45	0.05 - 2.08	6	0.11, 0.1	0.04 - 0.17	10	1.07, 0.2	0.06 - 6.95	4	0.85, 0.44	0.16 - 2.37	4	0.3, 0.19	0.11 - 0.74
BDE_184	9	0.64, 0.36	0.05 - 3.05	10	0.08, 0.07	0.02 - 0.16	10	0.17, 0.18	0.02 - 0.44	7	0.98, 0.32	0.08 - 3.45	3	0.14, 0.13	0.1 - 0.19
BDE_183	10	5.96, 3.23	0.08 - 16.4	12	0.78, 0.69	0.16 - 1.65	12	3.58, 2.32	0.25 - 9.35	11	3.29, 0.95	0.03 - 23.1	11	0.73, 0.4	0.03 - 2.4
BDE_191	11	1.13, 0.43	0.03 - 6.02	12	0.25, 0.26	0.07 - 0.47	12	0.82, 0.33	0.14 - 4.79	12	0.51, 0.24	0.02 - 2.53	11	0.23, 0.28	0.03 - 0.61
BDE_180	9	0.99, 0.73	0.05 - 4.05	8	0.15, 0.13	0.03 - 0.32	11	0.47, 0.24	0.08 - 1.3	7	1.18, 0.24	0.12 - 5.7	4	0.2, 0.19	0.13 - 0.29
BDE171.190	9	0.86, 0.46	0.06 - 2.81	8	0.19, 0.13	0.06 - 0.65	10	0.46, 0.21	0.07 - 1.73	6	0.67, 0.7	0.21 - 1.29	4	0.27, 0.28	0.14 - 0.37
BDE_201	11	1.35, 0.55	0.01 - 8.4	12	0.13, 0.11	0.02 - 0.31	12	0.31, 0.24	0.04 - 0.74	11	3.6, 0.28	0.01 - 31.2	9	0.13, 0.09	0.01 - 0.3
BDE_197	11	2.19, 0.93	0.02 - 9.89	12	0.27, 0.29	0.05 - 0.55	12	1.05, 0.61	0.1 - 2.61	11	3.01, 0.32	0.02 - 24.9	11	0.2, 0.11	0.02 - 0.64
BDE_203	10	0.93, 0.68	0.04 - 3.47	12	0.16, 0.17	0.03 - 0.3	12	0.5, 0.28	0.05 - 1.37	10	3.2, 0.28	0.02 - 26.2	11	0.16, 0.07	0.01 - 0.51
BDE_196	10	2.81, 2.0	0.05 - 10.4	12	0.31, 0.33	0.07 - 0.58	12	1.03, 0.63	0.16 - 2.82	10	5.48, 0.57	0.03 - 44.7	7	0.48, 0.38	0.03 - 1.02
BDE_208	11	3.57, 1.44	0.02 - 23.3	12	0.39, 0.49	0.07 - 0.6	12	0.94, 0.83	0.2 - 2.14	11	6.48, 0.44	0.02 - 59.5	12	0.23, 0.08	0.02 - 0.99
BDE_207	11	7.13, 2.73	0.02 - 46.5	12	0.68, 0.8	0.13 - 1.15	12	1.91, 1.52	0.34 - 4.87	12	10.4, 0.68	0.03 – 103	12	0.4, 0.13	0.03 - 1.73
BDE_206	11	7.32, 3.83	0.04 - 45.6	12	1.09, 1.01	0.16 - 2.67	12	2.73, 2.1	0.64 - 5.85	12	14.8, 0.69	0.05 – 155	12	0.72, 0.15	0.05 - 4.37
BDE_209	11	160, 26.2	0.15 –1152	12	15.8, 12.4	1.29 – 36.0	12	51.1, 29.9	4.68 – 147	12	85.3, 8.68	0.15 – 881	12	6.62, 1.72	0.34 - 40.9
Σ_{27}PBDEs		**230, 65.3**	**1.79 -1460**		**23.8, 20.3**	**3.01 - 53.3**		**128, 45.0**	**8.25 – 822**		**148, 19.5**	**1.66 – 1407**		**17.0, 5.82**	**1.54 - 95.2**
PBB_153	1	3.32, 3.32	3.32 - 3.32	N.D.			N.D.			N.D.			N.D.		
PBB_156	9	5.0, 5.0	1.0 - 9.0	7	4.0, 4.0	1.0 - 7.0	9	5.0, 5.0	1.0 - 9.0	6	3.5, 3.5	1.0 - 6.0	6	3.5, 3.5	1.0 – 6.0
HxBBz	9	3.23, 1.11	0.03 - 18.8	10	0.53, 0.09	0.01 - 4.61	11	0.95, 0.1	0.02-6.94	6	0.07, 0.05	0.04 - 0.15	4	0.08, 0.06	0.02 - 0.17
HBCDDs	**9**	**69.8, 13.3**	**1.41 – 461**	**11**	**6.92, 6.41**	**1.2 - 14.9**	**12**	**9.74, 5.01**	**0.42 - 34.4**	**9**	**3.87, 3.26**	**0.77 - 8.65**	**7**	**14.0, 6.25**	**0.29 - 41.3**

Det*= Detected, N.D.= not detected

Table 4.18: Descriptive statistics of BFRs at sampling cities of KPK, Sindh and Baluchistan Provinces (ng/gm dw)

BFRs	**Peshawar (n=16)**			**Karachi (n=20)**			**Hyderabad (n=12)**			**Quetta (n=20)**		
	Det*	**Mean, median**	**Range**	**Det***	**mean, median**	**Range**	**Det***	**mean, median**	**Range**	**Det***	**mean, median**	**Range**
BDE_17	5	0.06, 0.05	0.02 - 0.12	9	29.2, 0.16	0.04 - 260	2	0.04, 0.04	0.04 - 0.04	3	0.16, 0.04	0.04 - 0.4
BDE_28	5	0.08, 0.08	0.04 - 0.12	11	105, 0.4	0.09 – 1143	3	0.1, 0.09	0.04 - 0.18	6	0.5, 0.05	0.03 - 2.7
BDE_49	14	0.23, 0.23	0.11 - 0.39	17	83.9, 0.56	0.09 – 1404	9	0.21, 0.14	0.06 - 0.57	13	0.41, 0.21	0.08 - 3.19
BDE_71	13	0.08, 0.07	0.03 - 0.16	17	1.83, 0.1	0.04 - 28.9	9	0.07, 0.05	0.03 - 0.18	12	0.07, 0.07	0.03 - 0.18
BDE_47	16	0.39, 0.29	0.08 - 1.22	18	126, 0.78	0.16 – 2206	10	0.22, 0.17	0.05 - 0.6	17	0.89, 0.25	0.05 - 11.3
BDE_66	11	0.08, 0.07	0.04 - 0.15	13	75.5, 0.35	0.08 – 971	5	0.08, 0.07	0.02 - 0.15	8	0.33, 0.08	0.03 - 2.09
BDE_100	16	0.12, 0.1	0.03 - 0.32	16	16.5, 0.26	0.05 – 257	5	0.06, 0.05	0.04 - 0.09	12	0.16, 0.15	0.04 - 0.51
BDE_99	16	0.51, 0.45	0.12 - 1.47	19	99.1, 1.01	0.11 – 1823	12	0.2, 0.13	0.06 - 0.65	19	0.48, 0.21	0.05 - 4.47
BDE_85	10	0.07, 0.06	0.04 - 0.1	10	28.7, 0.17	0.1 – 283	5	0.06, 0.06	0.04 - 0.09	11	0.1, 0.08	0.04 - 0.34
BDE_126	4	0.07, 0.06	0.05 - 0.12	6	0.56, 0.42	0.07 - 1.46	2	0.04, 0.04	0.04 - 0.05	2	0.12, 0.12	0.05 - 0.19
BDE_154	16	0.07, 0.07	0.02 - 0.16	16	9.65, 0.12	0.03 – 151	8	0.04, 0.04	0.01 - 0.07	14	0.07, 0.04	0.01 - 0.34
BDE_153	16	0.27, 0.25	0.04 - 1.11	18	43.7, 0.38	0.08 – 760	8	0.1, 0.08	0.03 - 0.2	15	0.2, 0.1	0.03 - 1.15
BDE_138	7	0.09, 0.09	0.04 - 0.15	10	14.8, 0.18	0.04 – 144	2	0.05, 0.05	0.04 - 0.06	3	0.18, 0.07	0.07 - 0.4
BDE_184	12	0.07, 0.07	0.03 - 0.12	10	0.59, 0.15	0.03 - 3.81	4	0.04, 0.04	0.03 - 0.05	5	0.06, 0.06	0.02 - 0.12
BDE_183	16	0.72, 0.61	0.07 - 2.66	19	8.28, 0.84	0.04 - 76.5	10	0.22, 0.19	0.04 - 0.68	14	0.39, 0.22	0.05 - 1.29
BDE_191	16	0.27, 0.22	0.08 - 0.98	19	0.63, 0.31	0.07 - 6.18	10	0.12, 0.1	0.03 - 0.27	17	0.15, 0.16	0.03 - 0.27
BDE_180	11	0.13, 0.11	0.05 - 0.26	11	0.7, 0.23	0.04 - 3.88	2	0.07, 0.07	0.06 - 0.09	7	0.12, 0.1	0.03 - 0.37
BDE171.190	9	0.16, 0.13	0.07 - 0.29	7	1.23, 0.29	0.1 - 3.82	4	0.06, 0.06	0.03 - 0.09	5	0.12, 0.11	0.05 - 0.23
BDE_201	16	0.11, 0.11	0.02 - 0.23	18	0.36, 0.12	0.02 - 3.14	9	0.04, 0.04	0.01 - 0.06	15	0.07, 0.04	0.01 - 0.17
BDE_197	16	0.21, 0.21	0.06 - 0.43	18	1.45, 0.25	0.03 - 15.5	9	0.06, 0.07	0.02 - 0.12	15	0.11, 0.07	0.01 - 0.31
BDE_203	16	0.17, 0.13	0.03 - 0.49	15	0.77, 0.2	0.03 - 5.99	8	0.06, 0.05	0.02 - 0.12	14	0.1, 0.06	0.03 - 0.27
BDE_196	15	0.35, 0.27	0.05 - 0.91	17	1.68, 0.35	0.06 - 15.4	8	0.12, 0.12	0.04 - 0.19	12	0.21, 0.13	0.06 - 0.47
BDE_208	16	0.4, 0.25	0.05 - 1.97	19	1.35, 0.22	0.03 - 13.9	9	0.09, 0.08	0.03 - 0.23	17	0.15, 0.1	0.02 - 0.49
BDE_207	16	0.67, 0.49	0.05 - 3.13	19	2.95, 0.37	0.04 - 30.7	11	0.14, 0.15	0.03 - 0.42	17	0.26, 0.17	0.02 - 0.84
BDE_206	16	2.09, 0.68	0.1 - 19.9	20	5, 0.53	0.08 – 55	12	0.26, 0.21	0.04 - 1.02	19	0.41, 0.26	0.04 - 1.83
BDE_209	16	40.7, 8.4	0.49 – 457	20	67.6, 8.95	0.29 – 565	12	2.08, 1.1	0.13 - 5.7	20	3.97, 2.67	0.14 - 14.1
Σ_{27}PBDEs		**48.1, 13.6**	**1.81 – 494**		**727, 17.7**	**1.84 - 10231**		**4.63, 3.29**	**1.01 – 12.0**		**9.79, 5.62**	**1.06 - 48.1**
PBB_153	N.D.			1	0.65, 0.65	0.65 - 0.65	N.D.			N.D.		
PBB_156	7	4.0, 4.0	1.0 – 7.0	8	4.5, 4.5	1.0 – 8.0	3	2.0, 2.0	1.0 – 3.0	4	2.5, 2.5	1.0 – 4.0
HxBBz	12	0.18, 0.05	0.01 - 0.99	9	5.02, 0.05	0.01 - 42.85	2	0.02, 0.02	0.02 - 0.02	4	0.06, 0.03	0.02 - 0.17
HBCDDs	**15**	**1.77, 1.58**	**0.37 - 3.64**	**13**	**8.96, 2.33**	**0.94 - 45.57**	**8**	**1.4, 1.2**	**0.3 - 2.87**	**11**	**3.06, 2.28**	**0.22 - 8.77**

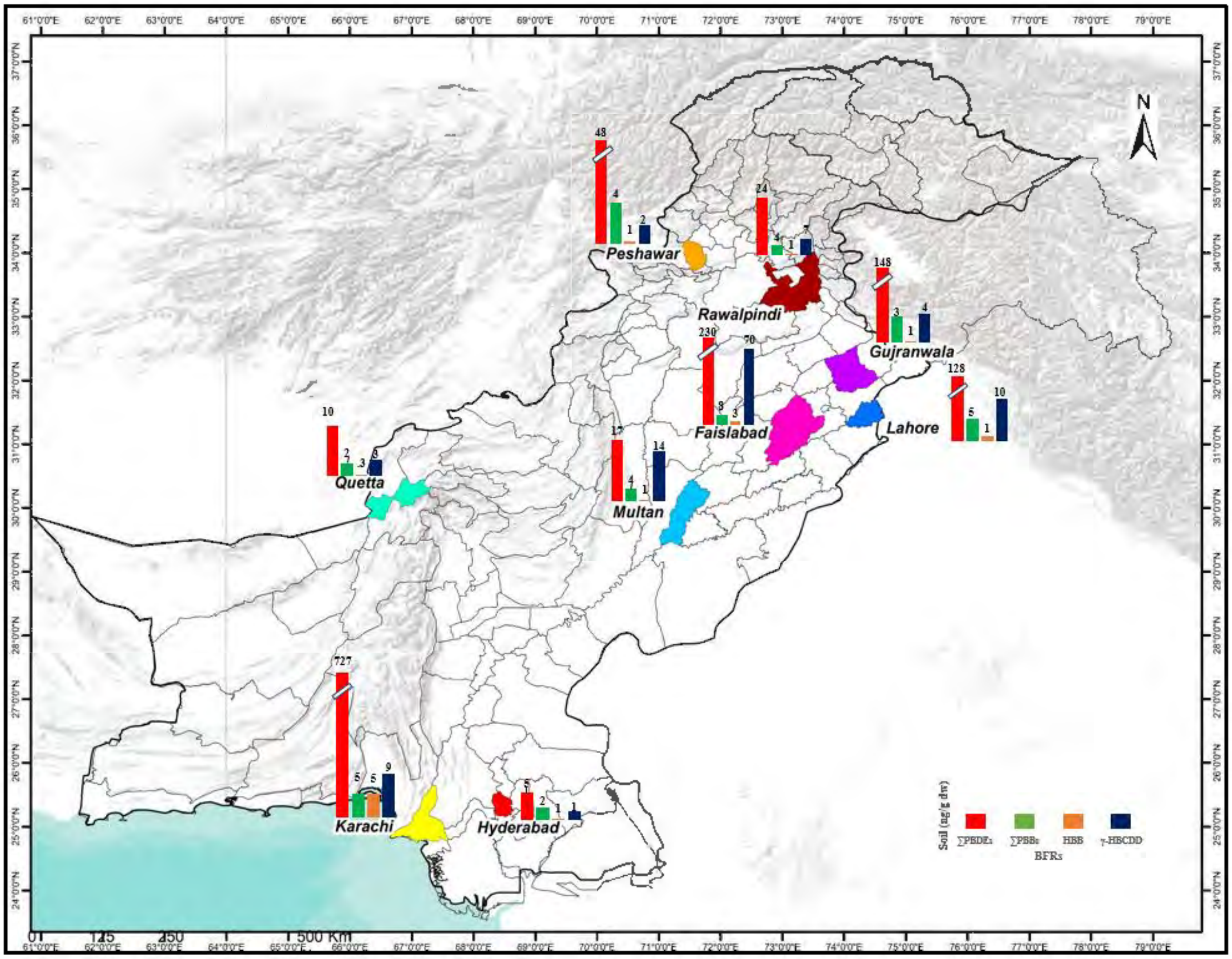


Figure 4.8: Spatial distribution of BFRs (mean) in soils from studied cities in Pakistan

Following Karachi, Faisalabad demonstrates the second-highest annual total level: 230, 65.3 (1.79 -1460), 11.5, 9.43 (4.35 - 31.1), and 69.8, 13.3 (1.41 – 461) ng/g for PBDEs, PBBs, and ∑HBCDD, respectively (Figure 4.8). Conversely, low levels were observed in Hyderabad city ranging from 1.01 – 12.0 ng/g dw, with a mean concentration of 4.63 ng/g dw for all PBDEs. Soil contamination levels in other cities were ranked as follows: Gujranwala > Lahore > Peshawar > Rawalpindi > Multan > Quetta > Hyderabad. Among individual sampling sites, S21 (Sher Shah) in Karachi city stood out for contamination with BFRs (Table 4.19), as it has been previously identified as one of the significant informal e-waste recycling centers in the city (Iqbal *et al.,* 2017; Imran *et al.,* 2017; Kazim *et al.,* 2023).

