



AN ABSTRACT OF THE THESIS OF

Leah R. Gonzales for the degree of Master of Science in Chemistry presented on May 31, 2011.

Title: Trace Analysis of Halogenated Polycyclic Aromatic Hydrocarbons from an Electronic Waste Recycling Area and Guangzhou, China.

Abstract approved:

---

Staci L. Simonich

Halogenated Polycyclic Aromatic Hydrocarbons (X-PAHs) are ubiquitous contaminants that are thought to be generated by processes such as chemical industries and incomplete combustion, including waste incineration and electronic waste (e-waste) burning. X-PAHs are a concern for environmental and human health because they are toxic, mutagenic, and are expected to be more lipophilic than the parent compounds. To study these compounds in the environment, an analytical method was developed, utilizing large-volume injection via a programmable

temperature vaporizing (PTV) inlet, using environmental samples from an e-waste area and in Guangzhou, China. The concentrations of 26 X-PAHs were measured in atmospheric particulate matter (PM), house dust (HD), and sediment. In general, the X-PAH concentrations in PM were low, with concentrations ranging from <0.078 to 41.81 pg/m<sup>3</sup>. There was no significant difference in X-PAH concentrations in PM between the e-waste area and Guangzhou. These concentrations are of the same order of magnitude as previous studies of X-PAHs in PM. These data suggest that e-waste activities are not a significant source of X-PAHs in atmospheric PM. The concentrations of X-PAHs in HD samples ranged from <0.0372 to 3575 pg/g dry weight. In general, there was no significant difference between E-waste and Guangzhou HD concentrations. The profiles of X-PAHs in PM and HD were different, suggesting that there are additional sources for X-PAHs inside homes other than outdoor air. The concentrations of X-PAHs in sediment samples from an e-waste site ranged from <104 to 2890 pg/g dry weight. The X-PAH profile in sediment more closely resembled the X-PAH profile of PM.

©Copyright by Leah R. Gonzales

May 31, 2011

All Rights Reserved

Trace Analysis of Halogenated Polycyclic Aromatic Hydrocarbons from an Electronic  
Waste Recycling Area and Guangzhou, China

by

Leah R. Gonzales

A THESIS

submitted to

Oregon State University

in partial fulfillment of

the requirements for the

degree of

Master of Science

Presented May 31, 2011

Commencement June 2011

Master of Science thesis of Leah R. Gonzales presented on May 31, 2011.

APPROVED:

---

Major Professor, representing Chemistry

---

Chair of the Department of Chemistry

---

Dean of the Graduate School

I understand that my thesis will become part of the permanent collection of Oregon State University libraries. My signature below authorizes release of my thesis to any reader upon request.

---

Leah R. Gonzales, Author

## ACKNOWLEDGEMENTS

I would like to thank Dr. Staci Simonich for her continued support and guidance over the course of this project, and my graduate committee: Dr. William Baird, Dr. Jennifer Field, and Dr. Vincent Remcho. I would also like to thank Dr. Shejun Chen and his lab at the Guangzhou Institute of Geochemistry in China for organizing sample collection, and for help with sample preparation. I am very thankful to Dr. Takeshi Ohura at the University of Shizuoka in Japan for generously supplying the halogenated PAH standards. I would like to thank my labmates: Julie Denham, Narumol "On" Jariyasopit, Yuling Jia, Carlos Manzano, and Oleksii Motorykin for their support and friendship. A special thanks to Jill Schrlau for her friendly advice and Jing Wang for his help with sample preparation and analysis. I am deeply grateful to my husband, Jozef Gonzales for his unending support, love, and assuaging words. Finally, I would like to thank the Superfund Research Program (SRP) for funding this research.

## CONTRIBUTION OF AUTHORS

Dr. Staci Simonich provided experimental design and edits (for all chapters). Dr. Shejun Chen organized field collection of samples.



## TABLE OF CONTENTS

	<u>Page</u>
Chapter 1: Introduction.....	1
Sources of X-PAHs.....	1
Physical Chemical Properties.....	4
Analytical Methods .....	6
X-PAHs and the Environment .....	7
X-PAHs and Human Health .....	13
Research Objectives .....	16
References .....	31
Chapter 2: Trace Analysis of Halogenated Polycyclic Aromatic Hydrocarbons in Particulate Matter From an E-waste Site and an Urban Area in China .....	34
Abstract .....	35
Introduction.....	36
Materials and Methods .....	38
Results and Discussion.....	42
Conclusions.....	48
References .....	70
Chapter 3: Conclusions .....	74

## LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
1.1. Structures of Studied Cl-PAHs .....	18
1.2. Structures of Studied Br-PAHs .....	19
2.1. Map of Sampling Locations.....	49
2.2. Structures of Cl-PAHs studied.....	50
2.3. Structures of Br-PAHs studied.....	51
2.4. Chromatogram of one $\mu$ L splitless injection of X-PAH standard in EI mode.....	52
2.5. Chromatogram of one $\mu$ L splitless injection of X-PAH standard in NCI mode....	53
2.6. Structures of Cl-PAHs not ionized in NCI ionization .....	54
2.7. Chromatogram of X-PAH standard using 1 $\mu$ L splitless injection (and NCI ionization) .....	55
2.8. Chromatogram of X-PAH standard using 3 $\mu$ L solvent vent injection using a PTV inlet (and NCI ionization).....	56
2.9. Chromatogram of four different PTV injection volumes for m/z=286 for 6-ClBaP (using NCI ionization) .....	57
2.10. X-PAH Profile in Particulate Matter and House Dust from Guangzhou and an E-waste area .....	58
2.11. Relationship between X-PAH Concentrations in Particulate Matter from an E-waste Area and Guangzhou, China .....	59
2.12. Relationship between X-PAH Concentrations in House Dust from an E-waste Area and Guangzhou, China .....	60
2.13. X-PAH Profile for Particulate Matter, House Dust, and Sediment from an E-waste Area .....	61
2.14. Relationship between X-PAH Concentrations in Dust and Particulate Matter from an E-waste Area.....	62

LIST OF FIGURES, CONTINUED

2.15. Relationship between X-PAH Concentrations in House Dust and Particulate  
Matter from Guangzhou, China ..... 63

## LIST OF TABLES

<u>Table</u>	<u>Page</u>
1.1. EPI-Suite Estimated Constants and Properties of Studied X-PAHs and Corresponding Parent PAH.....	20
1.2. Concentrations of Cl-PAHs in Environmental Samples.....	22
1.3. Concentrations of Br-PAHs in Environmental Samples.....	26
1.4. Direct Photolysis Data of X-PAHs .....	27
1.5. Gas/Particle Partitioning of Cl-PAHs.....	28
1.6. AhR-Mediated Activities of X-PAHs.....	29
1.7. TEQs of X-PAHs.....	30
2.1. X-PAHs Listed in Elution Order with Abbreviations, NCI Ions Monitored, Method Recoveries, and Estimated Detection Limits .....	64
2.2. Signal to Noise Ratios for Different Injection Volumes of a Beijing Atmospheric Particulate Matter Sample.....	65
2.3. X-PAH Concentrations in Particulate Matter from Guangzhou, China and an E-waste Area.....	66
2.4. Comparison of Literature X-PAH Particulate Matter Concentrations with This Study .....	67
2.5. X-PAH Concentrations in House Dust from Guangzhou, China and an E-waste Area .....	68
2.6. X-PAH Concentrations in Lake Sediment from an E-waste Area.....	69

To, for, and with, Jozef

## CHAPTER 1: Introduction

PAHs are ubiquitous environmental contaminants, composed of two or more fused aromatic rings. In addition to parent PAH structures, multi-substituted PAHs are also produced, including halogenated polycyclic aromatic hydrocarbons (X-PAHs). X-PAHs are composed of a parent PAH structure with at least one halogen (chlorine or bromine) substituent. The structures of the chlorinated polycyclic aromatic hydrocarbons (Cl-PAHs) studied in the course of this research are shown in Figure 1.1, and the structures of the brominated polycyclic aromatic hydrocarbons (Br-PAHs) are shown in Figure 1.2.

### **Sources of X-PAHs**

X-PAHs are produced primarily from incomplete combustion, and are produced from a variety of sources. While some PAH sources also produce X-PAHs, some sources are unique to X-PAHs. Temporal trend data for PAHs and X-PAHs do not show a correlation, implying that X-PAHs are produced by additional sources [1]. In addition, there is no correlation between the type of waste materials incinerated (municipal, industrial or hazardous operations) and the X-PAH concentrations measured in the ash samples [2]. Therefore, it is believed that X-PAHs are not released from the waste components, but are formed during their incineration [2].

X-PAH sources include chemical industries [3], waste incinerators (especially older, fixed grate-type incinerators) [2, 4, 5], leaded gasoline automobile exhaust [6], water chlorination facilities [7], and Kraft Mills [8, 9]. Previous studies suggest that the incineration of electronic waste (e-waste) during the e-waste recycling process (e-cycling) is also a sources of X-PAHs [3]. E-cycling emissions are of concern due to the magnitude of the waste involved and the conditions under which the workers labor.

E-waste consists of electronic equipment that is no longer wanted or useable, such as computers, televisions, cell phones, toys, and household appliances [10]. E-waste is a mixture of hundreds of compounds, many of them toxic. Some of these compounds are metals such as mercury, lead, cadmium, and chromium [11]. Other toxic components include polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) and PAHs [3, 12-14]. In addition, e-waste also includes flame retardants such as polybrominated biphenyls (PBBs) and polybrominated diphenyl ethers (PBDEs) [11].