Table 4.19: Yearly averaged concentration of studied BFR groups at individual sampling sites (ng/g dw)

Site Code	**Σ_{27}PBDEs (n=4)**		**Σ_{3}PBBs (n=4)**		**g-HBCDD (n=4)**	
	Mean, Median	**Range**	**Mean, Median**	**Range**	**Mean, Median**	**Range**
S1	10.6, 10.5	2.2 - 19.4	1.75, 1.56	1.02 - 2.66	1.58, 1.17	1.04 - 2.52
S2	19.2, 17.7	3.14 - 38.2	2.06, 2.05	1.02 - 3.11	2.66, 3.09	1.29 - 3.15
S3	20.2, 19.9	4.26 - 36.5	0.36, 0.08	0.01 - 0.99	0.82, 0.68	0.37 - 1.58
S4	142, 37.6	3.41 – 490	1.53, 1.54	1.02 - 2.04	1.96, 1.81	0.59 - 3.64
S5	452, 176	15.0 – 1436	12.7, 12.7	4.67 - 20.8	259, 259	58.2 - 461
S6	99.3, 76.6	36.7 – 207	6.62, 6.76	4.52 - 8.45	16.7, 9.87	1.41 - 45.5
S7	125, 57.5	12.6 – 305	3.12, 2.09	1.03 - 6.26	14.2, 6.35	2.35 - 34.0
S8	25.7, 26.2	5.64 - 44.6	1.56, 1.55	1.03 - 2.11	6.84, 7.59	2.96 - 9.24
S9	20.2, 17.2	3.34 - 43.3	2.09, 2.1	1.01 - 3.14	3.93, 2.32	1.2 - 8.28
S10	25.2, 21.6	4.79 - 52.8	3.1, 1.67	1.02 - .61	9.23, 8.94	4.16 - 14.9
S11	95.2, 97.9	27.1 – 158	2.68, 2.66	1.03 - 4.38	7.84, 7.39	2.17 - 14.4
S12	20.7, 20.1	9.12 - 33.5	2.39, 1.67	1.06 - 4.43	5.13, 4.16	0.42 - 11.8
S13	265, 104	35.4 – 817	3.77, 2.07	1.02 - 9.94	16.2, 12.9	4.81 - 34.4
S14	6.08, 1.81	0.81 - 19.8	N.D.	N.D.	0.77, 0.77	0.77 - 0.77
S15	363, 17.6	7.32 – 1407	1.56, 1.56	1.04 - 2.07	2.81, 2.23	0.93 - 5.87
S16	61.3, 48.4	23.2 – 125	2.57, 2.55	1.04 - 4.15	5.7, 6.46	1.23 - 8.65
S17	1.54, 1.47	1.02 - 2.00	N.D.	N.D.	N.D.	N.D.
S18	15.9, 13.5	3.3 - 33.1	2.11, 2.11	1.04 - 3.17	12.7, 4.54	0.29 - 41.3
S19	30.8, 12.5	2.59 - 94.3	2.04, 2.04	1.02 - 3.06	15.8, 11.4	5.04 - 31.1
S20	31.1, 10.5	4.01 - 98.9	1.71, 1.71	1.66 - 1.76	2.59, 2.59	2.07 - 3.12
S21	**3536, 1277**	**17.4 - 10231**	**16.9, 3.89**	**1.04 - 45.9**	**29.3, 41.0**	**1.27 - 45.6**
S22	40.1, 15.8	3.96 – 111	0.2, 0.2	0.2 - 0.2	2.84, 1.09	0.94 - 6.48
S23	13.6, 11.4	4.66 - 26.5	1.0, 1.0	1.0 - 1.0	2.33, 2.33	2.33 - 2.33
S24	44.4, 31.5	19.6 - 94.6	2.03, 2.02	1.02 - 3.05	3.15, 3.23	1.11 - 5.02
S25	6.96, 7.68	1.79 - 10.7	1.52, 1.52	1.02 - 2.02	1.29, 1.2	0.39 - 2.4
S26	2.13, 1.63	0.86 - 4.08	N.D.	N.D.	1.58, 1.58	0.3 - 2.87
S27	4.28, 3.54	1.56 - 8.46	1.02, 1.02	1.02 - 1.02	1.43, 1.43	0.52 - 2.34
S28	19.7, 12.2	9.11 - 40.0	1.02, 1.02	1.02 - 1.02	6.88, 6.88	6.88 - 6.88
S29	1.19, 1.13	0.99 - 1.46	N.D.	N.D.	N.D.	N.D.
S30	13.8, 13.2	5.89 - 23.0	1.53, 1.53	1.03 - 2.03	2.99, 2.85	2.04 - 4.22
S31	6.4, 6.95	3.7 - 8.0	N.D.	N.D.	0.95, 1.03	0.22 - 1.51
S32	8.57, 5.5	2.72 - 20.4	1.09, 1.09	1.02 - 1.17	5.53, 5.53	2.28 - 8.77

Other notable sites include S5 (Rax city) in Faisalabad, S15 (Industrial area) in Gujranwala, and S13 (Abid Market) adjacent to S11 (Hall Road) in Lahore, which also showed high levels of PBDEs due to large-scale e-waste related operations in these areas (Kazim *et al.,* 2023; Sheikh *et al.,* 2021; Umair *et al.,* 2016).

To date, most studies reporting ΣPBDE soil contamination near e-waste recycling activities originate from China, where informal processes like burning and acid-leaching are common (Luo *et al.,* 2009; Wang *et al.,* 2014). Table 2.2 in review of literature section presents regional comparison studies targeting e-waste related contamination of BFRs in soil. Levels of Σ_{23}PBDE ranging from 191−9156 ng/g; mean: 2689 (Luo *et al.,* 2009) and Σ_{41}PBDE; 13.9−13300 ng/g; mean; 898 ng/g (Wang *et al.,* 2014) outside 1300 electronics dismantling workshops at Guangdong Province, China were broadly comparable to those measured near e-waste sites in Karachi, Gujranwala, and Faisalabad cities in the present study. Relatively lower concentrations of Σ_{8}PBDEs (including all relevant congeners) were reported in soil at an informal processing site in Ghana (mean: 54.8, range: 15.6−96.8 ng/g) (Akortia *et al.,* 2017) and at an open burning site in Vietnam (mean:14; range: 1.66−62 ng/g) (Matsukami *et al.,* 2017) while ΣPBDEs ranged 37−9200 (mean: 590) ng/g outside a processing workshop from the same Vietnamese study. These comparisons suggest that informal e-waste recycling facilities in Pakistan may have a similar potential to contaminate adjacent soils as widespread and informal practices in regions of Asia and Africa.

As discussed, PBDEs, PBBs, and HBCDDs concentrations differed among the e-waste sites listed in Table 4.19. Total BFRs levels were significantly higher in samples from Karachi, Gujranwala, Faisalabad, and Lahore due to the extent of informal recycling operations in these megacities. These results were expected because PBDEs and other BFRs are mainly associated with electrical and electronic products and as flame retardants (Covaci *et al.,* 2011), and the scale of recycling operations was found to be higher in these cities. Moreover, different types of e-waste products used for recycling operations define the spatial occurrence of related BFRs. Detailed analyses to determine possible relationships between the type of e-waste recycled and the level and pattern of BFRs contamination should be focused on in future studies due to the complex nature of e-waste operations in these recycling sites and the fact that a specific e-waste type is not limited to one site.

4.3.2.3 Seasonal variability

The total BFRs levels in the soil at e-waste recycling sites were strikingly higher than those at the reference site. Winter levels of ΣBFRs were about 3 times that of the rest of seasons, possibly due to the different meteorological conditions between seasons (Han *et al.*, 2009). Total concentrations of ΣBFRs were ranked as winter (11620 ng/g)> spring (3874 ng/g)> Autumn (3139 ng/gm)> Summer (1207 ng/g). The concentrations of ΣBFRs in autumn were significantly correlated with spring and summer ($P < 0.05$) while winter being unexpectedly high contaminated season did not correlate with other seasons (Table 4.20). Nevertheless, in subsequent research, Zhang et al. (2012) reported that the higher concentrations of FRs observed in summer while the variability of BFRs among seasons could possibly be due to different emission/deposition mechanisms. Over manifold difference of BFRs between the maximum (winter) and minimum (summer) indicated that the sampling period is a vital influencing factor for further investigations of human exposure risk assessment. Another potential explanation could be that Pakistan undergoes a dry winter characterized by reduced precipitation, which may diminish the leaching of contaminants from the soil, consequently leading to higher levels of pollutants in surface soils.

Table 4.20: Correlation analysis of ΣBFRs among sampling seasons

	Autumn	**Winter**	**spring**	**summer**
Autumn	1			
Winter	0.270098	1		
spring	0.938906	0.389127	1	
Summer	0.981185	0.313495	0.98265	1

🟩 Correlation is significant at the 0.01 level (2-tailed).

□ Correlation is significant at the 0.05 level (2-tailed)

4.3.2.4 Human Health Exposure

Human exposure to target BFRs through soil ingestion was assessed using average concentrations derived from soil samples collected across all cities in the Punjab province, as well as KPK, Sindh, and Baluchistan, employing ingestion factors recommended by the USEPA (Assessment, 1992). RfDs by the ingestion route were sourced from the US Environmental Protection Agency's Integrated Risk Information System for certain BDE data, while other BDE congeners were treated as equivalent reference doses with the same number of bromine atoms (Luo *et al.*, 2014), as detailed in Table 3.15 in methodology section.

Table 4.21: Human health exposures of FRs to e-waste laborers at sampling cities of Punjab cities (Ingestion: ng/kg/day)

BFRs	**Faisalabad**		**Rawalpindi**		**Lahore**		**Gujranwala**		**Multan**	
	ADD	**LADD**	**ADD**	**LADD**	**ADD**	**LADD**	**ADD**	**LADD**	**ADD**	**LADD**
BDE_17	0.00027	0.00013	0.00004	0.00002	0.00012	0.00006	0.00010	0.00004	0.00005	0.00003
BDE_28	0.00063	0.00029	0.00007	0.00003	0.00025	0.00011	0.00018	0.00008	0.00006	0.00003
BDE_49	0.00125	0.00058	0.00024	0.00011	0.00059	0.00027	0.00048	0.00022	0.00034	0.00015
BDE_71	0.00021	0.00010	0.00006	0.00003	0.00012	0.00005	0.00009	0.00004	0.00007	0.00003
BDE_47	0.00545	0.00251	0.00039	0.00018	0.01013	0.00468	0.00095	0.00044	0.00072	0.00033
BDE_66	0.00080	0.00037	0.00008	0.00004	0.00032	0.00015	0.00025	0.00012	0.00021	0.00009
BDE_100	0.00159	0.00073	0.00017	0.00008	0.00338	0.00156	0.00036	0.00017	0.00029	0.00014
BDE_99	0.00771	0.00356	0.00077	0.00036	0.02059	0.00950	0.00152	0.00070	0.00159	0.00073
BDE_85	0.00053	0.00025	0.00008	0.00004	0.00151	0.00070	0.00029	0.00013	0.00026	0.00012
BDE_126	0.00170	0.00078	0.00005	0.00003	0.00035	0.00016	0.00042	0.00020	0.00008	0.00003
BDE_154	0.00114	0.00053	0.00008	0.00004	0.00133	0.00061	0.00042	0.00019	0.00017	0.00008
BDE_153	0.00243	0.00112	0.00027	0.00012	0.00340	0.00157	0.00075	0.00034	0.00042	0.00019
BDE_138	0.00050	0.00023	0.00008	0.00003	0.00073	0.00034	0.00058	0.00027	0.00021	0.00009
BDE_184	0.00044	0.00020	0.00005	0.00003	0.00012	0.00005	0.00067	0.00031	0.00010	0.00004
BDE_183	0.00408	0.00188	0.00053	0.00025	0.00245	0.00113	0.00225	0.00104	0.00050	0.00023
BDE_191	0.00077	0.00036	0.00017	0.00008	0.00056	0.00026	0.00035	0.00016	0.00016	0.00007
BDE_180	0.00068	0.00031	0.00010	0.00005	0.00032	0.00015	0.00081	0.00037	0.00014	0.00006
BDE171.190	0.00059	0.00027	0.00013	0.00006	0.00032	0.00015	0.00046	0.00021	0.00018	0.00009
BDE_201	0.00092	0.00043	0.00009	0.00004	0.00021	0.00010	0.00247	0.00114	0.00009	0.00004
BDE_197	0.00150	0.00069	0.00018	0.00009	0.00072	0.00033	0.00206	0.00095	0.00014	0.00006
BDE_203	0.00064	0.00029	0.00011	0.00005	0.00034	0.00016	0.00219	0.00101	0.00011	0.00005
BDE_196	0.00192	0.00089	0.00021	0.00010	0.00071	0.00033	0.00375	0.00173	0.00033	0.00015
BDE_208	0.00245	0.00113	0.00027	0.00012	0.00064	0.00030	0.00444	0.00205	0.00016	0.00007
BDE_207	0.00488	0.00225	0.00047	0.00021	0.00131	0.00060	0.00714	0.00330	0.00027	0.00013
BDE_206	0.00501	0.00231	0.00075	0.00034	0.00187	0.00086	0.01012	0.00467	0.00049	0.00023
BDE_209	0.10973	0.05065	0.01082	0.00499	0.03499	0.01615	0.05843	0.02697	0.00453	0.00209
PBDEs	0.15784	0.07285	0.01627	0.00751	0.08737	0.04032	0.10154	0.04687	0.01166	0.00538
PBB_153	0.00227	0.00105	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
PBB_156	0.00342	0.00158	0.00274	0.00126	0.00342	0.00158	0.00240	0.00111	0.00240	0.00111
PBBs	0.00570	0.00263	0.00274	0.00126	0.00342	0.00158	0.00240	0.00111	0.00240	0.00111
HxBBz	0.00221	0.00102	0.00036	0.00017	0.00065	0.00030	0.00005	0.00002	0.00005	0.00003
HBCDDs	0.04782	0.02207	0.00474	0.00219	0.00667	0.00308	0.00265	0.00122	0.00961	0.00444
BFRs	**0.21357**	**0.09857**	**0.02412**	**0.01113**	**0.09812**	**0.04528**	**0.10664**	**0.04922**	**0.02372**	**0.01095**

Table 4.22: Human health exposures of FRs to e-waste laborers at sampling cities of KPK, Sindh and Baluchistan Province (Ingestion: ng/kg/day)

BFRs	**Peshawar**		**Karachi**		**Hyderabad**		**Quetta**	
	ADD	**LADD**	**ADD**	**LADD**	**ADD**	**LADD**	**ADD**	**LADD**
BDE_17	0.00004	0.00002	0.01998	0.00922	0.00003	0.00001	0.00011	0.00005
BDE_28	0.00005	0.00003	0.07197	0.03321	0.00007	0.00003	0.00034	0.00016
BDE_49	0.00016	0.00007	0.05744	0.02651	0.00014	0.00007	0.00028	0.00013
BDE_71	0.00005	0.00003	0.00125	0.00058	0.00005	0.00002	0.00005	0.00002
BDE_47	0.00027	0.00012	0.08616	0.03977	0.00015	0.00007	0.00061	0.00028
BDE_66	0.00005	0.00003	0.05168	0.02385	0.00005	0.00003	0.00023	0.00010
BDE_100	0.00008	0.00004	0.01133	0.00523	0.00004	0.00002	0.00011	0.00005
BDE_99	0.00035	0.00016	0.06788	0.03133	0.00014	0.00006	0.00033	0.00015
BDE_85	0.00005	0.00002	0.01967	0.00908	0.00004	0.00002	0.00007	0.00003
BDE_126	0.00005	0.00002	0.00038	0.00018	0.00003	0.00001	0.00008	0.00004
BDE_154	0.00005	0.00002	0.00661	0.00305	0.00003	0.00001	0.00005	0.00002
BDE_153	0.00018	0.00009	0.02995	0.01382	0.00007	0.00003	0.00014	0.00006
BDE_138	0.00006	0.00003	0.01012	0.00467	0.00003	0.00002	0.00012	0.00006
BDE_184	0.00005	0.00002	0.00040	0.00019	0.00003	0.00001	0.00004	0.00002
BDE_183	0.00049	0.00023	0.00567	0.00262	0.00015	0.00007	0.00027	0.00012
BDE_191	0.00018	0.00009	0.00043	0.00020	0.00008	0.00004	0.00010	0.00005
BDE_180	0.00009	0.00004	0.00048	0.00022	0.00005	0.00002	0.00008	0.00004
BDE171.190	0.00011	0.00005	0.00084	0.00039	0.00004	0.00002	0.00008	0.00004
BDE_201	0.00008	0.00003	0.00025	0.00011	0.00003	0.00001	0.00005	0.00002
BDE_197	0.00014	0.00007	0.00099	0.00046	0.00004	0.00002	0.00008	0.00003
BDE_203	0.00012	0.00005	0.00053	0.00024	0.00004	0.00002	0.00007	0.00003
BDE_196	0.00024	0.00011	0.00115	0.00053	0.00008	0.00004	0.00014	0.00007
BDE_208	0.00027	0.00013	0.00092	0.00043	0.00006	0.00003	0.00010	0.00005
BDE_207	0.00046	0.00021	0.00202	0.00093	0.00010	0.00004	0.00018	0.00008
BDE_206	0.00143	0.00066	0.00342	0.00158	0.00018	0.00008	0.00028	0.00013
BDE_209	0.02786	0.01286	0.04629	0.02137	0.00142	0.00066	0.00272	0.00126
PBDEs	0.03298	0.01522	0.49784	0.22977	0.00317	0.00146	0.00671	0.00309
PBB_153	N/A	N/A	0.00045	0.00021	N/A	N/A	N/A	N/A
PBB_156	0.00274	0.00126	0.00308	0.00142	0.00137	0.00063	0.00171	0.00079
PBBs	0.00274	0.00126	0.00353	0.00163	0.00137	0.00063	0.00171	0.00079
HxBBz	0.00012	0.00006	0.00344	0.00159	0.00001	0.00001	0.00004	0.00002
HBCDDs	0.00121	0.00056	0.00614	0.00283	0.00096	0.00044	0.00210	0.00097
BFRs	**0.03705**	**0.01710**	**0.51095**	**0.23582**	**0.00551**	**0.00254**	**0.01055**	**0.00487**

N/A= Not available

ADD and LADD for the sampling cities of the Punjab province are detailed in Table 4.21, while those for KPK, Sindh, and Baluchistan are provided in Table 4.22. For all FRs combined, exposure through ingestion was notably high at 0.51095 ng/kg/day in Karachi city, as anticipated. Karachi exhibited the highest ADD levels for PBDEs (0.49784 ng/kg/day), followed by HBB (0.00344 ng/kg/day) among all the contaminants.

Human exposure to contaminated soil in other cities was ranked as follows: Faisalabad > Gujranwala > Lahore > Peshawar > Rawalpindi > Multan > Quetta > Hyderabad. Faisalabad city was noted for high ADD doses for PBBs (0.00570 ng/kg/day) and HBCDDs (0.00614 ng/kg/day), respectively. Among individual BFRs, BDE-209 showed the highest ingestion value of 0.10973 ng/kg/day in Faisalabad, followed by BDE-47 (0.08616 ng/kg/day) and BDE-99 (0.06788 ng/kg/day) in Karachi city. The daily and lifetime intake of all other BFRs through soil ingestion was negligible compared to the RfD (reference dose) derived from toxicological research and estimates provided by the EPA (EPA US, 2014; Luo *et al.*, 2014; Ali *et al.*, 2012). It is important to note that exposure estimates entail numerous uncertainties that may influence the magnitude of exposure, including personal habits, dietary preferences, and occupational settings (Iqbal *et al.*, 2017).

The findings suggest that workers might be exposed to BFRs if they spend more time in recycling operations than currently assumed. Moreover, the informal e-waste recycling industry in Pakistan is expected to expand due to the absence of legislative policies specifically addressing e-waste management. Additionally, the growing prevalence of such informal e-waste recycling facilities could lead to increased exposure to toxic chemicals. Therefore, there is a possibility of heightened contamination of BFRs, potentially exposing laborers and nearby populations. Further investigations considering additional contaminants and other exposure pathways are warranted to evaluate appropriate measures for more environmentally sustainable e-waste management in Pakistan.

4.4 Part-IV

Investigating Brominated Flame Retardants (BFRs) in Informal E-Waste Recycling Facilities: An Assessment of Source, Distribution, and Human Exposure in Pakistan

This section is under preparation for a possible submission to a scientific journal.

4.4.1 Methodology

Details about field sampling and laboratory analysis, statistical analysis and QC/QA of FRs in air are given in Chapter-3 (section 3.2).

4.4.2 Results and Discussion

4.4.2.1 Occurrence and Distribution Pattern

While previous research on FRs in Pakistan has focused on indoor environmental matrices (Ali *et al.,* 2014; Ali *et al.,* 2012) and/or examining FRs levels at urbanized area or at small scale (Syed *et al.,* 2020; Iqbal *et al.,* 2017) this study represents the first investigation conducted at country level on selected BFRs originating from informal e-waste recycling facilities in Pakistan. In this study, nine PBDEs congeners, HBB and HBCDD compounds were identified and quantified in ambient air from 40-informal e-waste recycling sites in 9 mega cities of Pakistan. The detection frequency of selected BFRs in all investigated environmental matrixes is presented in Figure 4.9. The results and basic description of levels of selected BFRs in air are briefed in Table 4.23 and Appendix-10. Spatially, measured concentrations (mean (range)) in all sampling compartments i.e., particulate (flux (ng/m^2.day)) and gaseous (pg/m^3)) among all PBDEs were higher near the biggest recycling cities i.e., Karachi, (24.9 (0.44-721) and (26.4 (0.32-864), Lahore (4.78 (0.30-69.2) and (10.2 (0.26-516)), Peshawar, (2.24 (0.35-18.8)) and (2.47 (0.30-49.4)), Gujranwala, (15.8 (0.49-501)) and (5.31 (0.30-29.7)) and Faisalabad, (6.0 (0.27-73.4)) and (11.7 (0.35-261)), respectively (Appendix-10). In the case of individual PBDEs, BDE-209 (16 (0.46-400)) and (20.7 (1.17-516)), BDE-47, (17.6 (0.59-721)) and (17.8 (0.99-864)), BDE-99, (9.58 (0.40-437)) and (9.58 (0.57-394)) and BDE-28, (10.7 (0.43-241)) and (11.4 (0.58-375)) were detected in higher concentrations in particulate (flux (ng/m^2.day)) and gaseous (pg/m^3)) phase respectively (Table 4.23).

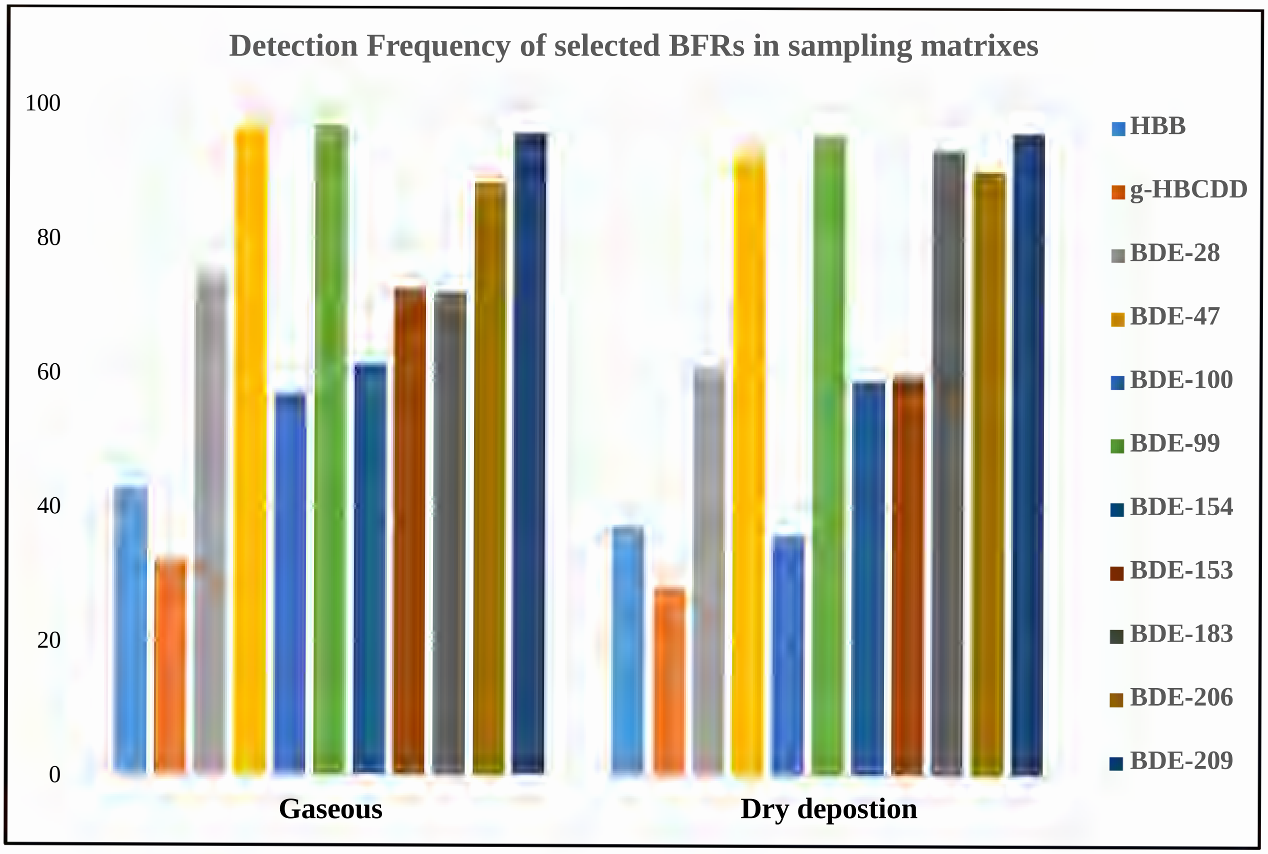


Figure 4. 9: Detection frequency of selected BFRs in air

The concentration level at reference site (COMSATS University, Islamabad) detected lower level of selected BFRs ranging, n.d-5.35 and n.d-2.28 with a detection frequency of 52.3 % and 56.8 % for gaseous, particulate phase samples respectively (Figure 4.9).

4.4.2.2 PBDEs in air

Table 4.23 summarizes the selected BFRs average concentration in gaseous and particulate phases. The yearly average concentration level of Σ_9PBDEs in all sites were 74.8 (5.39-2418) pg/m^3 and 69.8(3.65-2020) flux = ng/m^2.day) for the gaseous and particulate phase, respectively. In the air, BDE-209, BDE-47, BDE-28 and BDE-99 were dominant congeners present in concentration i.e., 20.7 pg/m^3 and 16 flux = ng/m^2.day), 17.8 pg/m^3 and 17.6 flux = ng/m^2.day), 11.4 pg/m^3 and 10.7 flux = ng/m^2.day), and 9.58 pg/m^3 and 9.58 flux = ng/m^2.day) for gaseous and particulate phase, respectively. Concentration level of remaining selected PBDEs were ranked as BDE-206 >BDE-183 >BDE-100 >BDE-153 >BDE-154 in gaseous phase and BDE-53 >BDE-100 >BDE-183 >BDE-206 >BDE-154 in particulate phase (Table 4.23).

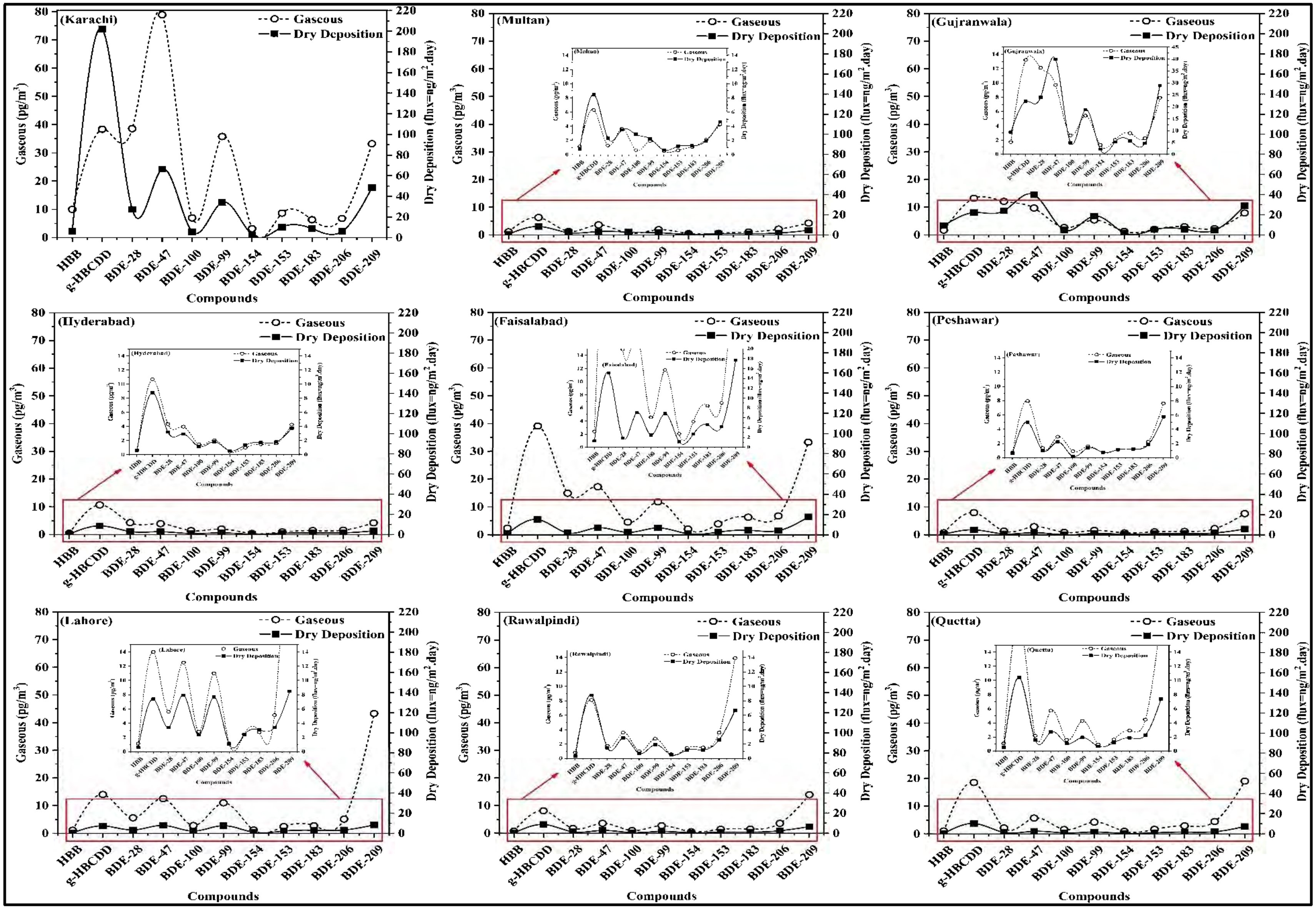


Figure 4.10: Summary of basic descriptive statistics of BFRs concentration levels

Table 4.23: Descriptive statistics of selected BFRs combined at all sites in studied environmental matrixes

Compounds	Gaseous (pg/m^3) (n=160)						Particulate (flux= ng/m^2.day) (n=160)					
	Mean	Median	S. D	Min	Max	Detected	Mean	Median	S. D	Min	Max	Detected
HBB	3.02	1.01	8.83	0.34	59.9	70	3.68	0.72	14.7	0.22	106	59
g-HBCDD	15.7	8.14	33.2	0.78	248	51	14.0	8.53	15.8	3.92	69.0	45
Σnon-PBDE	**18.8**	**9.15**	**42.0**	**1.12**	**308**	-	**17.7**	**9.26**	**30.5**	**4.14**	**175**	-
BDE-28	11.4	2.07	40.8	0.58	375	119	10.7	2.10	37.3	0.43	241	97
BDE-47	17.8	4.32	78.8	0.99	864	155	17.6	3.74	83.3	0.59	721	148
BDE-100	3.29	1.45	7.50	0.48	68.3	91	3.73	1.87	6.12	0.48	32.8	57
BDE-99	9.58	2.64	35.7	0.57	394	155	9.58	2.20	42.7	0.40	437	152
BDE-154	1.47	0.69	2.89	0.23	25.6	98	1.37	0.71	2.60	0.23	16.6	94
BDE-153	3.00	1.24	7.82	0.36	74.2	116	3.81	1.49	11.3	0.35	93.2	99
BDE-183	3.59	1.68	7.41	0.46	60.2	115	3.67	1.75	7.17	0.40	47.4	115
BDE-206	3.95	2.47	5.45	0.55	40.7	141	3.30	2.17	4.23	0.30	31.2	144
BDE-209	20.7	6.61	55.3	1.17	516	153	16.0	4.96	51.8	0.46	400	153
ΣPBDE	**74.8**	**23.2**	**242**	**5.39**	**2418**		**69.8**	**21.0**	**246**	**3.65**	**2020**	-

Most of the PBDEs were presents in the gaseous monitoring, excluding a few sites (site J40 at Hyderabad for (BDE-28, BDE-100, BDE-154), site J28 at Multan & site J38 at Hyderabad for (BDE-100), site J10 at Rawalpindi, site J28 at Multan, and site J38 at Hyderabad for (BDE-183). PBDEs, on the other hand, were detected in particulate phase in all sampling cities except Peshawar (BDE-100). Some PBDEs, however, were not found in specific samples, including BDE-28 in 6 samples, BDE-47, BDE-99, BDE-183, BDE-206, and BDE-209 in 1, BDE-100 in 12, and BDE-154 and BDE-153 in 3 samples.