E-waste is the fastest growing component of municipal solid waste. The world generates between 22 to 55 million tons of e-waste each year, and the volume of waste increases approximately 4% annually [11]. The United States alone generated 3.16 million tons of e-waste in 2008, which is 1.3% of the total municipal solid waste generated in the U.S. for that year [15]. The majority of this e-waste (approximately 80%) is disposed of by being buried in landfills [15]. Not all e-waste is disposed of in

this manner; e-waste is also e-cycled in the U.S. using modern equipment and appropriate regulations. However, not all e-waste collected for recycling is actually e-cycled in the U.S., approximately 50 -80% of U.S. e-waste is exported (sometimes illegally) to developing countries to be e-cycled there [11, 16-19]. China is the world's largest importer and recycler of e-waste [20].

The e-cycling process is not recycling in the conventional sense of turning a useless item into a useful one; but entails only the removal of the valuable metal components (i.e.: gold and copper) for resale, and the subsequent disposal of the remaining materials [10, 14]. Using proper equipment and precautions, e-cycling is safe. However, this is often not the case when the e-waste recycling occurs in a developing country, where there are lax or unenforced environmental regulations and health protocols [10, 11, 14].

While processing materials, e-cycling workers first dismantle and sort the electronic equipment. Next, the metals are salvaged using techniques such as the dry roasting of circuit boards, use of open acid baths, and the burning of cables. The waste is disposed of by the open air shredding, melting and burning of plastics, and the subsequent disposal (dumping) of the resulting materials in nearby fields and riverbanks [10, 14]. In addition, printer toner is recovered for re-sale using bare hands and a paintbrush. As e-waste recycling is a household business, the recovery and disposal processes are carried out in the homes and yards of workers. Not only do the



workers perform these tasks without adequate personal protection equipment, in some cases they use cooking pots and utensils to process the waste [10, 14, 21].

Despite these risks, workers travel from great distances to villages where e-waste is recycled for financial gain. A worker can make several times the money recycling e-waste than other common rural professions, such as farming. Daily wages earned for e-waste recycling are approximately \$1.50 [19, 22].

These conditions have disastrous consequences for the environment. The e-waste recycling village of Guiyu in Guangdong, China, has the highest documented values of PCDD/Fs abundances in ambient air in the world [13]. Local streams and lakes (previous sources of fresh water) are black, acrid, and clogged with waste, such that they are unusable. Fresh water for drinking and bathing has to be shipped in from nearby villages at great expense [19].

### **Physical Chemical Properties**

There is a significant correlation between parent PAH concentrations and Cl-PAH concentrations in urban particulate matters [23]. It is likely that the major mechanism by which Cl-PAHs are formed is the direct chlorination of the parent PAH [2, 23]. However, no such correlation has been found between parent PAH concentrations and Br-PAH concentrations in the same samples [23]. The lack of

correlation may be due to the different sources and halogen concentrations present in the waste materials, and/or the stability of the bromine substituent [2, 23].

There have been a limited number of studies on X-PAHs in the environment due to the lack of commercially available standards. Therefore, few physical-chemical properties of X-PAHs have been measured experimentally. These properties were estimated for X-PAHs using the EPI-Suite program [24], in comparison with their parent PAHs (Table 1.1) [24].

In general, the EPI-Suite estimations of X-PAH physical-chemical properties were similar to those of the parent PAHs (Table 1.1). The range of estimated X-PAH vapor pressures are  $7.20 \times 10^{-3}$  to  $7.92 \times 10^{-7}$  Pa, which is slighter lower than the estimated parent PAH vapor pressures of  $4.40 \times 10^{-2}$  to  $1.31 \times 10^{-7}$  Pa [24]. These ranges are reasonable; as molecular weight increases, vapor pressure decreases [25]. The X-PAHs also followed this general trend, especially the higher molecular weight X-PAHs.

The Henry's Law Constant (HLC) is used to estimate the partitioning of a compound between air and water. The range of HLC values for X-PAHs was  $6.67 \times 10^{-5}$  to  $6.00 \times 10^{-7}$  ———. This range is similar to the PAH HLC range of  $1.67 \times 10^{-4}$  to  $8.30 \times 10^{-6}$  ——— (Table 1.1). This range of HLC values for both PAHs and X-PAHs

( $\sim 10^{-7}$  to  $10^{-5}$ ) is consistent with values for compounds that have a slow-volatilization from water [26].

X-PAH and PAH  $K_{oc}$  and water solubility's were also estimated (Table 1.1).  $K_{oc}$  describes the extent that a compound will partition between water and an organic carbon phase (such as soil or sediment). The range of the X-PAH  $K_{oc}$  values is from  $1.82 \times 10^4$  to  $2.16 \times 10^6$ . This range is similar to the PAH range of  $4.24 \times 10^3$  to  $2.09 \times 10^5$ . These ranges show that in a system composed of only water and an organic carbon phase, both PAHs and X-PAHs will have a high potential to sorb to soil or sediment. Further, the range of the X-PAH water solubility data is  $1.30 \times 10^{-1}$  to  $6.57 \times 10^{-4}$  mg/L which shows that X-PAHs are even less water soluble than their parent compounds, which have a range of 1.34 to  $2.64 \times 10^{-2}$  mg/L (Table 1.1).

While the majority of measured X-PAHs were found in air, if they are discharged into water, the  $K_{oc}$  values suggest that they would partition into sediment, with possible deleterious effects to the aquatic ecosystem. The low HLC value suggests that once the X-PAHs have partitioned into water, they will not volatilize quickly.

### **Analytical Methods**

The majority of the environmental studies focusing on X-PAHs measured the X-PAH concentrations in atmospheric particulate matter [1, 2, 4-6, 23, 27-32]. The X-

PAHs were extracted from the air filters by either centrifugation using dichloromethane (DCM) as a solvent or Soxhlet extraction with toluene, sometimes as a mixture with methanol or ethanol [1, 23, 30, 32]. The extracts were then concentrated and purified using silica solid phase extraction [1-3, 23, 30]. The extracts were concentrated, and analyzed by GC-MS in electron impact (EI) mode. A range of environmental samples (leaves, soil, dust), as well as electronic shredder waste, were dried with sodium sulfate and extracted by soxhlet extraction using a ratio of 3:1 DCM: hexane. These samples were also filtered with a silica gel/ activated charcoal mix after silica SPE [3]. For water samples, the X-PAHs were extracted using a continuous liquid-liquid extractor (with hexane as a solvent), and the resulting extract was concentrated using a rotary evaporator [7]. Snow samples were first filtered to remove particles. The filters were then rinsed with acetone, followed by toluene, to ensure no X-PAHs were left on the filters. The two fractions were combined, and extracted with water to remove all water and acetone. The samples were purified using silica-SPE [6].

### **X-PAHs and the Environment**

The limited environmental studies available reveal that X-PAHs are ubiquitous contaminants. They have been detected in a wide variety of matrices including air, snow, soil, vegetation, tap water, dust, and sediment [1, 3, 6, 7, 23, 27, 29, 30, 32]. The most common matrix that Cl-PAHs have been studied in is

atmospheric particulate matter (PM) [1, 5, 6, 23, 27, 29, 30, 32]. While most of the Cl-PAHs in PM are below the detection limit (DL) or low pg/ $\mu$ L range, there are some Cl-PAHs that are often found at higher concentrations, such as 1-chloropyrene and 6-chlorobenzo(a)pyrene (6-ClBaP). 6-ClBaP has been measured in atmospheric PM at concentrations that are greater than the other Cl-PAHs [1-3, 23]. The highest Cl-PAH concentration measured was 6-ClBaP, which was measured in concentrations up to 137 pg/m<sup>3</sup>. Furthermore, 6-ClBaP does not show the same temporal variation as other Cl-PAHs [1]. From this data, it is clear that 6-ClBaP has different sources and/or atmospheric fate than the other Cl-PAHs [1]. Of the matrices that Cl-PAHs have been measured in, the highest X-PAH concentrations were measured in fly ash from a waste incinerator. In this matrix, the highest X-PAH concentrations were 6-ClBaP, which was measured in concentrations as high as 5290 ng/g dry weight, and 6-chlorochrysene which was measured in concentrations as high as 1156 ng/g dry weight [2].

While the environmental concentrations of Cl-PAHs are considerably lower than those of their parent compounds (by approximately 100-times), some Cl-PAH concentrations are higher than PCDD/Fs and polychlorinated biphenyls (PCBs) concentrations in environmental matrices [3, 30, 31]. A summary of the published environmental concentrations of Cl-PAHs are shown in Table 1.2.

Br-PAHs have not been measured as frequently as Cl-PAHs, and therefore, have only been identified in two matrices: urban air from Shizuoka, Japan and incinerator ash recovered from South Korea [2, 23]. The concentrations of Br-PAHs in air were generally low, with most compounds below the DL. However, the Br-PAH concentrations varied significantly. Of the Br-PAHs, 5,7-dibromobenz[a]anthracene, was measured in urban air at the highest concentrations [23]. The incinerator ash samples were composed of two types of ash: fly ash and bottom ash. The bottom ash samples contained very few detectable Br-PAHs, however the fly ash contained several Br-PAHs at measurable amounts [2]. 1-bromopyrene was measured at the highest concentration, up to 758 ng/g dry weight [2]. A summary of the published environmental concentrations of Br-PAHs are shown in Table 1.3.

The atmospheric fate of Cl-PAHs is expected to be similar to that of the parent PAHs, including atmospheric transport. For air samples collected in Japan in 2002 the air mass back trajectories reveal that air masses containing measurable concentrations of Cl-PAHs originated in China [30].

When X-PAHs are released into the environment, many factors can alter the concentrations. These include atmospheric transport, seasonal emission sources (such as indoor heating which occurs during cooler temperatures), degradation of compounds (i.e.: photolysis that is associated with the longer more intense hours of sunlight during the summer months, and photochemical reactions involving radical

species), meteorological conditions or events (wet or dry deposition), and/or gas-to-particle partitioning [1, 30, 32]. Of these processes, photolysis is considered the greatest route of degradation for parent PAHs [23].