In both phases (particulate and gaseous) the prevalence of lower PBDEs, such as BDE-47 (mean= 17.8 pg/m^3 and 17.6 ng/m^2.day), BDE-28 (11.4 pg/m^3 and 10.7 ng/m^2.day), BDE-99 (9.58 pg/m^3 and 9.58 ng/m^2.day), and deca-BDEs (BDE-209= 20.7pg/m^3 and 16.0 ng/m^2.day), exceeded that of octa-BDEs in the atmosphere (Table 4.23). This can be attributed to their higher volatility and the presence of informal recycling processes of e-waste as a trace of technical deca-BDE. These findings align with a previous study conducted on atmospheric emissions due to informal e-waste recycling in Karachi (Iqbal *et al.,* 2017). However, the average concentration of BDE-209 in this study surpassed that of other studies conducted at e-waste sites, such as Guangzhou, China, where BDE-209 ranged from 0.26 to 4.20 ng/m^3 (Chen *et al.,* 2006), Guiyu (1.95 ng/m^3) (Chen *et al.,* 2009), and Taizhou (0.18 ng/m^3) (Han *et al.,* 2009).

The stated pattern with comparatively elevated levels of volatile PBDEs in the atmosphere, could possibly be due to combination of primary and secondary sources (Gouin *et al.,* 2006), and attributed to e-waste activities happening in these locations which are involved in old electronic equipment recycling containing penta-BDE & octa-BDE formulations, extensively manufactured and employed in market previously. Printed Circuit boards (PCBs), contain relatively higher amounts of tetra- BDE & penta-BDEs (Liu *et al.,* 2019), release lighter BDEs into the atmosphere when they are melted & grilled to attain precious metals inside (Cai *et al.,* 2019). Furthermore, debromination can occur to BDE-209 results further contaminated and lower PBDEs due to burning process more common activity in informal sector (Nie *et al.,* 2015). Thus, several variables such as debromination, the presence of primary and secondary sources (Iqbal *et al.,* 2017), might be responsible for the comparatively high levels of lower BDEs observed in current study.

4.4.2.3 non-PBDEs

The yearly average concentration of HBB and HBCDD detected was 3.02 (0.34-59.9) pg/m^3 and 15.7 (0.78-248) pg/m^3 for gaseous phase, while 3.68 (0.22-106) ng/m^2.day and 14 (3.92-69) ng/m^2.day for particulate phase (Table 4.23). Both compounds were detected in 44 % and 32 % in gaseous phase and 37 % and 28 % of samples taken from particulate (Figure 4.9). The marginal lower detection frequency of HBB and HBCDD in the particulate phase compared to the gaseous phase may be attributed to their lower volatility, which makes them less prone to vaporization and subsequent release into the atmosphere during e-waste recycling processes. This reduced volatility limits their potential for atmospheric emissions and subsequent deposition (Esplugas *et al.,* 2022).

In a global context, atmospheric concentrations of HBB around e-waste sites in southern China were found to have lower, with an average concentration of 0.15 ng/m^3 (Tian *et al.,* 2012).

Similarly, a study conducted in Taizhou, China, reported low levels of HBB (0.007 ng/m^3) (Zhang *et al.,* 2012). These reported levels are manifold lower compared to the concentrations measured in our study. Both HBB and HBCDD have been used as flame retardant in polymers, plastics, textiles, woods, and paper (Liu *et al.,* 2016), and e-waste recycling facilities have been identified as potential sources of HBB (Venier *et al.,* 2012). In summary, the elevated concentrations of these BFRs found in the vicinity of e-waste recycling sites can be attributed to the scale and intensity of the informal processes carried out in these areas.

4.4.2.4 Spatio-temporal variation of FRs

The descriptive summary of the selected FRs in gaseous and particulate phase in each sampling city is presented in Table 4.24 and 4.25 respectively, for all sampling cities. Among cities, high levels were detected at Karachi with yearly mean concentration of Σ_9PBDEs (mean=227, range= 10.5-2185) ng/m^3 in gaseous and (210 (9.21-2020) flux (ng/m^2.day) particulate phase. After Karachi, high levels (101 (7.29-550) ng/m^3 and 48.6 (6.63-172) flux (ng/m^2.day) were detected at Faisalabad, (86.5 (10.3-721) ng/m^3, 39.8 (7.48-174) flux (ng/m^2.day) at Lahore and 46.4 (7.23-142) ng/m^3 and 134 (12.3-1458) flux (ng/m^2.day) at Gujranwala for gaseous and particulate phase, respectively. Regarding Σnon-PBDEs, high levels were detected at Karachi 48.4 (4.75-308) ng/m^3 in gaseous and at Gujranwala 31.5, 10.6 (5.80-171) flux (ng/m^2.day in particulate phase. High level of HBB and HBCDD in particulate phase (flux (ng/m^2.day)) were detected at Karachi (6.43 (0.33-42.5)) and 202 ((4.60-69.0)) Gujranwala (9.27 (0.50-106)) and (22.2 (5.30-64.9)) and Faisalabad (1.29 (0.39-2.47)) and (15.1 (6.89-32.0)) (Table 4.24), while Karachi (10.0 (0.34-1.59)) and (38.4 (4.41-248)), Faisalabad (2.40 (0.68-7.60)) and (39.1 (5.69-68.8)) and Lahore (1.14 (0.77-2.27)) and (14.0 (7.86-23.6)) reported high level in gaseous phase ((pg/m^3))) (Table 4.25), respectively. The details of variability in concentration level of FRs air are given in the following sections.

Elevated levels at Karachi and Faisalabad are consistent with prior study that found high concentration of several FRs, such as PBDEs, in these cities (Iqbal *et al.,* 2017; Syed *et al.,* 2013). In comparison, Peshawar, Hyderabad, Multan, Quetta, and Rawalpindi exhibit lower concentration levels in all sampling matrixes (Table 4.24 and 4.25). $\sum_9$PBDE levels in Karachi were many orders of magnitude higher than those at other cities. Elevated levels of target compounds in Karachi could possibly the outcomes of specific type of recycling operations and type of e-waste.

The atmospheric level of PBDEs and non-PBDEs were also consistent in each sampling city reported in this study (The details are presented in Table 4.24 and 4.25). Contribution rank of other cities was Faisalabad >Lahore >Quetta >Rawalpindi>Peshawar >Hyderabad >Multan for gaseous and Faisalabad >Lahore >Quetta >Multan >Rawalpindi >Hyderabad >Peshawar for particulate phase. Previously, few localized studies have also been conducted in Pakistan which indicate contamination of FRs in different environmental matrix, but the reported levels were lower to what is reported in this study (Ali *et al.,* 2014; Syed *et al.,* 2013; Ali *et al.,* 2015; Mahmood *et al.,* 2015; Zehra *et al.,* 2015, Syed at al., 2020). However, these studies also provide the evidence that these cities are highlighted for e-waste operations as hotspot within the country (Syed *et al.,* 2020; Shaikh *et al.,* 2020; Akbar *et al.,* 2020; Akram *et al.,* 2019; Sajid *et al.,* 2019; Imran *et al.,* 2017; Iqbal *et al.,* 2017; Umair *et al.,* 2016). Addition to the informal e-waste recycling, these cities have been reported for mega-scale manufacturing which potentially utilize FRs, e.g., manufacturing of EEE, in plastic products, in textiles and preservatives as well. Faisalabad is famous for its garment manufacturing and textile units (Hafeez *et al.,* 2021), while Gujranwala is well-known for multi-industries. Such highlighted characteristics of these mage cities can result elevated levels of FRs more possibly. However, comparatively low level of FRs in Multan, Hyderabad, Peshawar, and Rawalpindi could be due to lower informal e-waste recycling practices and lesser industrial production.

Table 4.24: Descriptive summary [Mean, Median (Min-Max)] of BFRs in gaseous phase from Nine Pakistani cities (ng/m^3)

Compounds	Peshawar	Faisalabad	Rawalpindi	Lahore	Karachi	Gujranwala	Multan	Quetta	Hyderabad
HBB	0.74, 0.66 (0.47-1.19)	2.40, 1.16 (0.68-7.60)	0.81, 0.78 (0.58-1.17)	1.14, 1.04 (0.77-2.27)	10.0, 0.88 (0.34-1.59)	1.72, 1.56 (0.64-3.61)	1.16, 1.17 (0.62-1.86)	1.09, 1.03 (0.62-2.03)	0.55, 0.55 (0.55-0.55)
g-HBCDD	7.96, 7.15 (4.09-13.5)	39.1, 45.3 (5.69-68.8)	8.11, 7.68 (5.87-11.2)	14.0, 11.6 (7.86-23.6)	38.4, 16.9 (4.41-248)	13.2, 7.29 (6.37-30.6)	6.30, 6.30 (5.52-7.07)	18.5, 17.5 (11.4-33.6)	10.7, 10.7 (8.43-13.0)
ΣnonPBDE	**8.71, 7.80 (4.57-14.6)**	**41.5, 46.4 (6.38-76.4)**	**8.92, 8.45 (6.44-12.4)**	**15.1, 12.7 (8.63-25.8)**	**48.4, 17.8 (4.75-308)**	**14.9, 8.85 (7.01-34.2)**	**7.46, 7.47 (6.14-8.93)**	**19.5, 18.5 (12.0-35.6)**	**11.3, 11.3 (8.98-13.6)**
BDE-28	1.36, 1.11 (0.66-2.26)	14.9, 6.98 (0.58-72.0)	1.76, 1.67 (0.74-2.89)	5.60, 5.09 (1.35-11.6)	38.6, 2.48 (1.02-375)	12.1, 12.1 (0.93-36.2)	1.31, 1.29 (0.73-1.92)	2.18, 1.42 (0.96-5.83)	4.34, 1.45 (0.84-13.4)
BDE-47	2.95, 2.97 (1.31-4.68)	17.2, 10.0 (1.26-73.7)	3.59, 3.31 (1.38-6.37)	12.5, 9.30 (2.19-47.1)	78.9, 7.95 (2.14-864)	9.71, 5.86 (1.14-29.7)	3.65, 3.14 (1.25-8.22)	5.72, 4.39 (1.53-15.3)	3.96, 2.69 (0.99-15.1)
BDE-100	0.91, 0.93 (0.55-1.14)	4.57, 2.40 (0.48-13.3)	1.00, 1.04 (0.69-1.26)	2.82, 1.71 (0.69-11.8)	6.98, 2.45 (0.69-68.3)	2.66, 2.52 (0.74-6.11)	0.66, 0.71 (0.48-0.82)	1.60, 1.17 (0.60-4.49)	1.45, 1.45 (0.87-2.03)
BDE-99	1.61, 1.44 (1.04-2.96)	11.8, 7.01 (0.83-38.6)	2.73, 2.62 (0.79-5.92)	11.0, 5.37 (1.54-73.6)	35.8, 4.54 (1.17-394)	5.41, 3.96 (0.58-16.8)	1.93, 1.77 (0.99-3.73)	4.28, 2.99 (0.87-12.9)	2.04, 1.90 (0.57-4.62)
BDE-154	0.72, 0.59 (0.30-175)	2.07, 1.33 (0.35-6.45)	0.59, 0.55 (0.34-1.03)	1.19, 0.73 (0.26-4.42)	3.19, 0.93 (0.32-25.6)	1.31, 1.02 (0.30-4.94)	0.53, 0.57 (0.35-0.67)	0.95, 0.69 (0.44-2.32)	0.43, 0.42 (0.23-0.65)
BDE-153	1.11, 0.92 (0.45-2.35)	3.91, 2.56 (0.56-15.6)	1.45, 1.46 (0.94-1.99)	2.46, 1.69 (0.71-9.20)	8.65, 1.81 (0.66-74.2)	2.02, 1.62 (0.46-4.60)	0.63, 0.64 (0.55-0.72)	1.64, 1.08 (0.68-4.54)	0.98, 0.99 (0.36-2.01)
BDE-183	1.22, 0.99 (0.65-2.53)	6.32, 3.36 (0.68-34.8)	1.52, 1.40 (0.72-3.20)	2.75, 2.27 (0.97-6.18)	6.32, 3.36 (0.68-34.8)	2.97, 2.01 (0.60-8.68)	1.09, 1.03 (0.71-1.58)	2.91, 1.92 (0.70-10.4)	1.47, 1.37 (0.46-3.51)
BDE-206	2.24, 1.83 (1.19-5.13)	6.77, 3.24 (0.95-34.6)	3.57, 2.95 (0.58-9.12)	5.14, 2.32 (0.75-40.7)	6.77, 3.24 (0.95-34.6)	2.26, 1.74 (0.96-5.45)	2.11, 1.96 (1.13-3.73)	4.47, 3.57 (1.40-11.5)	1.60, 1.25 (0.71-3.83)
BDE-209	7.63, 4.75 (2.22-49.4)	33.3, 15.0 (1.60-261)	13.9, 7.07 (2.45-61.3)	43.3, 9.09 (1.87-516)	33.3, 15.0 (1.60-261)	7.91, 6.57 (1.53-29.5)	4.27, 4.67 (1.85-7.43)	19.0, 11.9 (3.40-63.7)	4.25, 2.87 (1.17-14.2)
ΣPBDE	**19.7, 15.5 (8.38-72.2)**	**101, 51.9 (7.29, 550)**	**30.1, 22.1 (8.62-93.1)**	**86.5, 37.6 (10.3-721)**	**227, 37.1 (10.5-2185)**	**46.4, 37.4 (7.23-142)**	**16.2, 15.8 (8.05-28.8)**	**42.8, 29.1 (10.6-131)**	**20.5, 14.4 (6.21-59.3)**

Table 4.25: Descriptive summary [Mean, Median (Min-Max)] of BFRs in Particulate phase from Nine Pakistani cities (Flux (ng/m^2.day)

Compounds	Peshawar	Faisalabad	Rawalpindi	Lahore	Karachi	Gujranwala	Multan	Quetta	Hyderabad
HBB	0.63, 0.63 (0.54-0.72)	1.29, 0.96 (0.39-2.47)	0.33, 0.33 (0.24-0.42)	0.60, 0.43 (0.22-1.51)	6.43, 0.80 (0.33-42.5)	9.27, 1.28 (0.50-106)	0.82, 0.75 (0.28-1.79)	0.52, 0.51 (0.40-0.64)	0.62, 0.60 (0.44-0.82)
g-HBCDD	4.98, 4.35 (4.09-6.48)	15.1, 13.0 (6.89-32.0)	8.77, 8.77 (8.53-9.00)	7.38, 6.90 (4.55-10.4)	20.2, 11.1 (4.60-69.0)	22.2, 9.37 (5.30-64.9)	8.48, 8.48 (4.42-12.5)	10.4, 11.2 (7.28-12.8)	8.78, 10.8 (3.92-11.6)
Σnon-PBDE	**5.61, 4.98 (4.63-7.20)**	**16.4, 13.9 (7.28-34.5)**	**9.10, 9.10 (8.78-9.42)**	**7.98, 7.33 (4.77-11.9)**	**26.6, 11.9 (4.93-112)**	**31.5, 10.6 (5.80-171)**	**9.30, 9.24 (4.70-14.3)**	**10.9, 11.7 (7.69-13.4)**	**9.40, 11.4 (4.36-12.5)**
BDE-28	1.03, 0.93 (0.52-2.32)	1.92, 1.68 (0.61-5.37)	1.49, 1.27 (0.43-3.74)	3.41, 2.34 (0.98-9.20)	27.3, 3.52 (1.17-241)	24.0, 8.75 (1.97-214)	2.33, 1.52 (0.56-5.73)	1.59, 1.41 (0.86-3.06)	3.18, 2.81 (1.55-4.51)
BDE-47	2.23, 1.94 (1.04-5.39)	7.04, 5.52 (1.00-19.4)	2.88, 3.19 (1.07-4.61)	7.93, 4.86 (1.72-36.2)	66.3, 8.81 (1.96-721)	39.9, 7.04 (2.64-501)	3.49, 2.57 (0.80-9.61)	2.71, 2.33 (1.12-5.74)	2.90, 2.64 (0.59-6.40)
BDE-100	N.D	2.48, 2.59 (0.68-4.11)	0.71, 0,79 (0.48-0.86)	2.35, 1.28 (0.58-10.7)	5.74, 2.41 (0.87-32.8)	4.89, 2.92 (1.01-28.3)	2.87, 2.87 (2.46-3.28)	1.09, 0.88 (0.74-1.64)	1.14, 1.14 (0.85-1.44)
BDE-99	1.38, 1.26 (0.60-2.36)	6.85, 1.90 (0.67-24.4)	1.92, 1.97 (0.77-3.02)	7.68, 3.08 (1.23-69.2)	34.2, 5.09 (0.70-437)	18.7, 5.00 (1.61-2.218)	2.24, 1.51 (0.73-5.99)	1.94, 1.48 (0.80-4.04)	1.81, 1.17 (0.40-6.16)
BDE-154	0.76, 0.55 (0.35-1.48)	1.15, 1.04 (0.27-2.61)	0.50, 0.41 (0.25-1.04)	1.09, 0.65 (0.47-4.32)	2.68, 1.11 (0.44-16.5)	2.13, 1.08 (0.49-15.4)	0.65, 0.48 (0.41-1.02)	0.68, 0.70 (0.41-0.91)	0.54, 0.41 (0.23-1.69)
BDE-153	1.14, 1.02 (0.35-2.24)	2.68, 2.14 (0.85-8.01)	1.16, 1.12 (0.46-2.22)	2.39, 1.67 (0.70-10.1)	10.2, 2.15 (1.14-93.2)	5.26, 1.64 (1.15-46.0)	1.20, 1.17 (0.56-1.80)	1.19, 1.02 (0.49-2.32)	1.35, 0.92 (0.80-4.89)
BDE-183	1.21, 1.06 (0.49-2.83)	4.61, 2.20 (0.70-17.1)	1.20, 1.11 (0.51-2.04)	3.06, 3.13 (0.52-5.59)	8.68, 4.02 (0.63-47.4)	5.73, 2.13 (0.93-41.2)	1.27, 1.37 (0.69-1.82)	1.88, 1.37 (0.49-6.12)	1.72, 1.09 (0.40-4.92)
BDE-206	1.84, 1.74 (0.64-4.44)	4.18, 2.52 (0.54-17.2)	2.58, 2.47 (0.91-4.70)	3.40, 2.76 (0.30-8.43)	6.03, 3.72 (0.63-31.2)	4.69, 2.43 (0.84-29.8)	1.95, 1.93 (0.64-4.17)	2.27, 2.04 (0.46-6.68)	1.79, 1.46 (0.52-4.26)
BDE-209	5.76, 4.31 (1.38-18.8)	17.7, 6.87 (1.31-73.4)	6.67, 4.32 (1.33-24.6)	8.47, 6.60 (0.98-20.1)	48.4, 12.2 (1.67-400)	28.9, 7.02 (1.68-364)	4.65, 3.80 (1.85-13.3)	7.39, 5.74 (1.87-18.7)	3.74, 2.55 (0.46-12.9)
ΣPBDE	**15.3, 12.8 (5.38-39.8)**	**48.6, 26.4 (6.63-172)**	**19.1, 16.7 (6.21-46.8)**	**39.8, 26.4 (7.48-174)**	**210, 43.0 (9.21-2020)**	**134, 38.0 (12.3-1458)**	**20.6, 17.2 (8.69-46.7)**	**20.7, 16.9 (7.24-49.2)**	**18.2, 14.2 (5.80-47.1)**

4.4.2.5 Temporal variations

In the Air (Gaseous and particulate), the average concentration levels of 11BFRs in warm seasons (summer and autumn) were significantly higher than those in the cold season (winter). The comparative description of BFRs levels in studied matrixes among seasons is presented in Table 4.26 and Figure 4.11. The results from the atmospheric samples demonstrated a much clearer seasonal trend. The gaseous phase exhibited higher levels during the summer season (Average = 13.1 pg/m^3, median = 3.81 pg/m^3, range = 0.30-516 pg/m^3), whereas the particulate phase showed higher levels during autumn (Average = 11.7. median = 2.66, Range = 0.23-721 (ng/m^2.day). The seasonal trend of 11BFRs levels in air was as summer > winter > spring > autumn and autumn > summer > spring > winter for gaseous and particulate phase, respectively. In the air, temperature could be a significant parameter, suggesting that the levels of BFRs in the gas-phase and particle-phase were highly temperature dependent. The levels of BFRs in the atmosphere showed a similar seasonal variation, with low mass BFRs dominating in the air in warmer seasons. This finding suggests that atmospheric concentrations of BFRs in high-temperature seasons at the e-waste site are strongly controlled by temperature-driven evaporation from contaminated surfaces in the local surroundings of these sites (Liu *et al.,* 2016; Tian *et al.,* 2011; Wania *et al.,* 1998).

Table 4.26: Seasonal variations of studied compounds

Sampling	Description	Autumn	Winter	Spring	Summer
Particulate (ng/m^2.day)	**Average**	11.7	5.15	8.04	10.7
	Median	2.66	2.37	2.06	1.82
	Range	0.23-721	0.28-119	0.23-524	0.24-501
Gaseous (ng/m^3)	**Average**	5.37	12.5	7.06	13.1
	Median	1.87	1.92	2.53	3.81
	Range	0.33-154	0.23-864	0.26-309	0.30-516

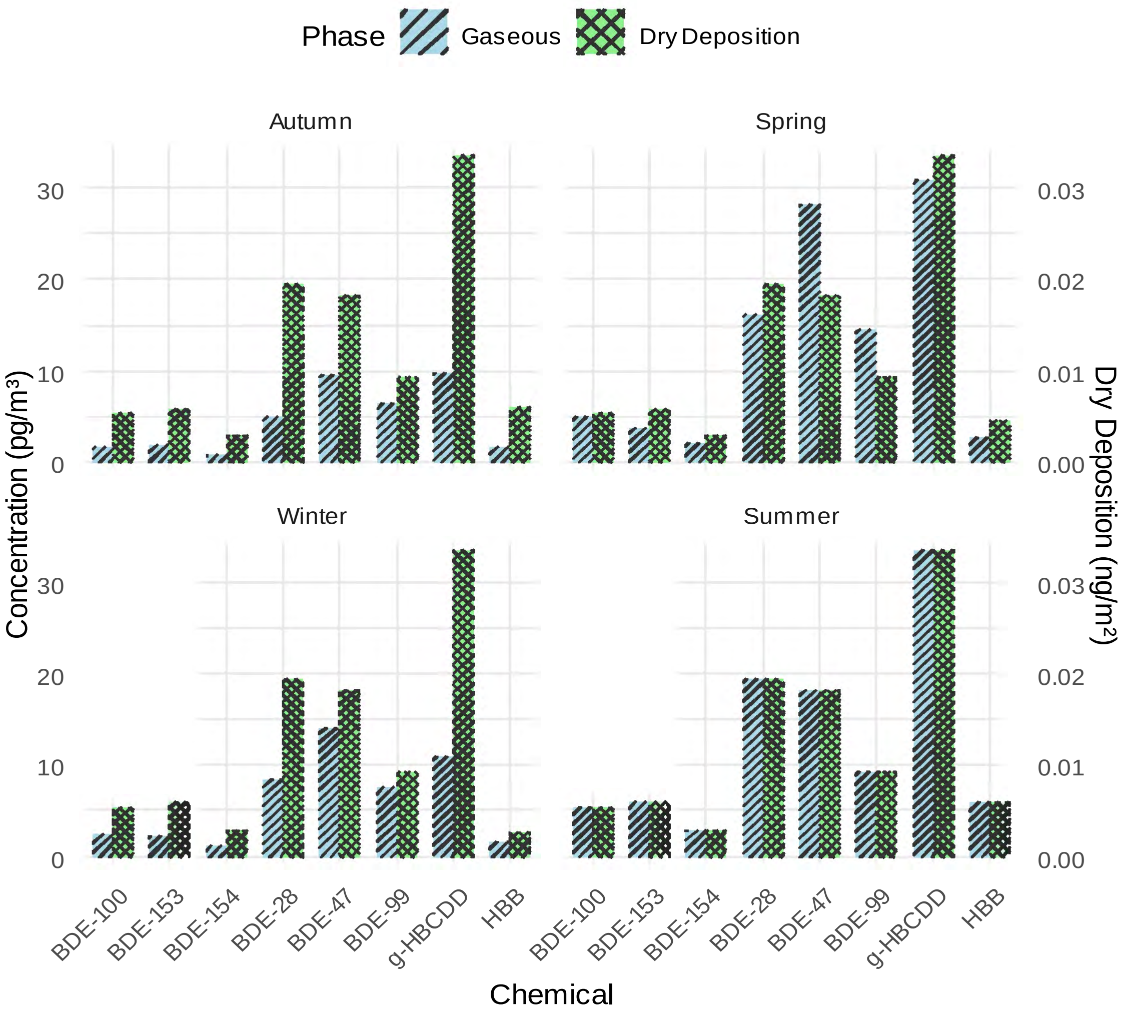


Figure 4.11: Seasonal variation of BFRs in air

4.4.2.6 Health Risk Assessment

The average ADD for 9PBDEs, HBB and g-HBCDD were estimated as 6.25 pg/kg-BW/day, 0.21 pg/kg-BW/day and 1.65 pg/kg-BW/day for air inhalation (Table 4.27). Generally, the high ADD calculated from the samples taken from Karachi, tailed by Faisalabad, Lahore & Gujranwala. Previously Iqbal et al. (2017), described provides ADD for sum 8-PBDEs in outdoor air ingestion near e-waste recycling sites at Karachi (ADDgas = 19.1 ng/kg/day which are higher to the estimation reported in this study. However, our ADD estimates are higher to sum 8-PBDEs values reported earlier from major urban cities in Pakistan (Syed *et al.*, 2020). Similarly, Fromme et al. reported an estimated ADD for outdoor air of BDE-209 for an average adult in Germany, UK, and U.S. as 0.6, 0.6, and 0.3 pg/ kg-BW/day respectively (Fromme *et al.*, 2016). Levels of BDE-209 in present study (1.86 pg/kg-BW/day) were lower than Guangzhou

(12 pg/kg-BW/day) (Liu *et al.,* 2016). It is important to recognize that several factors introduce uncertainties in exposure assessments, thereby influencing the level of exposure experienced by individuals. These factors include personal habits, dietary preferences, occupational environments, and others.

The inhalation exposure risk associated with FRs calculated in current study are potentially lower than that of previous similar studies & RfDs suggested by EPA (USEPA, 2004; Wayne & Lance, 2006). However, if laborers and persons who use more time at such e-waste operational factories than indicated in model, the uptake doses potentially go up. In addition, it is estimated that Pakistan's e-waste recycling business would rise, resulting the high risk of BFR toxicity and significant exposure to laborers and adjacent communities.

Table 4.27: Average daily dose exposure of inhalation (pg/kg BW/day) of BFRs at Nine Pakistani cities

Cities	Exposure	HBB	g-HBCDD	BDE-28	BDE-47	BDE-100	BDE-99	BDE-154	BDE-153	BDE-183	BDE-206	BDE-209	City's ΣPBDEs
Peshawar	ADDgas	0.07	0.76	0.13	0.28	0.09	0.15	0.07	0.11	0.12	0.21	0.73	**1.88**
Faisalabad	ADDgas	0.23	3.72	1.42	1.64	0.44	1.12	0.20	0.37	0.60	0.64	3.17	**9.60**
Rawalpindi	ADDgas	0.08	0.77	0.17	0.34	0.09	0.26	0.06	0.14	0.14	0.34	1.32	**2.86**
Lahore	ADDgas	0.11	1.33	0.53	1.17	0.27	1.05	0.11	0.23	0.26	0.49	4.12	**8.23**
Karachi	ADDgas	0.95	3.66	3.68	7.51	0.66	3.41	0.30	0.82	0.69	0.53	4.06	**21.66**
Gujranwala	ADDgas	0.16	1.25	1.15	0.92	0.25	0.51	0.13	0.19	0.28	0.22	0.75	**4.41**
Multan	ADDgas	0.11	0.60	0.12	0.35	0.06	0.18	0.05	0.06	0.10	0.20	0.41	**1.54**
Quetta	ADDgas	0.10	1.76	0.21	0.54	0.15	0.41	0.09	0.16	0.28	0.43	1.81	**4.07**
Hyderabad	ADDgas	0.05	1.02	0.41	0.38	0.14	0.19	0.04	0.09	0.14	0.15	0.40	**1.95**
	Avg.ADDgas	**0.21**	**1.65**	**0.87**	**1.46**	**0.24**	**0.81**	**0.12**	**0.24**	**0.29**	**0.36**	**1.86**	**6.25**

Chapter 5

Conclusion and Recommendations

5.1 General Comments

The present research study is a comprehensive survey of informal e-waste recycling facilities in major areas of Pakistan including Punjab Province (Lahore, Faisalabad, Rawalpindi, Multan and Gujranwala), KP Province (Peshawar), Sindh Province (Karachi, Hyderabad) and Baluchistan Province (Quetta) in four seasons (autumn, winter, spring, and summer) between September 2020 and December 2021. This research study provided baseline data of GEM in air, HMs and FRs data in air and soil. In general, the current thesis highlighted the spatio-temporal information on the source and distribution of target compounds emitting from informal e-waste recycling processes at country level. The study area (Pakistan) highly populated country with 241 million people, is the most significant ecological area in the Indian sub-continent (South Asia). Regardless of its significance for the region, informal e-waste recycling facilities in Pakistan are more common due lack of legislative framework and soft imports in the name of donation or charity. Therefore outcome of the present research work emphasizes the status of hazardous compounds and offer understanding on levels, sources, distribution, environmental re-cycling and human health related consequences.

5.2 GEM

Passive air sampling methodology was employed first time at thirty-two informal e-waste recycling centers spread across nine major cities in Pakistan to monitor GEM levels on spatial and temporal scale. Passive air sampling was carried out for a period of one year i.e., splitting it into four seasons between October 2020 to September 2021. Yearly average GEM concentrations ranged from <1.60 to 92.0 ng/m3. Among all studied cities, higher concentrations were measured in the air samples from Karachi (Mean ± S.D =16.4 ± 9.30 ng/m3) followed by Lahore (14.3 ± 1.40 ng/m3), while lowest concentration levels were reported from Hyderabad (6.2 ± 4.1ng/m3). Temporally, higher concentration levels were recorded during autumn (13.8 ± 4.90 ng/m3) while lower GEM levels were measured during the spring season (8.10 ± 3.20 ng/m3). Meteorological parameters observed to have a significant role over sampling rate (SR) i.e., temperature (R2 = 0.982, p< 0.05)) and wind (R2 = 0.980, p< 0.05)), however, no significant difference was observed among GEM emission levels in different seasons. Here, our findings revealed that how GEM concentrations and emissions to the atmosphere varies at informal e-waste recycling facilities across Pakistan. Results also confirmed that informal e-waste recycling facilities might be a potential source of GEM emissions into the atmosphere.

The study reported 1st time GEM inventory data due to current informal recycling practices of e-waste in Pakistan. Based on the emission levels, the study implied that these practices are major contributor of GEM pollution across the country. Uncontrolled and informal ways of e-waste treatment procedures are a potential threat to human health and environmental compartments. Being the signatory of the Mina-Mata convention, Pakistan needs to restrict the emission levels by devising e-waste management plan.

5.3 Heavy metals in air and soil

This is the first comprehensive study, where passive air samplers were deployed at 40 e-waste recycling facilities across multiple cities (n=9) for a year-long continuous sampling of heavy metals (Cr, Ni, Pb, Cu, Mn, Zn and Cd). Simultaneously, the soil samples were also taken from the same sites, once in each season. Comparatively, the major urban centers i.e., Karachi, Lahore, Gujranwala, and Faisalabad showed the highest levels of HMs in air and soil. Based on air sample data, especially from Karachi, Zn (1410), Pb (410) and Mn (231) showed the higher average deposition fluxes ($\mu g/m^2$.day). Similarly, soils samples from Faisalabad, Lahore, and Karachi showed elevated average level (µg/g dw) of Mn (477), Cu (514), and Pb (172), respectively. Additionally, re-waste sampling location demonstrated higher HM levels ($p=0.05$) than reference sites, concluding that such processes are the major source of target chemicals. In the case of I_{geo} index Karachi, Lahore, and Gujranwala, showed moderate to extremely polluted levels of Cu, Pb, Cd, & Ni. It was determined that Pb has higher human health risk if ingested, trailed by dermal and inhalation route. For all HMs ingestion was found to be the prime human exposure pathway. As suggested by the ILCR model moderate to low cancer risks are associated with workers. Temporally, dry and cold seasons have elevated levels of HMs in both sampling matrices than rainy and humid seasons.