Laboratory studies revealed that Cl-PAHs and Br-PAHs undergo direct photolysis via a first-order reaction model [23, 30]. The data shows that Br-PAHs are slightly less photostable than the Cl-PAHs, which are less photostable than the parent PAHs. The range of photo degradation half-lives is large. The most photostable Cl-PAH (3-chlorofluoranthene) which has a half-life of 29 hours, is approximately 50-times more stable than the least stable Cl-PAH (6-ClBaP), with a half-life of 0.57 hours. There is a similar, though smaller, range for Br-PAHs: the most photostable Br-PAH (6-bromobenzo(a)pyrene), which has a half-life of 2.25 hours is roughly 30-times more stable than the least stable (measurable) Br-PAH (2-bromofluorene), with a half-life of 0.07 hours. It is interesting to note that one of the least photostable compounds (6-chlorobenzo(a)pyrene) is often detected in environmental samples at high concentrations, while one of the most photostable compounds (3-chlorofluoranthene) has been detected in environmental samples, but often at low concentrations. Clearly, the concentrations of the Cl-PAHs cannot be explained by photostability data alone, and other causes, such as emission rates must play a role as well. The photo degradation half-lives of X-PAHs are shown in Table 1.4 [23, 30].

While photolysis does decrease the concentration of X-PAHs, it does not necessarily form inert by-products. Rather than a de-chlorinated parent structure, photolysis of Cl-PAHs is believed to create oxidized chlorinated by-products which are more toxic and mutagenic than their precursor due to the high reactivities of the products that are formed [30]. In contrast, the decay of Br-PAHs forms a de-brominated structure, which might then undergo fragmentation, most likely due to the relative weakness of the C-Br bond — as compared to the C-Cl bond — [23]. While important, direct photolysis does have its limitations; it is most effective for lower chlorinated Cl-PAHs. As the number of chlorine atoms on the parent structure increases, photolysis is less likely to occur [23]. Indeed, the parent structure is stabilized by chlorination. In contrast, the rate of photolysis increased with increasing bromination; the photolysis rate of 7,12-dibromobenz[a]anthracene completed within one minute [23].

Another important route of X-PAH degradation in the atmosphere is indirect photolysis. There are several photochemical oxidants that can react with atmospheric particulate-bound compounds; such as  $O_3$ ,  $NO_x$ , and the OH radical [25]. Of these species, reactions with the OH radical are the most relevant to X-PAHs, as the OH radical is both quite reactive, and the least selective [25]. As the X-PAH hydroxyl radical reaction rate constants ( $k'_{OH}$ ) have not been experimentally measured, these constants were estimated using the EPI-Suite program (see Table 1.1). The hydroxyl



radical rate constant for both X-PAHs and PAHs are nearly identical. The PAH range from  $5.00 \times 10^{-11}$  to  $8.85 \times 10^{-12}$  ———, and the X-PAH range from  $1.03 \times 10^{-11}$  to  $5.83 \times 10^{-12}$  ——— [24]. The similarity in between PAH and X-PAH constants suggests that the addition of a halogen to the PAH skeleton does not alter (either increase or decrease) its reactivity with the hydroxyl radical.

As X-PAHs are semi-volatile compounds, with estimated vapor pressures ranging from  $3.42 \times 10^{-3}$  to  $7.23 \times 10^{-7}$  Pa (see Table 1.1), they partition between the gaseous and the particle phase in the atmosphere. The variables that influence the partitioning of the compounds are ambient temperature, the concentration of the aerosol, and the interactions that occur between the compound and the aerosol [32]. In general, the greater the molecular weight, the lower the vapor pressure, and the higher the partitioning into the particle phase. The experimentally determined gas-to-particle percentages for a range of Cl-PAHs is given in Table 1.5 [32]. The range of particle percentage is 8% for 9-chloroanthracene to 82% for 6-chlorobenzo(a)pyrene.

On average, the Cl-PAH concentrations in the gas phase exceed the particulate phase concentrations by approximately ten times [32]. However, some of this disparity is because the majority of the compounds studied were lower molecular weight, higher vapor-pressure Cl-PAHs, which would pre-dispose these compounds to the gas phase. Included in this study were several additional compounds with a greater number of aromatic rings. For Cl-PAHs, the gas to particle partitioning ratio

is dependent on the PAH skeleton (the number of aromatic rings) rather than the degree of halogenation [32]. Therefore, the compounds in this study would display an increased preference for the particle phase.

Although X-PAHs are quite abundant in the gaseous phase, the particulate matter phase is of more importance to human health, as it is the particle-bound contaminants that are breathed deep into the lungs, where they are absorbed by the alveoli [33].

While the atmospheric concentrations of both the gaseous and particulate Cl-PAHs in Japan were higher in the cold season and lower in the warm season, the gas to particle partitioning differed. The particulate matter Cl-PAH concentrations were elevated in the cold seasons, while the gaseous Cl-PAH concentrations were elevated in the warm seasons [32]. It has been suggested that this phenomenon is due, in part, to the re-volatilization of Cl-PAHs from environmental sinks [32]. Similarly, parent PAH particulate concentrations have been shown to increase in the winter, while the gaseous PAH concentrations are elevated in the summer months [34].

### **X-PAHs and Human Health**

X-PAHs are of concern not only for the environment but also for human health. X-PAHs are toxic and mutagenic [2]. The log  $K_{ow}$  values, which describes the affinity for a compound to partition between water and an organic phase (such as a

living organism) for the X-PAHs are slightly higher than those of the parent PAH (see Table 1.1). The range of the log  $K_{ow}$  values for X-PAHs is 4.91 to 7.30, and the range for PAHs is 4.02 to 6.11. An increase in log  $K_{ow}$  values describes a greater affinity for a compound to partition into lipids. Therefore, X-PAHs are expected to be more lipophilic than their parent structures, making the X-PAHs more likely to bioaccumulate and biomagnify [23].

The chief step in the metabolic activation of X-PAHs is associated with the aryl hydrocarbon receptor (AhR) [35]. The AhR is a transcription factor, a protein involved in the replication of DNA [36]. The AhR is usually (and ideally) inactive. When ligands such as dioxin or dioxin-like compounds bind to the AhR, cellular transformation occurs [37]. AhR activity is therefore a measure of the mutagenicity of a compound. Many X-PAHs have been shown to display AhR-mediated activities, sometimes in contrast to the corresponding parent PAH [38]. Cl-PAHs with a fewer number of aromatic rings have been shown to have increased AhR activity in relation to the parent PAH, as the number of chlorine atoms is increased [39]. However, Cl-PAHs with a greater number of aromatic rings tend to have decreased AhR activity in relation to the parent PAH, as the number of chlorine atoms increased [39]. In the case of Br-PAHs, the structures with fewer rings have increased AhR activities in relation to the parent PAH, while structures with more rings have decreased AhR

activity in relation to the parent PAHs [23]. From this data, it is clear that the position of the halogen is very important in determining AhR activity.

One of the ways that AhR activity is measured is by the median effective concentration ( $EC_{50}$ ). This value represents the concentration of a compound (such as an X-PAH) that elicits a response in 50% of test organisms in a specified population under a defined set of conditions [40]. A compound that has a lower  $EC_{50}$  is therefore a more potent compound, as less of it is required to elicit a response. The lowest  $EC_{50}$  value for a Cl-PAH and Br-PAH are 0.03 and 0.07  $\mu\text{M}$ ; which represent 6-chlorochrysene and 7-bromobenz[a]anthracene, respectively [23]. These values are comparable to the lowest PAH  $EC_{50}$  value of 0.05  $\mu\text{M}$  for benz[a]anthracene [23]. The  $EC_{50}$  values of parent and X-PAHs are shown in Table 1.6 [23, 39].

Toxic equivalencies (TEQs) are calculated values that are used to determine the toxicity of mixtures of dioxin and dioxin-like compounds by measuring each component of the compound in relation to the most toxic dioxin: 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) [41]. TEQs can be calculated for any sample that has specific congener concentration data and a toxicity value [42]. This value could either be an experimentally derived relative potency value (REP) or a determined TCDD equivalency factor (TEF) which is derived from many potency values [42].

The X-PAH TEQs were calculated from individual  $REP_{\text{BaP}}$  values and the corresponding X-PAH concentration [23]. The REP values were calculated in

comparison to benzo(a)pyrene (BaP). Most X-PAHs have REP values considerably lower than BaP; however, 6-chlorochrysene has a higher REP value of 2.1. The TEQs for X-PAHs show a range of values, which show similarities based on the matrix the compound was analyzed in. For atmospheric particulate matter, the TEQs of total PAHs, Cl-PAHs, and Br-PAHs were 11500, 44.1, and 27.5 fg/m<sup>3</sup>, respectively [23], which are much lower than those found in other matrices, such as soil and dust. The TEQs for PAHs, Cl-PAHs, and PCDD/Fs for floor dust from an e-waste site were 127, 518, and 1070 pg-TEQ/g, respectively [3]. In contrast, the concentrations in soil from the same site are 19.1, 92.3, and 70.6, pg-TEQ/g. The Cl-PAH TEQs from environmental samples, (leaves, soil, and dust), from an e-waste area estimate that they are more toxic than the corresponding parent PAH, and are similar to that of dioxin [2]. In addition, Cl-PAH TEQs from urban particulate matter estimate that Cl-PAHs are 30-50 times more toxic than dioxins [39]. This is of concern, because some X-PAHs have been measured in greater concentrations than dioxins.