5.4 FRs in soil and air

The findings reveal the prevailing contamination of BFRs in soils from informal e-waste recycling facilities throughout major urban cities in Pakistan. This study showed alarmingly higher levels of PBDEs, PBBs, and ∑HBCDD in soil samples collected from e-waste recycling sites. The mean concentrations (ng/g) of $\sum_{27}$PBDEs (polybrominated diphenyl ethers), $\sum_{2}$PBB (polybrominated biphenyls), HBB (hexabromobiphenyl), and ∑HBCDD (hexabromocyclododecane) were 176 (range: 0.76 – 11141), 31.0 (0.65-58.0), 1.39 (0.01 - 42.8), and 12.0 (0.22 – 461), respectively. These levels were substantially higher (six to ten-fold) than those at background sites. Karachi, Faisalabad, Gujranwala, and Lahore exhibited high levels of all BFRs. Notably, BDE-209 (mean = 45.5 ng/g) ranged (0.13 – 1152) ng/g) was the most prevalent congener in soil samples. Seasonally, total ΣBFR concentrations ranked higher in winter (11620 ng/g), followed by spring (3874 ng/g), autumn (3139 ng/g), and summer (1207 ng/g) indicating a seasonal impact of recycling activities. The average daily dose for soil ingestion was estimated for BDE-209 (0.10973 ng/kg/day) in Faisalabad, followed by BDE-47 (0.08616 ng/kg/day) and BDE-99 (0.06788 ng/kg/day) in Karachi.

In both soil and air, the concentrations of the majority of BFRs were consistently found to be high. The spatial patterns observed for these compounds strongly advocate that informal e-waste recycling facilities play an important role as a potential key source of BFR emissions. The spatio-temporal trends observed for PBDEs, HBB, and HBCDD point towards common emission sources for these compounds. These sources are likely associated, at least in part, with informal recycling processes such as the burning of scrap materials, which is a common practice at the e-waste sites under study. The prevalence of BDE-209 in the soils and air surrounding the sites strongly suggests that e-waste originating from FR- products containing technical deca-BDE has been processed in all major cities of Pakistan.

Seasonal variability further accentuated the challenges posed by e-waste pollution, with higher concentrations observed during winter months, possibly due to different emission mechanisms and meteorological conditions. These compounds, widely used in EEE, pose significant threats to ecosystems and human health due to their bioaccumulation potential, persistence, and toxicity. The dynamic nature of BFRs on spatial and temporal scale underscore the complex nature of e-waste contamination in Pakistan. Karachi, Faisalabad, Gujranwala, and Lahore emerged as hotspots of BFR contamination, highlighting the need for targeted interventions in these megacities. Human health exposure assessments revealed potential risks associated with soil ingestion, particularly for workers at informal e-waste recycling sites.

Pakistan is highlighted among the top importer of e-waste with several hundred laborers involved in this business activity. Domestic generation in Pakistan is about 558 kilotons in 2024 and is predictable to grow at 10.2 % yearly (Balde *et al.,* 2024; Sheikh, 2021), the country could be in one of the starring regions of e-waste generation, which needs for regulatory strengths to reduce possibly dangerous impacts on environment and human health. Though there is no potential damage to human health from inhaling or ingesting BFRs through the soil is concluded, however there are still other potential routes of human exposure that need to be focused into more (such as direct skin contact and nutrition

5.5 Recommendations and forthcoming approaches

The current research was directed effectively and described the firsthand information on GEM poisons in air, Heavy metals pollution in air and soil and POPs FRs data in soil from informal e-waste recycling units in nine major urbanized cities of Pakistan. The presented findings depicted concentration to the reality that pollution of target compounds must be judged as an significant environmental problem due to their undue use in the electrical & electronic equipment sector. Present work can be a way forward for very useful future studies to safeguard human health and environmental degradation due to such informal e-waste operations, future recommendations are as follows.

1. For GEM contamination in air further research should focused on the specific e-waste facility that involves total emission. It is also necessary to determine the spatial concentration variability within the informal e-waste processing sites.
2. Regarding heavy metals pollution in the country, it is suggested to be more detailed sampling, especially reference sites in every studied city would help in forming a clearer spatial trend.
3. Transect studies for air and soil would also help to delineate the extent to which these hot spots of HMs exert effects on local populations and the environment.
4. In addition, exploring bioavailability of HMs in air (particulate matter) and soil may also be an additional source to determine the potential harmful risks caused by synergistic effects by presence of HMs in several environmental matrices. For instance, oxidative potential of airborne particulate matter has been shown to be driven by high levels of certain HMs such as Fe and Cu, among others.

5. HMs associated with particulate matter, when inhaled, lead to the formation of reactive oxygen species, which negatively impact health through damage of cardiovascular and respiratory tissues (Cohen *et al.,* 2015; Shahpoury *et al.,* 2021).
6. Regarding FRs in soil, additional research is warranted to explore other exposure pathways and toxins associated with e-waste recycling activities. PCBs, dioxins, PAHs, and various other toxic compounds represent potential contaminants that merit further investigation to comprehensively assess the risks posed by informal e-waste recycling in Pakistan.
7. E-waste policies, laws and regulations should be introduced, implemented, and monitored.
8. Research and assessment of improved management procedures can be aided by recording and updating data on the overall amount of e-waste imported and exported.
9. The e-waste management industry's unorganized sector has to be improved and elevated with the aid of capacity building programs.
10. With the use of social, economic, and life cycle evaluations, a comparative study of various waste management strategies should be conducted before developing the E-waste management system.
11. All government agencies, including revenue, customs, and regulatory offices, should encourage formal e-waste recycling through incentives including credit ratings, compensation, and subsidies.
12. Future studies should also target exposures from a broader range of well-known toxins either formed or released because of informal e-waste activities, such as PCBs, dioxins, PAHs, and various metals (e.g., mercury, lead, and cadmium).

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List of Appendices

Appendix-1

Table: Meteorological parameters (Average temperature and wind speed)

	Autumn		Winter		Spring		Summer	
Sampling Cities	Avg. Temp (^{0}C)	Avg Wind Speed (m/s)	Avg. Temp (^{0}C)	Avg Wind Speed (m/s)	Avg. Temp (^{0}C)	Avg Wind Speed (m/s)	Avg. Temp (^{0}C)	Avg. Wind Speed (m/s)
	18	3.0	17	3.4	29	3.7	32	4.2
Faisalabad	19	4.6	17	5.0	30	6.2	32	5.3
Rawalpindi	18	5.8	16	5.4	27	9.1	29	9.8
Lahore	20	5.5	18	5.9	30	6.2	31	6.8
Karachi	24	4.5	23	4.2	32	8.3	31	9.0
Gujranwala	17	2.1	16	1.6	28	3.0	30	2.6
Multan	20	1.4	19	1.8	32	3.4	33	2.5
Quetta	10	2.3	10	6.1	24	2.9	28	11.6
Hyderabad	24	7.2	23	6.0	33	11.7	32	12.0

Appendix-2

Table: Details on sampling periods, meteorological conditions, and site-specific sampling rates for sapling GEM in study area

			Deplyment	Harvest	Total Days	Avrg. T (^{0}C)	Avrg Wind Speed (m/s)	R (m^3/day)	Deplyment	Harvest	Total Days	Avrg. T (^{0}C)	Avrg Wind Speed (m/s)	R (m^3/day)
City	**Site name**	**Site Code**	**Autumn**						**Winter**					
Peshawar	Gula Ji	J1	16/09/2020	24/12/2020	99	18	3.0	0.141	24/12/2020	24/03/2021	90	17	3.4	0.142
Peshawar	P. Saddar	J2	16/09/2020	24/12/2020	99	18	3.0	0.141	24/12/2020	24/03/2021	90	17	3.4	0.142
Peshawar	Ring Road	J3	16/09/2020	24/12/2020	99	18	3.0	0.141	24/12/2020	24/03/2021	90	17	3.4	0.142
Peshawar	Karkhany	J4	22/09/2020	01/01/2021	101	18	3.0	0.141	01/01/2021	27/03/2021	85	17	3.4	0.142
Faisalabad	Rax City	J5	22/09/2020	01/01/2021	101	19	4.6	0.147	01/01/2021	02/04/2021	91	17	5.0	0.146
Faisalabad	Sargodha road	J6	22/09/2020	01/01/2021	101	19	4.6	0.147	01/01/2021	27/03/2021	85	17	5.0	0.146
Faisalabad	Motor market	J7	22/09/2020	01/01/2021	101	19	4.6	0.147	01/01/2021	27/03/2021	85	17	5.0	0.146
Rawalpindi	COMSATS University	Background	25/09/2020	31/12/2020	97	18	5.8	0.149	31/12/2020	03/04/2021	93	16	5.4	0.146
Rawalpindi	Dubai Plaza	J8	25/09/2020	30/12/2020	96	18	5.8	0.149	31/12/2020	03/04/2021	93	16	5.4	0.146
Rawalpindi	Collage Road	J9	25/09/20 20	31/12/2020	97	18	5.8	0.149	31/12/2020	03/04/2021	93	16	5.4	0.146
Rawalpindi	Pindi Sadder	J10	25/09/2020	31/12/2020	97	18	5.8	0.149	31/12/2020	03/04/2021	93	16	5.4	0.146
Lahore	Hall Road	J11	24/09/2020	30/12/2020	97	20	5.5	0.150	30/12/2020	03/04/2021	94	18	5.9	0.149
Lahore	Misri Shah	J12	24/09/2020	30/12/2020	97	20	5.5	0.150	30/12/2020	03/04/2021	94	18	5.9	0.149
Lahore	Abid Market	J13	24/09/2020	30/12/2020	97	20	5.5	0.150	30/12/2020	03/04/2021	94	18	5.9	0.149
Karachi	Sher Shah	J14	23/09/2020	29/12/2020	97	24	4.5	0.151	29/12/2020	04/04/2021	96	23	4.2	0.149
Karachi	Bhens Colony	J15	23/09/2020	29/12/2020	97	24	4.5	0.151	29/12/2020	04/04/2021	96	23	4.2	0.149
Karachi	Layari	J16	23/09/2020	29/12/2020	97	24	4.5	0.151	29/12/2020	04/04/2021	96	23	4.2	0.149
Karachi	Gulshe e Hadeed	J17	25/09/2020	31/12/2020	97	24	4.5	0.151	31/12/2020	03/04/2021	93	23	4.2	0.149
Karachi	Orangi Town	J18	25/09/2020	31/12/2020	97	24	4.5	0.151	31/12/2020	03/04/2021	93	23	4.2	0.149
Gujranwala	Kamoki	J19	25/09/2020	31/12/2020	97	17	2.1	0.138	31/12/2020	03/04/2021	93	16	1.6	0.136
Gujranwala	Industrial Estate	J20	18/10/2020	17/01/2021	91	17	2.1	0.138	17/01/2021	17/04/2021	90	16	1.6	0.136
Gujranwala	Parao road	J21	22/10/2020	22/01/2021	92	17	2.1	0.138	22/01/2021	22/04/2021	90	16	1.6	0.136
Multan	Aziz hotel	J22	19/10/2020	19/01/2021	92	20	1.4	0.139	19/01/2021	19/04/2021	90	19	1.8	0.138
Multan	Rasheed abad	J23	19/10/2020	19/01/2021	92	20	1.4	0.139	19/01/2021	19/04/2021	90	19	1.8	0.138
Multan	Khan Plaza	J24	18/10/2020	18/01/2021	92	20	1.4	0.139	18/01/2021	18/04/2021	90	19	1.8	0.138
Quetta	Western bypass	J25	28/10/2020	28/01/2021	92	10	2.3	0.132	28/01/2021	28/04/2021	90	10	6.1	0.143
Quetta	Suraj gang	J26	24/10/2020	25/01/2021	93	10	2.3	0.132	25/01/2021	27/04/2021	92	10	6.1	0.143

Quetta	Wapda Colony	J27	24/10/2020	24/01/2021	92	10	2.3	0.132	24/01/2021	27/04/2021	93	10	6.1	0.143
Quetta	Madrsa Road	J28	31/10/2020	29/01/2021	90	10	2.3	0.132	29/01/2021	28/04/2021	89	10	6.1	0.143
Quetta	Sabzal Road	J29	31/10/2020	28/01/2021	89	10	2.3	0.132	28/01/2021	28/04/2021	90	10	6.1	0.143
Hyderabad	Sepa office	J30	13/11/2020	13/02/2021	92	24	7.2	0.158	13/02/2021	14/06/2021	121	23	6.0	0.154
Hyderabad	Metha Ram	J31	15/10/2020	15/01/2021	92	24	7.2	0.158	15/01/2021	12/04/2021	87	23	6.0	0.154
Hyderabad	Naseem market	J32	10/11/2020	11/01/2021	62	24	7.2	0.158	11/01/2021	12/04/2021	91	23	6.0	0.154
City	**Site name**	**Site Code**	**Spring**						**Summer**					
Peshawar	Gula Ji	J1	24/03/2021	03/07/2021	101	29	3.7	0.153	03/07/2021	03/10/2021	92	32	3.7	0.156
Peshawar	P. Saddar	J2	24/03/2021	03/07/2021	101	29	3.7	0.153	03/07/2021	03/10/2021	92	32	3.7	0.156
Peshawar	Ring Road	J3	24/03/2021	03/07/2021	101	29	3.7	0.153	03/07/2021	03/10/2021	92	32	3.7	0.156
Peshawar	Karkhany	J4	27/03/2021	04/07/2021	99	29	3.7	0.153	04/07/2021	03/10/2021	91	32	3.7	0.156
Faisalabad	Rax City	J5	27/03/2021	04/07/2021	99	30	6.2	0.161	04/07/2021	03/10/2021	91	32	5.3	0.161
Faisalabad	Sargodha road	J6	27/03/2021	04/07/2021	99	30	6.2	0.161	04/07/2021	03/10/2021	91	32	5.3	0.161
Faisalabad	Motor market	J7	27/03/2021	04/07/2021	99	30	6.2	0.161	04/07/2021	03/10/2021	91	32	5.3	0.161
Rawalpindi	COMSATS University	Background	10/04/2021	21/08/2021	133	27	9.1	0.167	21/08/2021	19/12/2021	120	29	9.8	0.170
Rawalpindi	Dubai Plaza	J8	10/04/2021	21/08/2021	133	27	9.1	0.167	21/08/2021	19/12/2021	120	29	9.8	0.170
Rawalpindi	Collage Road	J9	10/04/2021	21/08/2021	133	27	9.1	0.167	21/08/2021	19/12/2021	120	29	9.8	0.170
Rawalpindi	Pindi Sadder	J10	10/04/2021	21/08/2021	133	27	9.1	0.167	21/08/2021	19/12/2021	120	29	9.8	0.170
Lahore	Hall Road	J11	09/04/2021	22/08/2021	135	30	6.2	0.162	22/08/2021	01/12/2021	101	31	6.8	0.164
Lahore	Misri Shah	J12	09/04/2021	22/08/2021	135	30	6.2	0.162	22/08/2021	01/12/2021	101	31	6.8	0.164
Lahore	Abid Market	J13	09/04/2021	22/08/2021	135	30	6.2	0.162	22/08/2021	01/12/2021	101	31	6.8	0.164
Karachi	Bhens Colony	J15	04/04/2021	07/07/2021	94	32	8.3	0.169	07/07/2021	10/10/2021	95	31	9.0	0.170
Karachi	Layari	J16	04/04/2021	07/07/2021	94	32	8.3	0.169	07/07/2021	10/10/2021	95	31	9.0	0.170
Karachi	Gulshe e Hadeed	J17	03/04/2021	08/07/2021	96	32	8.3	0.169	08/07/2021	09/10/2021	93	31	9.0	0.170
Karachi	Orangi Town	J18	04/03/2021	08/07/2021	126	32	8.3	0.169	08/07/2021	09/10/2021	93	31	9.0	0.170
Gujranwala	Kamoki	J19	04/03/2021	08/07/2021	126	28	3.0	0.151	08/07/2021	09/10/2021	93	30	2.6	0.151
Karachi	Bhens Colony	J15	04/04/2021	07/07/2021	94	32	8.3	0.169	07/07/2021	10/10/2021	95	31	9.0	0.170
Gujranwala	Industrial Estate	J20	05/05/2021	05/09/2021	123	28	3.0	0.151	08/07/2021	09/10/2021	93	30	2.6	0.151
Gujranwala	Parao road	J21	05/05/2021	13/09/2021	131	28	3.0	0.151	08/07/2021	09/10/2021	93	30	2.6	0.151

Multan	Aziz hotel	J22	05/05/2021	04/09/2021	122	32	3.4	0.155	05/09/2021	05/12/2021	91	33	2.5	0.154
Multan	Rasheed abad	J23	05/05/2021	07/09/2021	125	32	3.4	0.155	05/09/2021	05/12/2021	91	33	2.5	0.154
Multan	Khan Plaza	J24	05/05/2021	06/09/2021	124	32	3.4	0.155	05/09/2021	05/12/2021	91	33	2.5	0.154
Quetta	Western bypass	J25	Sampler was vandalised						29/08/2021	08/12/2021	101	28	11.6	0.175
Quetta	Suraj gang	J26	27/04/2021	28/08/2021	123	24	2.9	0.147	28/08/2021	05/12/2021	99	28	11.6	0.175
Quetta	Wapda Colony	J27	27/04/2021	27/08/2021	101	29	3.7	0.153	27/08/2021	08/12/2021	103	28	11.6	0.175
Quetta	Madrsa Road	J28	28/04/2021	30/08/2021	101	29	3.7	0.153	30/08/2021	07/12/2021	99	28	11.6	0.175
Quetta	Sabzal Road	J29	28/04/2021	29/08/2021	101	29	3.7	0.153	29/08/2021	08/12/2021	101	28	11.6	0.175
Hyderabad	Sepa office	J30	15/05/2021	25/08/2021	99	29	3.7	0.153	25/08/2021	25/11/2021	92	32	12.0	0.179
Hyderabad	Metha Ram	J31	22/04/2021	26/08/2021	99	30	6.2	0.161	26/08/2021	26/11/2021	92	32	12.0	0.179
Hyderabad	Naseem market	J32	22/04/2021	16/09/2021	99	30	6.2	0.161	16/09/2021	16/12/2021	91	32	12.0	0.179

Appendix-3

Table: Seasonal deployment duration of PAS-DDs at each sampling location

	Autumn		Winter		Spring		Summer	
Site Code	**Deployment Date**	**Harvesting Date**	**Deployment Date**	**Harvesting Date**	**Deployment Date**	**Harvesting Date**	**Deployment Date**	**Harvesting Date**
J1	16/09/2020	24/12/2020	24/12/2020	24/03/2021	24/03/2021	3/7/2021	3/7/2021	3/10/2021
J2	16/09/2020	24/12/2020	24/12/2020	24/03/2021	24/03/2021	3/7/2021	3/7/2021	3/10/2021
J3	16/09/2020	24/12/2020	24/12/2020	24/03/2021	24/03/2021	3/7/2021	3/7/2021	3/10/2021
J4	16/09/2020	24/12/2020	24/12/2020	24/03/2021	24/03/2021	3/7/2021	3/7/2021	3/10/2021
J5	22/09/2020	1/1/2021	1/1/2021	27/03/2021	27/03/2021	3/7/2021	3/7/2021	3/10/2021
J6	22/09/2020	1/1/2021	1/1/2021	2/4/2021	2/4/2021	4/7/2021	4/7/2021	3/10/2021
J7	22/09/2020	1/1/2021	1/1/2021	2/4/2021	2/4/2021	4/7/2021	4/7/2021	3/10/2021
J8	22/09/2020	1/1/2021	1/1/2021	27/03/2021	27/03/2021	4/7/2021	4/7/2021	3/10/2021
J9	22/09/2020	1/1/2021	1/1/2021	27/03/2021	27/03/2021	4/7/2021	4/7/2021	3/10/2021
BG	25/09/2020	30/12/2020	30/12/2020	3/4/2021	10/04/2021	21/08/2021	21/08/2021	19/12/2021
J10	25/09/2020	30/12/2020	30/12/2020	3/4/2021	10/04/2021	21/08/2021	21/08/2021	19/12/2021
J11	25/09/2020	31/12/2020	31/12/2020	3/4/2021	10/04/2021	21/08/2021	21/08/2021	19/12/2021
J12	25/09/2020	31/12/2020	31/12/2020	3/4/2021	10/04/2021	21/08/2021	21/08/2021	19/12/2021
J13	24/09/2020	30/12/2020	30/12/2020	3/4/2021	9/04/2021	22/08/2021	22/08/2021	1/12/2021
J14	24/09/2020	30/12/2020	30/12/2020	3/4/2021	9/04/2021	22/08/2021	22/08/2021	1/12/2021
J15	24/09/2020	30/12/2020	30/12/2020	3/4/2021	9/04/2021	22/08/2021	22/08/2021	1/12/2021
J16	24/09/2020	30/12/2020	30/12/2020	3/4/2021	9/04/2021	22/08/2021	22/08/2021	1/12/2021
J17	23/09/2020	29/12/2020	29/12/2020	4/4/2021	4/4/2021	7/7/2021	7/7/2021	10/10/2021
J18	23/09/2020	29/12/2020	29/12/2020	4/4/2021	4/4/2021	7/7/2021	7/7/2021	10/10/2021

J19	23/09/2020	29/12/2020	29/12/2020	4/4/2021	4/4/2021	7/7/2021	7/7/2021	10/10/2021
J20	23/09/2020	29/12/2020	29/12/2020	4/4/2021	4/4/2021	7/7/2021	7/7/2021	10/10/2021
J21	25/09/2020	31/12/2020	31/12/2020	3/4/2021	4/3/2021	8/7/2021	8/7/2021	9/10/2021
J22	25/09/2020	31/12/2020	31/12/2020	3/4/2021	3/4/2021	8/7/2021	8/7/2021	9/10/2021
J23	25/09/2020	31/12/2020	31/12/2020	3/4/2021	3/4/2021	8/7/2021	8/7/2021	9/10/2021
J24	25/09/2020	31/12/2020	31/12/2020	3/4/2021	3/4/2021	8/7/2021	8/7/2021	9/10/2021
J25	18/10/2020	17/1/2021	17/1/2021	17/4/2021	5/5/2021	5/9/2021	7/8/2021	9/10/2021
J26	22/10/2020	22/01/2021	22/01/2021	22/4/2021	5/5/2021	13/9/2021	7/8/2021	9/10/2021
J27	10/19/2020	19/1/2021	19/1/2021	19/4/2021	5/5/2021	4/9/2021	5/9/2021	5/12/2021
J28	10/19/2020	19/1/2021	19/1/2021	19/4/2021	5/5/2021	4/9/2021	5/9/2021	5/12/2021
J29	10/19/2020	19/1/2021	19/1/2021	19/4/2021	5/5/2021	7/9/2021	5/9/2021	5/12/2021
J30	18/10/2020	18/1/2021	18/1/2021	18/4/2021	5/5/2021	6/9/2021	28/8/2021	5/12/2021
J31	28/10/2020	28/1/2021	28/1/2021	28/4/2021	27/4/2021	28/8/2021	28/8/2021	5/12/2021
J32	28/10/2020	28/1/2021	28/1/2021	28/4/2021	27/4/2021	28/8/2021	28/8/2021	8/12/2021
J33	24/10/2020	25/1/2021	25/1/2021	27/4/2021	27/4/2021	28/8/2021	27/8/2021	5/12/2021
J34	24/10/2020	24/1/2021	24/1/2021	27/4/2021	27/4/2021	27/8/2021	30/8/2021	8/12/2021
J35	31/10/2020	29/1/2021	29/1/2021	28/4/2021	28/4/2021	30/8/2021	29/8/2021	7/12/2021
J36	31/10/2020	28/1/2021	28/1/2021	28/4/2021	28/4/2021	29/8/2021	25/8/2021	8/12/2021
J37	31/10/2020	13/2/2021	13/2/2021	14/6/2021	15/5/2021	25/8/2021	25/8/2021	25/11/2021
J38	31/10/2020	13/2/2021	13/2/2021	14/6/2021	15/5/2021	25/8/2021	26/8/2021	25/11/2021
J39	15/10/2020	15/1/2021	15/1/2021	12/4/2021	22/4/2021	26/8/2021	16/9/2021	26/11/2021
J40	10/11/2020	11/1/2021	11/1/2021	12/4/2021	22/4/2021	16/9/2021	28/8/2021	16/12/2021

Appendix-4

Table: Methods to determine soil moisture content, soil organic matter content and soil pH values

Parameter	Details
1. *Soil moisture content*	A 50 g soil sample, sieved through a steel sieve with a 2 mm pore size, was kept at 105ºC in the oven (approximately 16 hours) until it attained a steady weight and was calculated using the formula (Eq. 1). $\text{Moisture content (\%)} = \frac{(A-B)\times 100}{A}$ (1) where A: initial weight, B: dry weight
2. *Soil Organic Matter Content*	Soil samples with determined moisture content were placed in a muffle furnace and burned at 750 ºC (approximately 16 h) until the soil attained a steady weight. $\text{Organic Matter Content (\%)} = \frac{(A-B)\times 100}{A}$ (2) where, A: initial weight of dry soil, B: weight after burning at 750 ºC
3. *Soil pH measurement*	10 g of soil sample, sieved through a steel sieve with 2 mm pore size, was placed in a glass jar and 10 mL of distilled water meeting the ASTM Type III definition (provided by an ultrapure water device operating based on ion exchange and reverse osmosis) was added for 15 minutes. After mixing in a rotary mixer, it was rested for 1 hour then pH measurement was carried out.

Appendix-5

Table: Details on sampling periods, meteorological and physco-chemical conditions of the soil

Site Code	Autumn				Winter				
	Collection date	Moisture Content (%)	OM content (%)	Avg. T (^{0}C)	Collection date	Total Days	Moisture Content (%)	OM content (%)	Avg. T (^{0}C)
BS1	16-09-20	11.80	6.00	18	24-12-20	90	8.50	6.00	17
S1	16-09-20	8.80	11.00	18	24-12-20	90	11.40	8.00	17
S2	16-09-20	7.90	4.00	18	24-12-20	90	8.90	7.00	17
S3	16-09-20	11.20	18.00	18	24-12-20	90	11.30	5.00	17
S4	16-09-20	12.60	7.00	18	24-12-20	90	10.40	9.00	17
BS2	22-09-20	12.30	5.00	18	01-01-21	85	8.20	6.00	17
S5	22-09-20	11.80	6.00	19	01-01-21	91	11.20	4.00	17
S6	22-09-20	9.90	4.00	19	01-01-21	85	9.60	2.00	17
S7	22-09-20	8.80	7.00	19	01-01-21	85	7.90	6.00	17
BS3	25-09-20	9.60	5.00	18	31-12-20	93	8.80	3.00	16
S8	25-09-20	7.90	6.00	18	31-12-20	93	11.20	1.00	16
S9	25-09-20	8.80	3.00	18	31-12-20	93	8.90	8.00	16
S10	25-09-20	12.40	4.00	18	31-12-20	93	9.90	11.00	16
BS4	25-09-20	13.30	15.00	18	31-12-20	93	12.30	12.00	16
S11	25-09-20	12.10	4.00	18	31-12-20	93	8.80	8.00	16
S12	25-09-20	11.30	2.00	18	31-12-20	93	12.40	7.00	16
S13	25-09-20	10.40	5.00	18	31-12-20	93	7.90	5.00	16
BS5	24-09-20	7.90	3.00	20	30-12-20	94	11.50	7.00	18
S14	24-09-20	8.80	6.00	20	30-12-20	94	9.60	5.00	18
S15	24-09-20	12.70	9.00	20	30-12-20	94	11.20	3.00	18
S16	24-09-20	11.40	3.00	20	30-12-20	94	8.20	4.00	18
BS6	23-09-20	8.90	9.00	24	29-12-20	96	11.30	4.00	23
S17	23-09-20	12.10	5.00	24	29-12-20	96	9.60	2.00	23
S18	25-09-20	11.30	4.00	24	31-12-20	93	8.70	5.00	23
S19	25-09-20	10.40	6.00	24	31-12-20	93	8.80	8.00	23
BS7	25-09-20	8.20	3.00	24	31-12-20	93	9.20	9.00	23
S20	25-09-20	9.50	2.00	17	31-12-20	93	11.40	3.00	16
S21	18-10-20	11.80	11.00	17	17-01-21	90	9.30	4.00	16

S22	22-10-20	9.90	4.00	17	22-01-21	90	11.70	6.00	16
S23	22-10-20	8.80	7.00	17	22-01-21	90	8.80	5.00	16
S24	19-10-20	9.60	8.00	20	19-01-21	90	9.20	4.00	19
BS8	18-10-20	7.90	21.00	20	18-01-21	90	8.80	4.00	19
S25	18-10-20	8.80	11.00	20	18-01-21	90	8.30	13.00	19
S26	18-10-20	11.90	7.00	20	18-01-21	90	13.10	8.00	19
S27	28-10-20	12.60	18.00	10	28-01-21	90	9.90	6.00	10
BS9	24-10-20	8.20	5.00	10	25-01-21	92	9.70	2.00	10
S28	24-10-20	9.50	3.00	10	24-01-21	93	8.80	3.00	10
S29	31-10-20	11.80	4.00	10	29-01-21	89	7.90	5.00	10
S30	31-10-20	9.90	5.00	10	28-01-21	90	11.20	4.00	10
S31	31-10-20	8.80	2.00	10	28-01-21	90	10.10	2.00	10
S32	13-11-20	9.60	7.00	24	13-02-21	121	10.20	11.00	23

Site Code	**Spring**					**Summer**				
BS1	24-03-21	101	11.40	6.00	29	03-07-21	92	8.80	7.00	32
S1	24-03-21	101	12.10	11.00	29	03-07-21	92	8.80	8.00	32
S2	24-03-21	101	11.40	14.00	29	03-07-21	92	12.40	6.00	32
S3	24-03-21	101	8.80	13.00	29	03-07-21	92	8.30	5.00	32
S4	24-03-21	101	9.80	4.00	29	03-07-21	92	11.30	6.00	32
BS2	27-03-21	99	8.20	3.00	30	04-07-21	91	11.40	7.00	32
S5	27-03-21	99	11.20	2.00	30	04-07-21	91	7.90	4.00	32
S6	27-03-21	99	9.60	5.00	30	04-07-21	91	12.40	3.00	32
S7	27-03-21	99	7.90	1.00	30	04-07-21	91	8.20	2.00	32
BS3	10-04-21	133	8.80	3.00	27	21-08-21	120	9.50	7.00	29
S8	10-04-21	133	12.10	4.00	27	21-08-21	120	11.20	5.00	29
S9	10-04-21	133	8.80	2.00	27	21-08-21	120	7.90	6.00	29
S10	10-04-21	133	12.40	6.00	27	21-08-21	120	8.80	4.00	29
BS4	09-04-21	135	8.20	3.00	30	22-08-21	101	8.30	3.00	31
S11	09-04-21	135	8.90	4.00	30	22-08-21	101	10.20	6.00	31
S12	09-04-21	135	10.20	6.00	30	22-08-21	101	7.90	7.00	31
S13	09-04-21	135	7.90	3.00	30	22-08-21	101	8.80	5.00	31

BS5	04-04-21	94	9.60	2.00	32	07-07-21	95	11.40	9.00	31
S14	04-04-21	94	8.80	6.00	32	07-07-21	95	8.80	6.00	31
S15	04-04-21	94	11.20	8.00	32	07-07-21	95	12.40	5.00	31
S16	04-04-21	94	12.30	2.00	32	07-07-21	95	8.30	9.00	31
BS6	03-04-21	96	9.30	4.00	32	08-07-21	93	11.30	8.00	31
S17	04-03-21	126	10.20	7.00	32	08-07-21	93	11.40	6.00	31
S18	04-03-21	126	12.10	5.00	32	08-07-21	93	9.30	8.00	31
S19	04-03-21	126	9.50	3.00	28	08-07-21	93	7.90	10.00	31
BS7	05-05-21	123	11.30	8.00	28	08-07-21	93	8.20	3.00	30
S20	05-05-21	131	12.40	6.00	28	08-07-21	93	9.50	4.00	30
S21	05-05-21	131	8.80	9.00	28	08-07-21	93	8.20	6.00	30
S22	05-05-21	122	12.80	7.00	32	08-07-21	93	9.50	5.00	30
S23	05-05-21	125	8.20	5.00	32	08-07-21	93	8.20	4.00	30
S24	05-05-21	124	9.50	4.00	32	08-07-21	93	9.50	2.00	30
BS8	27-04-21	123	8.80	3.00	24	28-08-21	99	11.40	6.00	28
S25										
S26	27-04-21	123	9.50	10.00	24	28-08-21	99	11.20	4.00	28
S27	27-04-21	122	11.40	7.00	24	27-08-21	103	9.30	5.00	28
BS9	28-04-21	124	8.80	2.00	24	30-08-21	99	8.80	3.00	28
S28	28-04-21	123	9.40	3.00	24	29-08-21	101	8.20	7.00	28
S29	28-04-21	123	8.20	3.00	24	29-08-21	101	9.50	6.00	28
S30	15-05-21	102	9.50	8.00	33	25-08-21	92	12.40	8.00	32
S31	22-04-21	126	10.20	7.00	33	26-08-21	92	8.30	2.00	32
S32	22-04-21	147			33	16-09-21	92	11.30	3.00	32