### **Research Objectives**

The first goal of this research was to develop an analytical method to measure the X-PAH concentrations in atmospheric particulate matter, soil, sediment, and house dust. The analytical method includes a programmable temperature vaporizing inlet (PTV) which lowers the detection limit by allowing for a large volume injection.

The second goal of this research was to measure and compare the X-PAH concentrations of an e-waste site with a nearby densely populated urban area in Guangzhou, China. While there are no e-waste recycling facilities in Guangzhou, other potential X-PAH sources including municipal waste incinerators are present.

Fig 1.1: Structures of Cl-PAHs studied.

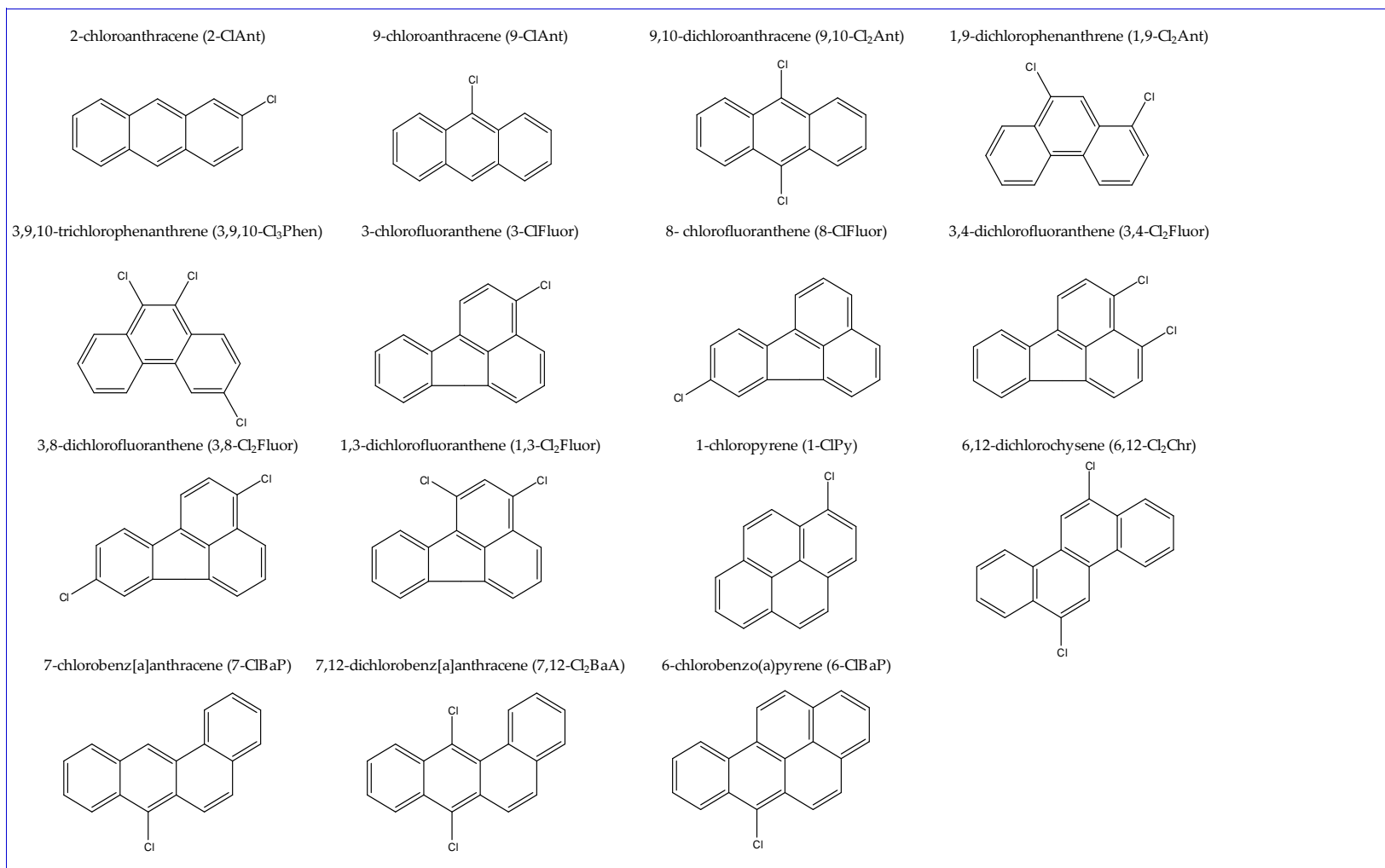


Fig 1.2: Structures of Br-PAHs studied.

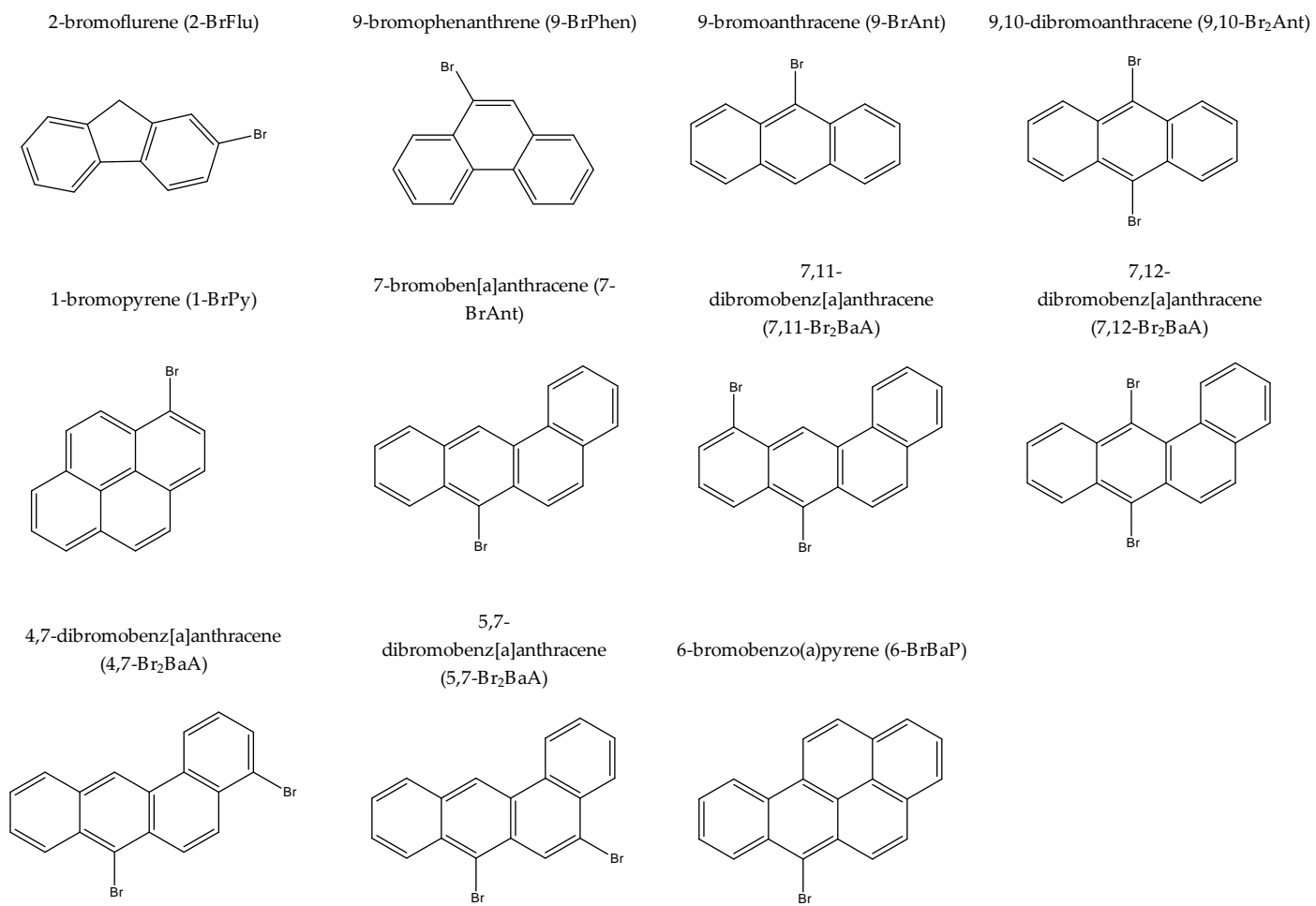




Table 1.1: EPI-Suite estimated constants and properties of the X-PAHs studied and the corresponding parent PAH [24].