Appendix-6

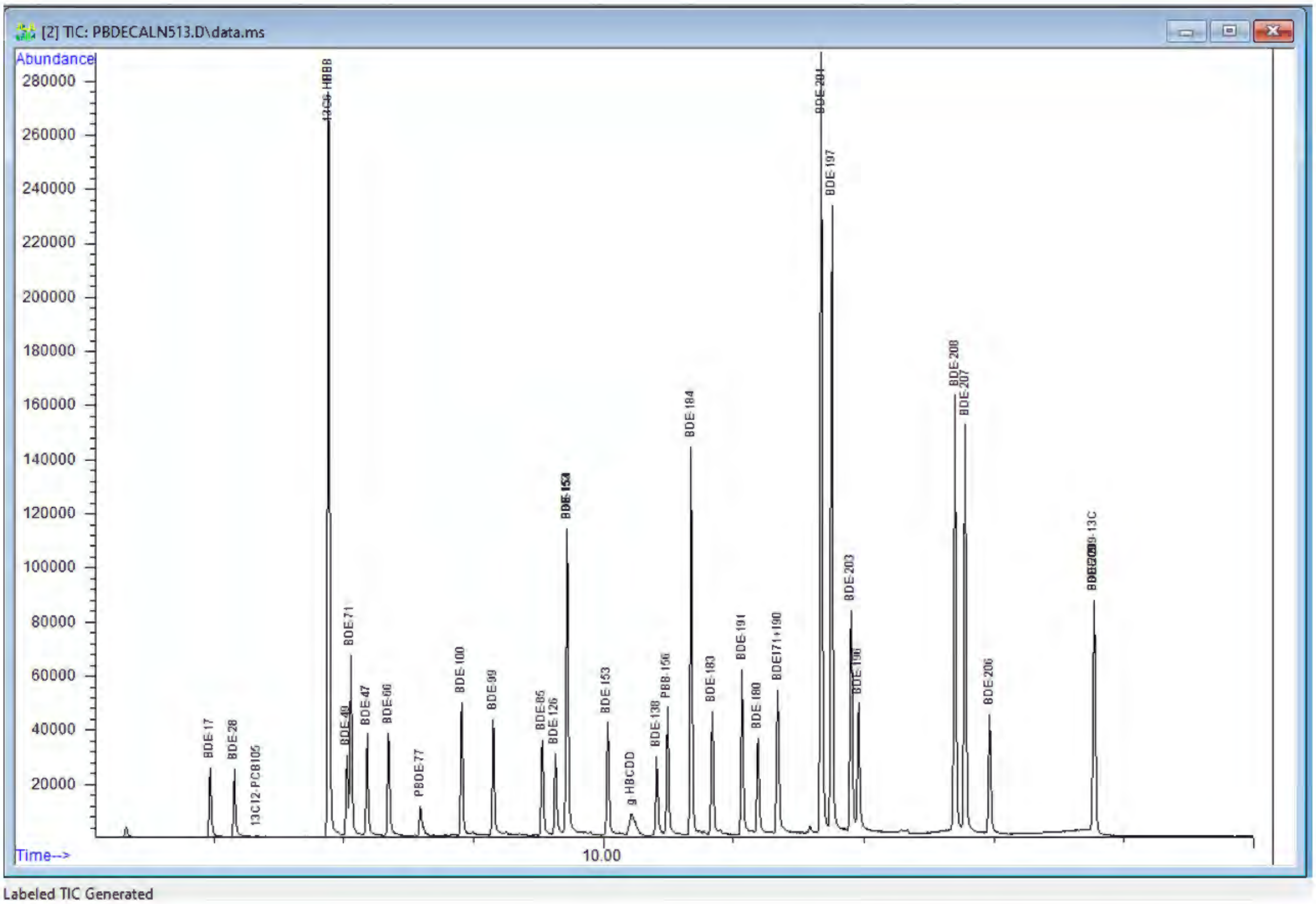

Figure: Sample chromatogram for the analyzed compounds (calibration level 5, analytes at 100 ng/ml, surrogate standards at 20 ng/ml concentrations)

Appendix-7

Table: Retention times, target and qualifier ions for target analytes, surrogate, and internals standards

Compound	Retention Time (min)	Category	Ionization Mode	Target Ion	Qualifier Ion 1	Qualifier Ion 2
PBDE-17	6.964	Target	NCI	79	81	160.8
PBDE-28	7.152	Target	NCI	79	81	160.8
PBDE-49	8.020	Target	NCI	79	81	160.8
PBDE-71	8.051	Target	NCI	79	81	160.8
PBDE-47	7.173	Target	NCI	79	81	160.8
PBDE-66	8.339	Target	NCI	79	81	160.8
PBDE-100	8.904	Target	NCI	79	81	160.8
PBDE-99	9.147	Target	NCI	79	81	160.8
PBDE-85	9.523	Target	NCI	79	81	160.8
PBDE-126	9.624	Target	NCI	79	81	
PBDE-154	9.719	Target	NCI	79	81	160.8
PBDE-153	10.032	Target	NCI	79	81	562.4
PBDE-138	10.410	Target	NCI	79	81	160.8
PBDE-184	10.675	Target	NCI	408.5	406.5	410.5
PBDE-183	10.838	Target	NCI	79	81	160.8
PBDE-191	11.066	Target	NCI	79	81	160.8
PBDE-180	11.186	Target	NCI	79	81	160.8
PBDE-171	11.340	Target	NCI	79	81	160.8
PBDE-190	11.340	Target	NCI	79	81	160.8
PBDE-201	11.678	Target	NCI	408.5	406.5	410.5
PBDE-197	11.757	Target	NCI	408.5	406.5	410.5
PBDE-203	11.900	Target	NCI	79	81	160.8
PBDE-196	11.957	Target	NCI	79	81	408.5
PBDE-208	12.698	Target	NCI	486.4	488.4	408.5
PBDE-207	12.779	Target	NCI	486.4	488.4	408.5
PBDE-206	12.967	Target	NCI	79	81	486.4
PBDE-209	13.771	Target	NCI	486.4	488.4	
HBB (PBB-153)	9.726	Target	NCI	627.4	629.4	
HBB (PBB-156)	10.492	Target	NCI	79	81	625.2
∑HBCDD	10.206	Target	NCI	79	81	159.7
PBDE-77	8.582	Surrogate	NCI	79	81	
$^{13}C_{12}$-PBDE-209	13.777	Surrogate	NCI	496.3	498.3	
$^{13}C_{6}$-HxBBz	7.879	Surrogate	NCI	559.3	561.3	
$^{13}C_{12}$-PCB-105	7.322	Internal	NCI	337.7	335.7	

Appendix-8

Table: RSD (%) values for CRM analysis

	mg/kg					
Contaminant	Certified Value	Result of Replicate Analysis 1	Result of Replicate Analysis 2	Average of Replicate Analysis	Stdev of Replicate Analysis	% RSD
Pb	106	124	118	121	4.08	14.4
Cr	158	166	169	167	2.14	5.95
Zn	222	213	210	211	1.91	4.77
Cd	125	115	114	114	0.66	8.32
Cu	102	117	102	110	11	7.42
Ni	130	130	125	127	3.78	1.96
Mn	287	282	284	283	1.77	1.38
					Overall RSD	6.31
					StDev	4.41

Appendix-9

Table: Nomenclature, MDLs and RfDs of target BFRs

BFRs	Molecule	RfDs	IDL (ng/g dw)	MDL (ng/g dw)
BDE17	2,2',4-Tribromodiphenyl ether	100	0.01	0.01
BDE28	2,4,4'-tribromodiphenyl ether	100	0.04	0.04
BDE49	2,2',4,5'-Tetrabromodiphenyl ether	100	0.01	0.01
BDE71	2,3',4',6-Tetrabromodiphenyl ether	100	0.01	0.01
BDE47	2,2'4,4'-tetrabromodiphenyl ether	100	0.02	0.02
BDE66	2,3'4,4'-tetrabromodiphenyl ether	100	0.01	0.01
BDE100	2,2'4,4',6-pentabromodiphenyl ether	100	0.02	0.02
BDE99	2,2'4,4',5-pentabromodiphenyl ether	100	0.01	0.01
BDE85	2,2',3,4,4'-pentabromodiphenyl ether	100	0.01	0.01
BDE126	3,3',4,4',5-Pentabromodiphenyl ether	100	0.01	0.01
BDE154	2,2',4,4',5,6'-hexabromodiphenyl ether	200	0.01	0.01
BDE153	2,2',4,4',5,5'-hexabromodiphenyl ether	200	0.01	0.01
BDE138	3,4,4′,5′-Hexabromodiphenyl ether	200	0.01	0.01
BDE184	2,2',3,4,4',6,6'-Heptabromodiphenyl ether	200	0.54	0.54
BDE183	2,2',3,4,4',5',6-heptabromodiphenyl ether	200	0.01	0.01
BDE191	2,3,3',4,4',5,6-heptabromodiphenyl ether	200	0.01	0.01
BDE180	2,2′,3,4,4′,5,5′-heptaheptabromodiphenyl ether	200	0.02	0.02
BDE171.190	2,2′,3,3′,4,4′,6-heptabromodiphenyl ether & 2,3,3',4,4',5,6-Heptabromodiphenyl ether	200	0.01	0.01
BDE201	2,2′,3,3′,4,5′,6,6′-Octabromodiphenyl ether)	200	0.01	0.01
BDE197	2,2',3,3',4,4',6,6'-Octabromodiphenyl ether	3000	0.01	0.01
BDE203	2,2’,3,4,4’,5,5’,6-octabromodiphenyl ether	3000	0.01	0.01
BDE196	2,2′,3,3′,4,4′,5,6′-octa- Bromodiphenyl ether	3000	0.01	0.01
BDE208	2,2',3,3',4,5,5',6,6'-nonabromodiphenyl ether	3000	0.01	0.01
BDE207	2,2',3,3',4,4',5,6,6'-nonabromodiphenyl ether	3000	0.01	0.01
BDE206	2,2’,3,3’,4,4’,5,5’,6-nonabromodiphenyl ether	3000	0.01	0.01
BDE209	2,2',3,3',4,4',5,5',6,6'-Decabromodiphenyl ether	7000	0.01	0.01
PBB153	2,2',4,4',5,5'-Hexabromobiphenyl	200	0.01	0.01
PBB156	2,3,3',4,4',5-Hexabromobiphenyl	200	0.01	0.01
HxBBz	Hexabromobenzene	2000	0.01	0.01
HBCDDs	Hexachlorocyclopentadienyl - dibromocyclooctane	200	0.03	0.03

Appendix-10

Table: Summary of basic descriptive statistics of BFRs concentration levels

Sample	BFRs	Statistics	Peshawar	Faisalabad	Rawalpindi	Lahore	Karachi	Gujranwala	Multan	Quetta	Hyderabad
Particulate phase Flux (ng/m^2.day)	**∑9PBDEs**	**Mean**	2.24	6.01	2.41	4.78	24.9	15.8	2.53	2.82	2.20
		Median	1.45	2.34	1.49	2.66	3.82	3.57	1.80	1.83	1.37
		Range	0.35-18.8	0.27-73.4	0.25-24.6	0.30-69.2	0.44-721	0.49-501	0.41-13.3	0.41-18.7	0.23-12.9
	∑Non-PBDEs	**Mean**	3.24	7.67	3.71	3.46	14.2	12.3	3.01	4.77	4.70
		Median	4.09	2.47	0.42	1.14	6.55	1.47	0.76	0.64	2.37
		Range	0.54-6.48	0.39-32.0	0.24-9.00	0.22-10.4	0.33-69.0	0.50-106	0.28-12.6	0.40-12.8	0.44-11.6
Gaseous phase (pg/m^3)	**∑9PBDEs**	**Mean**	2.47	11.74	3.81	10.2	26.4	5.31	2.21	5.37	2.58
		Median	1.59	4.03	2.02	3.67	3.55	2.79	1.70	2.79	1.55
		Range	0.30-49.4	0.35-261	0.34-61	0.26-516	0.32-864	0.30-29.7	0.35-8.22	0.44-63.7	0.23-15.1
	∑Non-PBDEs	**Mean**	4.35	13.2	4.13	7.23	23.6	5.53	2.44	9.20	7.33
		Median	2.64	2.83	1.17	2.27	8.65	2.47	1.41	2.03	8.43
		Range	0.47-13.5	0.68-68.9	0.58-11.2	0.77-23.6	0.34-248	0.64-30.6	0.62-7.07	0.62-33.6	0.55-13.0

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Research Paper

Gaseous elemental mercury emissions from informal E-Waste recycling facilities in Pakistan

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ABSTRACT

Detrimental effects of mercury (Hg) on ecosystems and human health have been well-documented. Whereas emissions of gaseous elemental mercury (GEM) from e-waste recycling have been reported in developed countries, much less is known about the situation in the Global South. Using a total of 132 passive air samplers, seasonally resolved concentrations of GEM in air were measured continuously at 32 informal e-waste recycling facilities and background location in Pakistan for a period of one year between September 2020 and December 2021. Annual average GEM concentrations at the studied locations ranged from 1.8 to 92 ng m^{-3}. Among the studied cities, higher concentrations were measured in Karachi (mean ± s.d: 17 ± 22, range: 4.2–92 ng m^{-3}), Lahore (16 ± 4.2, 8.2–22 ng m^{-3}) and Peshawar (15 ± 17, 4.9–80 ng m^{-3}), while lower levels were measured in Hyderabad (6.9 ± 6.2, 3.1–25 ng m^{-3}), consistent with a higher rate of informal recycling activities in metropolitan areas. Seasonally, higher GEM levels occurred during autumn (15 ± 16: 3.3–92 ng m^{-3}) and summer (13 ± 8.7: 1.8–80 ng m^{-3}) than in winter (12 ± 8.4: 2.5–49 ng m^{-3}) and spring (9.2 ± 7.3: 1.8–80 ng m^{-3}), possibly reflecting enhanced volatilization at higher temperatures and/or varying magnitude of recycling operations in different seasons. Policies and strict regulations related to e-waste management should be developed and implemented urgently in the country.

1. Introduction

With technological advancements and replacement of old electrical and electronic equipment (Forti et al., 2020), there is an increasing number of recycling operations designed to collect precious metals and enable secondary use of valuable resources. Globally, there is widespread export of e-wastes from some developed countries to developing countries, where informal and unregulated handling of e-waste can result in high worker exposure to mercury (Hg) and other hazardous substances (Wilson et al., 2018; Gravel et al., 2020).

Although Hg emissions to the environment have been reduced in some parts of the world, i.e., Europe and North America, it has risen in others, including Africa and Asia (Streets et al., 2019). Worldwide anthropogenic emissions of Hg to the atmosphere have been estimated

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Informal E -waste recycling in nine cities of Pakistan reveals significant impacts on local air and soil quality and associated health risks[☆]

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ABSTRACT

The global increase in electronic waste (e-waste) has led to a rise in informal recycling, emitting hazardous heavy metals (HMs) that threaten human health and ecosystems. This study presents the first comprehensive assessment of HM levels in dry deposition and soils at proximity of forty (40) informal e-waste recycling sites across Pakistan, between September 2020 to December 2021. Findings reveal that Zn (1410), Pb (410) and Mn (231) exhibited the higher mean deposition fluxes (μg/m^2.day), derived from air samples, particularly in Karachi. Similarly, soils showed higher mean concentrations (μg/g dw) of Mn (477), Cu (514) and Pb (172) in Faisalabad, Lahore, and Karachi, respectively. HMs concentrations were found higher in winter or autumn and lower in summer. In addition, HM levels were significantly ($p < 0.05$) higher at recycling sites compared to background sites year-round, highlighting the e-waste recycling operations as the major source of their emissions. The I_{geo} index indicated moderate to extremely contaminated levels of Cu, Pb, Cd, and Ni in Karachi, Lahore and Gujranwala. Ingestion was found as a leading human exposure route, followed by dermal and inhalation exposure, with Pb posing the greatest health risk. The Cumulative Incremental Lifetime Cancer Risk (ILCR) model suggested moderate to low cancer risks for workers. Strategic interventions recommend mitigating health and environmental risks, prioritizing human health and ecosystem integrity in Pakistan's e-waste management.

1. Introduction

Due to rapid technological advancements electronic and electrical equipment (EEE) production and use has experienced exponential growth in the last two decades which in turn has led to a rise in electronic and electrical waste (e-waste) (Kumar et al., 2017; Murthy and

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