Compound	Property or Constant											
	MW	Formula	MP (°C)	BP (°C)	Vapor Pressure (Pa)	Log K <sub>ow</sub>	Water Solubility (mg/L)	Henry's Law Constant	Log K <sub>aw</sub>	Log K <sub>oa</sub>	K <sub>oc</sub> (L/kg)	k' <sub>HO</sub> (cm <sup>3</sup> /mlcl x sec)
<b>fluorene</b>	<b>166.22</b>	<b>C<sub>13</sub>H<sub>10</sub></b>	<b>64</b>	<b>293</b>	<b>4.40E-02</b>	<b>4.02</b>	<b>1.34E+00</b>	<b>1.67E-04</b>	<b>-2.41</b>	<b>6.59</b>	<b>4.24E+03</b>	<b>8.85E-12</b>
2-bromofluorene	245.12	C <sub>13</sub> H <sub>9</sub> Br	100	330	7.20E-03	4.91	1.30E-01	6.67E-05	-2.56	7.47	1.82E+04	5.83E-12
<b>anthracene</b>	<b>178.24</b>	<b>C<sub>14</sub>H<sub>10</sub></b>	<b>78</b>	<b>327</b>	<b>2.89E-04</b>	<b>4.35</b>	<b>6.91E-01</b>	<b>5.13E-05</b>	<b>-2.64</b>	<b>7.09</b>	<b>7.27E+03</b>	<b>4.00E-11</b>
2-chloroanthracene	212.68	C <sub>14</sub> H <sub>9</sub> Cl	105	347	3.42E-03	4.99	1.60E-01	3.80E-05	-2.81	7.80	2.14E+04	2.81E-11
9-chloroanthracene	212.68	C <sub>14</sub> H <sub>9</sub> Cl	105	347	3.42E-03	4.99	1.60E-01	3.80E-05	-2.81	7.80	2.14E+04	2.81E-11
9,10-dichloroanthracene	247.13	C <sub>14</sub> H <sub>8</sub> Cl <sub>2</sub>	121	366	8.27E-04	5.63	2.94E-02	2.82E-05	-2.94	8.57	7.69E+04	8.22E-12
9-bromoanthracene	257.13	C <sub>14</sub> H <sub>9</sub> Br	114	359	1.41E-03	5.24	5.67E-02	2.05E-05	-3.08	8.32	3.53E+04	2.52E-11
9,10-dibromoanthracene	336.03	C <sub>14</sub> H <sub>8</sub> Br <sub>2</sub>	141	390	1.38E-05	6.13	3.43E-03	8.15E-06	-3.48	9.61	2.09E+05	7.22E-12
<b>phenanthrene</b>	<b>178.24</b>	<b>C<sub>14</sub>H<sub>10</sub></b>	<b>78</b>	<b>327</b>	<b>5.76E-03</b>	<b>4.35</b>	<b>6.77E-01</b>	<b>5.13E-05</b>	<b>-2.76</b>	<b>7.22</b>	<b>7.42E+03</b>	<b>1.30E-11</b>
1,9-dichlorophenanthrene	247.13	C <sub>14</sub> H <sub>8</sub> Cl <sub>2</sub>	121	366	8.27E-04	5.63	2.94E-02	2.82E-05	-2.94	8.57	7.69E+04	2.67E-12
3,9,10-trichlorophenanthrene	281.57	C <sub>14</sub> H <sub>7</sub> Cl <sub>3</sub>	135	384	2.10E-04	6.28	5.30E-03	2.09E-05	-3.07	9.35	3.49E+04	1.21E-12
9-bromophenanthrene	257.13	C <sub>14</sub> H <sub>9</sub> Br	114	359	4.59E-03	5.24	5.67E-02	2.05E-05	-3.08	8.31	3.53E+04	8.18E-12
<b>fluoranthene</b>	<b>202.26</b>	<b>C<sub>16</sub>H<sub>10</sub></b>	<b>120</b>	<b>372</b>	<b>4.17E-04</b>	<b>4.93</b>	<b>1.30E-01</b>	<b>8.30E-06</b>	<b>-3.44</b>	<b>8.60</b>	<b>3.01E+04</b>	<b>2.92E-11</b>
3-chlorofluoranthene	236.70	C <sub>16</sub> H <sub>9</sub> Cl	135	391	1.49E-04	5.58	3.75E-02	6.15E-06	-3.60	9.18	6.96E+04	1.19E-11
8-chlorofluoranthene	236.70	C <sub>16</sub> H <sub>9</sub> Cl	135	391	1.49E-04	5.58	3.75E-02	6.15E-06	-3.60	9.18	6.96E+04	2.85E-11
1,3-dichlorofluoranthene	271.15	C <sub>16</sub> H <sub>8</sub> Cl <sub>2</sub>	153	409	3.23E-05	6.22	6.79E-03	4.56E-06	-3.73	9.95	2.50E+05	4.49E-12
3,8-dichlorofluoranthene	271.15	C <sub>16</sub> H <sub>8</sub> Cl <sub>2</sub>	153	409	3.23E-05	6.22	6.79E-03	4.56E-06	-3.73	9.95	2.50E+05	1.13E-11
3,4-dichlorofluoranthene	271.15	C <sub>16</sub> H <sub>8</sub> Cl <sub>2</sub>	153	409	3.23E-05	6.22	6.79E-03	4.56E-06	-3.73	9.95	2.50E+05	5.15E-12

Table 1.1 (Continued): EPI-Suite estimated constants and properties of the X-PAHs studied and the corresponding parent PAH [20].

Compound	Property or Constant											
	MW	Formula	MP (°C)	BP (°C)	Vapor Pressure (Pa)	Log K <sub>ow</sub>	Water Solubility (mg/L)	Henry's Law Constant	Log K <sub>aw</sub>	Log K <sub>oa</sub>	K <sub>oc</sub> (L/kg)	k' <sub>HO</sub> (cm <sup>3</sup> /mlcl x sec)
<b>pyrene</b>	<b>202.26</b>	<b>C<sub>16</sub>H<sub>10</sub></b>	<b>120</b>	<b>372</b>	<b>4.59E-05</b>	<b>4.93</b>	<b>2.25E-01</b>	<b>8.30E-06</b>	<b>-3.31</b>	<b>8.19</b>	<b>1.72E+04</b>	<b>5.00E-11</b>
1-chloropyrene	236.70	C <sub>16</sub> H <sub>9</sub> Cl	135	391	1.49E-04	5.58	3.75E-02	6.15E-06	-3.60	9.18	6.96E+04	3.52E-11
1-bromopyrene	281.15	C <sub>16</sub> H <sub>9</sub> Br	147	403	5.50E-05	5.82	1.30E-02	3.31E-06	-3.87	9.69	1.12E+05	3.15E-11
<b>benz[a]anthracene</b>	<b>228.30</b>	<b>C<sub>18</sub>H<sub>12</sub></b>	<b>136</b>	<b>399</b>	<b>3.62E-05</b>	<b>5.52</b>	<b>2.91E-02</b>	<b>5.01E-06</b>	<b>-3.31</b>	<b>9.07</b>	<b>9.97E+04</b>	<b>5.00E-11</b>
7-chlorobenz[a]anthracene	262.74	C <sub>18</sub> H <sub>11</sub> Cl	151	418	2.14E-05	6.17	8.46E-03	3.71E-06	-3.82	9.99	2.62E+05	3.52E-11
7,12-dichlorobenz[a]anthracene	297.19	C <sub>18</sub> H <sub>10</sub> Cl <sub>2</sub>	164	437	5.26E-06	6.81	1.51E-03	2.75E-06	-3.95	10.76	8.13E+05	1.03E-11
7-bromobenz[a]anthracene	307.19	C <sub>18</sub> H <sub>11</sub> Br	163	430	7.78E-06	6.41	2.90E-03	2.00E-06	-4.09	10.50	3.66E+05	3.15E-11
7,11-dibromobenz[a]anthracene	386.09	C <sub>18</sub> H <sub>10</sub> Br <sub>2</sub>	187	461	7.23E-07	7.30	1.69E-04	7.96E-07	-4.49	11.79	2.16E+06	9.02E-12
7,12-dibromobenz[a]anthracene	386.09	C <sub>18</sub> H <sub>10</sub> Br <sub>2</sub>	187	461	7.23E-07	7.30	1.69E-04	7.96E-07	-4.49	11.79	2.16E+06	9.02E-12
4,7-dibromobenz[a]anthracene	386.09	C <sub>18</sub> H <sub>10</sub> Br <sub>2</sub>	187	461	7.23E-07	7.30	1.69E-04	7.96E-07	-4.49	11.79	2.16E+06	9.02E-12
5,7-dibromobenz[a]anthracene	386.09	C <sub>18</sub> H <sub>10</sub> Br <sub>2</sub>	187	461	7.23E-07	7.30	1.69E-04	7.96E-07	-4.49	11.79	2.16E+06	9.02E-12
<b>chrysene</b>	<b>228.30</b>	<b>C<sub>18</sub>H<sub>12</sub></b>	<b>136</b>	<b>399</b>	<b>2.08E-07</b>	<b>5.52</b>	<b>2.64E-02</b>	<b>5.01E-06</b>	<b>-3.67</b>	<b>9.48</b>	<b>1.10E+05</b>	<b>5.00E-11</b>
6,12-dichlorochrysene	297.19	C <sub>18</sub> H <sub>10</sub> Cl <sub>2</sub>	164	437	5.26E-06	6.81	1.51E-03	2.75E-06	-3.95	10.76	8.13E+05	1.03E-11
<b>benzo(a)pyrene</b>	<b>252.32</b>	<b>C<sub>20</sub>H<sub>12</sub></b>	<b>169</b>	<b>443</b>	<b>1.31E-07</b>	<b>6.11</b>	<b>1.04E-02</b>	<b>8.10E-07</b>	<b>-4.73</b>	<b>10.86</b>	<b>2.09E+05</b>	<b>5.00E-11</b>
6-chlorobenzo(a)pyrene	286.76	C <sub>20</sub> H <sub>11</sub> Cl	182	461	7.92E-07	6.75	1.94E-03	6.00E-07	-4.61	11.36	7.21E+05	3.52E-11
6-bromobenzo(a)pyrene	331.21	C <sub>20</sub> H <sub>11</sub> Br	193	473	2.91E-07	7.00	6.57E-04	3.23E-07	-4.88	11.88	1.19E+06	3.15E-11

Table 1.2: Concentrations of Cl-PAHs measured in environmental samples in previous studies.

Ref	Sampling Date and Location	Matrix (units)	Concentration of Chlorinated PAHs mean (range)								
			9 Cl Flu	9 Cl Phe	2 Cl Ant	9 Cl Ant	3 Cl Fluor	8 Cl Fluor	1 Cl Py	3,9 Cl <sub>2</sub> Phe	9,10 Cl <sub>2</sub> Ant + 1,9 Cl <sub>2</sub> Phe
[8]	Dec 1982-	Tap Water A (ng/L)	*	0.33	*	*	0.13	*	*	*	*
	Feb 1984 in	Tap Water A (ng/L)	*	0.18	*	*	0.14	*	*	*	*
	Tsukuba,	Tap Water B (ng/L)	*	*	*	*	0.17	*	*	*	*
	Japan	Lake Water (ng/L)	*	ND	*	*	ND	*	*	*	*
[2]	1992-2002 in Shizuoka, Japan	Urban Street Air-Particulate Matter (pg/m <sup>3</sup> )	*	2.7 (<1.3-8.2)	*	*	3.1 (<1.3-10)	ND	5.2 (0.72-19)	0.75 (<0.82-3.9)	*
[25]	1993? in Sweeden	Urban Street Air-Particulate (pg/m <sup>3</sup> )	*	*	*	*	2.6	0.7	4.9	*	*
		Urban Air- Semi-Volatile (pg/m <sup>3</sup> )	*	*	*	*	2	0.6	6.9	*	*
		Road Tunnel Air-Particulate (pg/m <sup>3</sup> )	*	*	*	*	10	4.4	14.7	*	*
		Road Tunnel Air- Semi-Volatile (pg/m <sup>3</sup> )	*	*	*	*	9.1	4.2	24.9	*	*
[26]	Jan- Dec 2002 in Shizuoka, Japan	Urban Air- Particulate Matter (pg/m <sup>3</sup> )	*	3.5 (2.1-6.8)	*	*	4.5 (2.2- 9.0)	*	7.5 (1.4-19)	2.7 (2.0-3.9)	*
[28]	Dec 2004 to Dec 2005 in Shizuoka, Japan	Urban Air-Gaseous Phase (pg/m <sup>3</sup> )	0.65 (<0.05- 2.1)	19 (2.2-45)	1.4 (<0.03-4.2)	13 (<0.02-71)	10 (<0.01-34)	3.8 (<0.01-30)	9.2 (<0.01-27)	1.3 (0.25-8.6)	2.2 (0.25-15)
		Urban Air- Particulate Phase (pg/m <sup>3</sup> )	0.20 (<0.05-0.30)	0.6 (<0.02-3.7)	0.36 (<0.03-2.1)	0.10 (<0.02-0.51)	2.0 (<0.01-13)	1.3 (<0.01-11)	3.8 (0.47-15)	1.9 (<0.23-1.9)	0.56 (<0.08-2.0)
		Urban Air- Combined Total (pg/m <sup>3</sup> )	0.62 (<0.05-2.1)	19 (2.3-45)	1.0 (<0.03-4.2)	9.9 (<0.02-71)	11 (0.97-39)	3.0 (<0.01-30)	13 (3.3-33)	1.4 (0.25-8.6)	2.4 (0.25-15)

ND = Not Detected \* = Not Analyzed

Table 1.2 (Continued): Concentrations of Cl-PAHs measured in environmental samples in previous studies.

Ref	Sampling Date	Matrix (units)	Concentration of Chlorinated PAHs mean (range)								
			9, 10 Cl <sub>2</sub> Phe	6 Cl Chr	7 Cl BaA	3,8 Cl <sub>2</sub> Fluor	3,4 Cl <sub>2</sub> Fluor	3,9,10 Cl <sub>3</sub> Phe	6 Cl BaP	6,12 Cl <sub>2</sub> Chr	7,12 Cl <sub>2</sub> BaA
[8]	Dec 1982-	Tap Water A (ng/L)	0.08	*	*	*	*	*	*	*	*
	Feb 1984 in	Tap Water A (ng/L)	0.04	*	*	*	*	*	*	*	*
	Tsukuba,	Tap Water B (ng/L)	0.18	*	*	*	*	*	*	*	*
	Japan	Lake Water (ng/L)	ND	*	*	*	*	*	*	*	*
[2]	1992-2002 in Shizuoka,	Urban Street Air-Particulate Matter (pg/m <sup>3</sup> )	1.9 (<1.1-23)	*	3.1 (<1.6-10)	ND	ND	ND	15 (<3.2-137)	*	*
[25]	1993? in Sweeden	Urban Street Air-Particulate (pg/m <sup>3</sup> )	*	*	0.4	*	*	*	1.9	*	*
		Urban Air- Semi-Volatile (pg/m <sup>3</sup> )	*	*	ND	*	*	*	ND	*	*
		Road Tunnel Air-Particulate (pg/m <sup>3</sup> )	*	*	2.3	*	*	*	6.1	*	*
		Road Tunnel Air- Semi-Volatile (pg/m <sup>3</sup> )	*	*	ND	*	*	*	ND	*	*
[26]	Jan- Dec 2002 in Shizuoka, Japan	Urban Air- Particulate Matter (pg/m <sup>3</sup> )	5.1 (3.4-8.3)	*	2.4 (<1.6-4.6)	*	*	*	5.6 (<3.2-12)	*	*
[28]	Dec 2004 to Dec 2005 in Shizuoka, Japan	Urban Air-Gaseous Phase (pg/m <sup>3</sup> )	0.45 (<0.04-2.7)	1.4 (<0.02-7.5)	13 (<0.02-83)	6.7 (<1.1-22)	4.0 (<1.9-7.8)	0.22 (<0.02-0.95)	2.3 (<0.55-9.8)	2.5 (<0.02-16)	14 (<0.05-87)
		Urban Air- Particulate Phase (pg/m <sup>3</sup> )	0.32 (<0.04-0.93)	0.6 (<0.028-2.9)	0.86 (<0.02-5.9)	2.4 (<1.1-4.9)	3.2 (<1.9-9.0)	0.082 (<0.02-0.36)	7.1 (<0.95-23)	0.26 (<0.02-1.8)	0.37 (<0.005-3.2)
		Urban Air- Combined Total (pg/m <sup>3</sup> )	0.54 (<0.04-2.9)	1.9 (0.12-7.6)	5.6 (<0.02-83)	6.0 (<1.1-22)	2.5 (<1.9-15)	0.24 (<0.02-1.1)	8.7 (1.9-23)	2.1 (<0.02-16)	14 (<0.05-87)

ND = Not Detected \* = Not Analyzed

Table 1.2 (Continued): Concentrations of Cl-PAHs measured in environmental samples in previous studies.

Ref	Sampling Date	Matrix (units)	Concentration of Chlorinated PAHs mean (range)								
			9 Cl Flu	9 Cl Phe	2 Cl Ant	9 Cl Ant	3 Cl Fluor	8 Cl Fluor	1 Cl Py	3,9 Cl <sub>2</sub> Phe	9,10 Cl <sub>2</sub> Ant + 1,9 Cl <sub>2</sub> Phe
[20]	Sept 2005- June 2006 in Shizuoka, Japan	Urban Air- Particulate Matter (pg/m <sup>3</sup> )	0.05 (<0.05-0.05)	0.62 (0.05-2.29)	0.11 (<0.03-0.59)	0.08 (<0.02-0.34)	1.56 (0.19-5.59)	0.35 (<0.02-2.14)	3.99 (0.22-11.32)	*	0.26 (<0.08-0.31)
[3]	2006-2007 in South Korea	Waste Incinerator: Fly Ash (ng/g)	<0.06	(<0.06-237)	(<0.06- 15)	(<0.06- 231)	(<0.06-1015)	(<0.06- 107)	(<0.06- 1113)	(<0.06- 46)	(<0.06- 276)
		Waste Incinerator: Bottom Ash (ng/g)	<0.06	(<0.06- 16)	(<0.06-0.68)	(<0.06- 1.0)	(<0.06- 4.0)	(<0.06- 1.1)	(<0.06- 2.6)	<0.06- 3.1	(<0.06- 8.8)
[4]	Sept 2007 in China	E-waste recycling facility: Electronic Shredder Waste (ng/g dry wt)	ND	ND	ND	ND	0.52 (0.46-0.65)	13.2 (8.23-20.4)	14.9 (7.48-26.7)	5.43 (4.19-6.39)	ND
		E-waste recycling facility: Leaf (ng/g dry wt)	ND	16.9 (3.67-28.1)	ND	ND	7.95 (1.24-16.5)	4.34 (1.27-7.80)	27.7 (15.8-44.8)	7.00 (3.73-11.7)	1.84 (0.75-2.64)
		E-waste recycling facility: Floor Dust (ng/g dry wt)	ND	ND	ND	ND	3.72 (2.44-5.91)	9.40 (1.31-15.6)	16.6 (6.86-31.8)	5.32 (ND-13.3)	1.38 (ND-6.88)
		E-waste Recycling Facility: Soil (ng/g dry wt)	ND	0.49 (ND-2.76)	ND	0.05 (ND-0.53)	0.49 (ND-2.67)	1.25 (ND-6.59)	4.06 (ND- 11.0)	1.87 (ND-5.69)	0.09 (ND- 0.51)
		E-waste recycling facility: Urban Soil (Reference) (ng/g dry wt)	ND	ND	ND	ND	ND	ND	ND	ND	ND
		Industrial Complex: Soil (ng/g dry wt)	ND	ND	ND	ND	0.73 (ND-2.50)	0.01 (ND-<0.14)	4.58 (ND-36.7)	0.20 (ND- 2.45)	ND
		Industrial complex: Rural Soil (Reference) (ng/g dry wt)	ND	ND	ND	ND	ND	ND	ND	ND	ND
Other Locations: Agricultural Soil (ng/g dry wt)	ND	ND	ND	ND	0.05 (ND-<0.13)	ND	ND	ND	ND		

ND = Not Detected \* = Not Analyzed

Table 1.2 (Continued): Concentrations of Cl-PAHs measured in environmental samples in previous studies.

Ref	Sampling Date	Matrix (units)	Concentration of Chlorinated PAHs mean (range)								
			9, 10 Cl <sub>2</sub> Phe	6 Cl Chr	7 Cl BaA	3,8 Cl <sub>2</sub> Fluor	3,4 Cl <sub>2</sub> Fluor	3,9,10 Cl <sub>3</sub> Phe	6 Cl BaP	6,12 Cl <sub>2</sub> Chr	7,12 Cl <sub>2</sub> BaA
[20]	Sept 2005- June 2006 in Shizuoka,	Urban Air- Particulate Matter (pg/m <sup>3</sup> )	0.14 (<0.04-0.24)	0.50 (0.04-1.39)	0.66 (0.04-3.47)	*	*	0.03 (<0.02-0.03)	7.17 (0.50- 39.54)	0.05 (<0.02-0.15)	0.07 (<0.05-0.37)
[3]	2006- 2007 in South Korea	Waste Incinerator: Fly Ash (ng/g)	(<0.06- 17)	(<0.06- 1156)	(<0.06- 874)	(<0.06- 410)	(<0.06- 131)	(<0.14- 706)	(<0.14- 5290)	(<0.14- 867)	(<0.14- 1133)
		Waste Incinerator: Bottom Ash (ng/g)	(<0.06- 8.6)	(<0.06- 7.9)	(<0.06- 0.92)	(<0.06- 2.9)	(<0.06- 0.76)	(<0.14- 3.4)	(<0.14-0.68)	(<0.14- 2.5)	(<0.14- 2.9)
[4]	Sept 2007 in China	E-waste recycling facility: Electronic Shredder Waste (ng/g dry wt)	ND	ND	10.6 (4.00-21.3)	ND	ND	5.43 (4.19- 6.39)	13.5 (5.84-25.3)	ND	ND
		E-waste recycling facility: Leaf (ng/g dry wt)	3.01 (1.58-5.09)	ND	9.64 (ND-40.6)	ND	ND	7.00 (3.73-11.7)	3.59 (ND-6.96)	ND	ND
		E-waste recycling facility: Floor Dust (ng/g dry wt)	0.73 (ND-2.22)	ND	22.5 (ND-33.8)	ND	ND	5.32 (ND-13.3)	43.3 (21.1-66.9)	ND	ND
		E-waste Recycling Facility: Soil (ng/g dry wt)	ND	ND	2.24 (ND-13.0)	ND	ND	1.87 (ND-5.69)	16.0 (ND-73.1)	0.09 (ND-0.85)	ND
		E-waste recycling facility: Urban Soil (Reference) (ng/g dry wt)	ND	ND	ND	ND	ND	ND	ND	ND	ND
		Industrial Complex: Soil (ng/g dry wt)	0.13 (ND-0.56)	ND	0.69 (ND-8.29)	ND	ND	0.20 (ND-2.45)	80.2 (6.73-231)	0.38 (ND-2.48)	0.71 (ND-4.75)
		Industrial complex: Rural Soil (Reference) (ng/g dry wt)	ND	ND	ND	ND	ND	ND	0.19 (ND-<0.27)	ND	ND
Other Locations: Agricultural Soil (ng/g dry wt)	ND	ND	ND	ND	ND	ND	0.10 (ND-<0.27)	ND	ND		

ND = Not Detected \* = Not Analyzed

Table 1.3: Concentrations of Br-PAHs measured in environmental samples in previous studies.

Ref	Sampling Date and Location	Matrix (units)	Concentration of Brominated PAHs mean (range)										
			2 Br Flu	9 Br Phe	9 Br Ant	9, 10 Br <sub>2</sub> Ant	1 Br Py	7 Br BaA	7,11 Br <sub>2</sub> BaA	7,12 Br <sub>2</sub> BaA	4,7 Br <sub>2</sub> BaA	5,7 Br <sub>2</sub> BaA	6 Br BaP
[20]	Sept 2005- June 2006 in Shizuoka, Japan	Urban Air- Particulate Matter (pg/m <sup>3</sup> )	ND	ND	ND	0.63 (<0.01-2.5)	1.78 (<0.45-9.45)	0.82 (<0.19-0.82)	ND	6.27 (<0.28-10.75)	0.19 (<0.14-0.27)	8.68 (<0.14-156.10)	3.27 (<0.60-6.68)
[3]	2006- 2007 in South Korea	Waste Incinerator: Fly Ash (ng/g)	<0.14	(<0.14- 133)	(<0.14- 19)	(<0.14- 2.0)	(<0.14-758)	(<0.14- 181)	<0.29	(<0.29- 147)		(<0.29- 6.8)	(<0.29-243)
		Waste Incinerator: Bottom Ash (ng/g)	<0.14	(<0.14- 0.25)	(<0.14- 0.65)	<0.14	<0.14	<0.14	<0.29	<0.29		<0.29	<0.29

ND = Not Detected \* = Not Analyzed

Table 1.4: Direct photolysis data for X-PAHs [23, 30].

<b>Compound</b>	<b>k (1/h)</b>	<b>R<sup>2</sup></b>	<b>half-life (h)</b>
<b>Fluorene</b>	<b>Not Measured</b>		
2-bromofluorene	9.390	0.998	0.07
<b>Phenanthrene</b>	<b>0.038</b>	<b>0.852</b>	<b>18.19</b>
9-chlorophenanthrene*	0.112	0.993	6.19
3,9-dichlorophenanthrene*	0.510	0.992	1.40
9,10-dichlorophenanthrene*	0.252	0.987	2.80
3,9,10-trichlorophenanthrene	0.324	0.982	2.10
9-bromophenanthrene	0.938	0.999	0.74
<b>Fluoranthene</b>	<b>Not Measured</b>		
3-chlorofluoranthene	0.024	0.987	29.00
8-chlorofluoranthene	0.054	0.915	13.00
3,4-dichlorofluoranthene	0.048	896	14.00
3,8-dichlorofluoranthene	0.054	0.804	13.00
5,7-dichlorofluoranthene*	0.078	0.983	8.90
<b>Anthracene</b>	<b>0.227</b>	<b>0.827</b>	<b>3.06</b>
9-bromoanthracene	0.540	0.972	1.28
9,10-dibromoanthracene	1.466	0.999	0.47
<b>Pyrene</b>	<b>0.196</b>	<b>0.946</b>	<b>3.53</b>
1-chloropyrene	0.720	0.961	1.91
1-bromopyrene	0.426	0.985	1.63
<b>Benz[a]anthracene</b>	<b>0.459</b>	<b>0.923</b>	<b>1.51</b>
7-chlorobenz[a]anthracene	0.558	0.931	1.20
7-bromobenz[a]anthracene	0.483	0.977	1.44
4,7-dibromobenz[a]anthracene	0.607	0.974	1.10
5,7-dibromobenz[a]anthracene	0.833	0.961	0.83
7,11-dibromobenz[a]anthracene	1.540	0.982	0.45
7,12-dibromobenz[a]anthracene			<0.01
<b>Benzo(a)pyrene</b>	<b>0.734</b>	<b>0.861</b>	<b>0.90</b>
6-chlorobenzo(a)pyrene	1.212	0.894	0.57
6-bromobenzo(a)pyrene	0.321	0.984	2.25

\* denotes a compound that was not studied in this research



Table 1.5: Gas/Particle partitioning of Cl-PAHs [32].

#	Compound	MW	% Gas Phase	% Particle Phase
1	9-chlorofluorene*	199.66	97	6
2	2-chloroanthracene	212.68	64	36
3	9-chloroanthracene	212.68	92	8
4	3-chlorophenanthrene*	212.68	97	3
5	3-chlorofluoranthene	236.7	86	14
6	8-chlorofluoranthene	236.7	70	30
7	1-chloropyrene	236.7	69	31
8	9,10-dichloroanthracene	247.13	89	11
9	1,9-dichlorophenanthrene	247.13	88	12
10	3,9-dichlorophenanthrene*	247.13	97	3
11	9,10-dichlorophenanthrene*	247.13	89	11
12	7-chlorobenz[a]anthracene	262.74	36	64
13	6-chlorochrysene*	262.74	55	45
14	1,3,5,7-tetrachloronaphthalene*	265.95	100	0
15	1,2,3,4-tetrachloronaphthalene*	265.95	92	8
16	1,3-dichlorofluoranthene	271.15	87	13
17	3,4-dichlorofluoranthene	271.15	71	29
18	3,8-dichlorofluoranthene	271.15	90	10
19	3,9,10-trichlorophenanthrene	281.57	71	29
20	6-chlorobenz[a]pyrene	286.76	18	82
21	6,12-dichlorochrysene	297.19	64	36
22	7,12-dichlorobenz[a]anthracene	297.19	87	13
23	pentachloronaphthalene*	300.4	98	2
24	hexachloronaphthalene*	334.85	86	14
25	septachloronaphthalene*	369.29	74	26
26	octachloronaphthalene*	403.74	73	27

\* denotes a compound that was not studied in this project

Table 1.6: AhR-Mediated activities of X-PAHs [3, 23, 39]

Compound	EC <sub>50</sub> (µM)	REP <sub>BaP</sub>	(fg-TEQ)/m <sup>3</sup>	Contribution (%)
<b>(Fluorene)</b>	<b>Not Measured</b>			
2-bromofluorene	3.3	0.02	nd	0
<b>Anthracene</b>	<b>9.38</b>	<b>0.01</b>	<b>3.45</b>	<b>0.03</b>
1-chloroanthracene*	1.78	0.04	Not Measured	
2-chloroanthracene	0.65	0.1	0.18	0.002
9-chloroanthracene	2.51	0.03	0.04	0.0004
9,10-dichloroanthracene	0.32	0.2	0.88	0.008
9-bromoanthracene	4.35	0.01	nd	0
<b>Phenanthrene</b>	<b>15.14</b>	<b>0.004</b>	<b>13.8</b>	<b>0.12</b>
9-chlorophenanthrene*	2.07	0.03	0.31	0.003
1,9-dichlorophenanthrene	0.54	0.12	0.53	0.005
3,9-dichlorophenanthrene*	0.2	0.32	Not Measured	
9,10-dichlorophenanthrene*	0.39	0.16	0.38	0.003
3,9,10-trichlorophenanthrene	0.08	0.77	0.44	0.004
9-bromophenanthrene	2.72	0.02	nd	0
<b>(Fluoranthene)</b>	<b>Not Measured</b>			
3-chlorofluoranthene	0.38	0.17	4.41	0.038
8-chlorofluoranthene	0.35	0.18	1.06	0.009
<b>(Chrysene)</b>	<b>Not Measured</b>			
6-chlorochrysene*	0.03	2.1	17.4	0.151
6,12-dichlorochrysene	2.35	0.03	0.03	0.0002
<b>Pyrene</b>	<b>1.27</b>	<b>0.05</b>	<b>325</b>	<b>2.81</b>
1-chloropyrene	0.66	0.1	6.64	0.057
1-bromopyrene	1.56	0.04	1.19	0.01
<b>Benz[a]anthracene</b>	<b>0.05</b>	<b>1.4</b>	<b>4450</b>	<b>38.5</b>
7-chlorobenz[a]anthracene	0.08	0.08	0.92	0.008
7,12-dichlorobenz[a]anthracene	0.66	0.1	12	0.001
7-bromobenz[a]anthracene	0.07	0.84	11.5	0.099
4,7-dibromobenz[a]anthracene	0.08	0.77	2.48	0.021
5,7-dibromobenz[a]anthracene	3.71	0.02	2.9	0.025
7,11-dibromobenz[a]anthracene	1.03	0.06	nd	0
7,12-dibromobenz[a]anthracene	0.65	0.09	9.41	0.081
<b>Benzo(a)pyrene</b>	<b>0.06</b>	<b>1</b>	<b>6690</b>	<b>57.9</b>
6-chlorobenzo(a)pyrene	0.69	0.09	10.8	0.093
6-bromobenzo(a)pyrene	31.97	0.002	0.11	0.001

\* denotes a compound not studied in this project

ND = Not Detected

Table 1.7: TEQ concentrations of PAHs and other halogenated compounds [3, 23]

Matrix	Units	TEQ Concentrations			
		$\Sigma$ PAHs	$\Sigma$ Cl-PAHs	$\Sigma$ Br-PAHs	$\Sigma$ PCDD/F
e- waste shredder waste		2.86	308	*	66.9
e-waste soil	pg/g dry weight	19.1	92.3	*	70.6
e-waste leaf		4.22	361	*	147
e-waste floor dust		127	518	*	1070
industrial complex-soil		178	146	*	5.35
urban air	fg/m <sup>3</sup>	11500	44.1	27.5	*

\* = Not Analyzed

## References

1. Kitazawa, A., et al., *Temporal Trends and Relationships of Particulate Chlorinated Polycyclic Aromatic Hydrocarbons and Their Parent Compounds in Urban Air*. Environ. Sci. Technol., 2006. **40**: p. 4592-4598.
2. Horii, Y., et al., *Occurance and Profiles of Chlorinated and Brominated Polycyclic Aromatic Hydrocarbons in Waste Incinerators*. Environ. Sci. Technol., 2008. **42**: p. 1904-1909.
3. Ma, J., et al., *Chlorinated and Parent Polycyclic Aromatic Hydrocarbons in Environmental Samples from an Electronic Waste Recycling Facility and a Chemical Industrial Complex in China*. Environ. Sci. Technol., 2009. **43**: p. 643-649.
4. Eklund, G., and Stromberg, B., *Detection of Polychlorinated Polynuclear Aromatics in Flue Gases from Coal Combustion and Refuse Incinerators*. Chemosphere, 1983. **12**: p. 657-660.
5. Samuelson, U.a.L., A., *Chlorinated Compounds in Emissions from Municipal Incineration*. Chemosphere, 1983. **12**: p. 665-668.
6. Haglund, e.a., *Analysis of Halogenated Polycyclic Aromatic Hydrocarbons in Urban Air, Snow, and Automobile Exhaust*. Chemosphere, 1987. **16**: p. 2441-2450.
7. Shiraishi, e.a., *Occurance of Chlorinated Polynuclear Aromatic Hydrocarbons in Tap Water*. Environ. Sci. Technol., 1985. **19**: p. 585-590.
8. Koistinen, J.e.a., *Chlorophenanthrenes, Alkylchlorophenanthrenes, and Alkylchloronaphthalenes in Kraft Pulp Mill Products and Discharges*. Chemosphere, 1994. **28**: p. 1261-1277.
9. Koistinen, J.e.a., *Chlorinated Fluorenes and Alkylfluorenes in Bleached Kraft Pulp and Pulp Mill Discharges*. Chemosphere, 1994. **28**: p. 2139-2150.
10. Wong, M.H., et al, *Export of Toxic Chemicals- A Review of the Case of Uncontrolled Electronic-Waste Recycling*. Environmental Pollution, 2007. **149**: p. 131-140.
11. Schwarzer, S., et al., *Environment Alert Bulletin: E-waste, the Hidden Side of IT Equipment's Manufactureing and Use*, UNEP, Editor. 2005.
12. Yu, X.Z., et al., *Distribution of polycyclic aromatic hydrocarbons in soils at Guiyu area of China, affected by recycling of electronic waste using primitive technologies*. Chemosphere, 2006. **65**: p. 1500-1509.
13. Li, H., et al., *Severe PCDD/F and PBDD/F Pollution in Air around an Electronic Waste Dismantling Area in China*. Environ. Sci. Technol., 2007. **41**: p. 5641-5646.
14. Puckett, J.e.a., *Exporting Harm: The High-Tech Trashing of Asia*, T.B.A. Network, Editor. 2002.
15. EPA, U.S., *Municipal Solid Waste Generation, Recycling, and Disposal in the United States: Detailed Tales and Figures for 2008*. 2009.
16. Dhanda, K., and Peters, A., *Reverse Logistics in the Computer Industry*. International Journal of Computers, Systems, and Signals, 2005. **6**: p. 57-67.

17. Arensmann, R., *Ready for Recycling*. Electronic Business, 2000. **26**: p. 108.
18. EPA, U.S., *Municipal Solid Waste Generation, Recycling, and Disposal in the United States: Detailed Tables and Figures for 2008*, U.S.E.O.o.R.C.a. Recovery, Editor. 2009.
19. Greenpeace. (2007) *Toxic tea Party*. Greenpeace.org.
20. Ni, H.-H.a.Z., Eddy, *Law Enforcement and Global Collaboration are the Keys to Containing E-waste Tsunami in China*. Environ. Sci. Technol., 2009. **43**: p. 3991-3994.
21. Carroll, C. (2008) *High-Tech Trash*. National Geographic.
22. Chi, X.e.a., *Informal electronic waste recycling: A sector review with special focus on China*. Waste Management, 2011. **31**: p. 731-742.
23. Ohura, T., et al., *Discovery of Novel Halogenated Polycyclic Aromatic Hydrocarbons in Urban Particulate Matters: Occurrence, Photostability, and AhR Activity*. Environ. Sci. Technol., 2009. **43**: p. 2269-2275.
24. EPA, U.S., *Estimation Programs Interface Suite™ for Microsoft® Windows, v 4.00*. 2010, United States Environmental Protection Agency, Washington DC, USA.
25. Schwarzenbach, R., et al., *Environmental Organic Chemistry*. Second Edition ed. 2003, Hoboken, NJ: Wiley-Interscience.
26. Opreko, D., *Review of Exposure Assessment Guidelines*, S.E.R.a.D. Program, Editor. 1996.
27. Ishaq, R.e.a., *PCBs, PCNs, PCDD/Fs, PAHs and Cl-PAHs in Air and Water Particulate Samples- Patterns and Variations*. Chemosphere, 2003. **50**: p. 1131-1150.
28. Lang, C., et al., *Atmospheric Transport and Outflow of Polycyclic Aromatic Hydrocarbons from China*. Environ. Sci. Technol., 2008. **42**: p. 5196-5201.
29. Nilsson, U.a.O., C., *Chlorinated Polycyclic Aromatic Hydrocarbons: Method of Analysis and Their Occurrence in Urban Air*. Environ. Sci. Technol., 1993. **27**: p. 1826-1831.
30. Ohura, T., et al., *Occurrence, Profiles, and Photostabilities of Chlorinated Polycyclic Aromatic Hydrocarbons Associated with Particulates in Urban Air*. Environ. Sci. Technol., 2005. **39**: p. 85-91.
31. Ohura, T., *Environmental Behavior, Sources, and Effects of Chlorinated Polycyclic Aromatic Hydrocarbons*. TheScientificWorldJOURNAL, 2007. **7**: p. 372-380.
32. Ohura, T., et al., *Chlorinated Polycyclic Aromatic Hydrocarbons in the Atmosphere: Seasonal Levels, Gas-Particle Partitioning, and Origin*. Environ. Sci. Technol., 2008. **42**: p. 3296-3302.
33. EPA, U.S. *Particulate Matter: Health and Environment*. 2010 August 06, 2010 [cited 2010 September, 24]; Available from: <http://www.epa.gov/particles/health.html>.

34. Ohura, T., et al, *Spatial Distributions and Profiles of Atmospheric Polycyclic Aromatic Hydrocarbons in Two Industrial Cities in Japan* Environ. Sci. Technol., 2004. **38**: p. 49-55.
35. Ohura, T., et al, *Differential Action of Chlorinated Polycyclic Aromatic Hydrocarbons on Aryl Hydrocarbon Receptor-Mediated Signaling in Breast Cancer Cells*. Environmental Toxicology, 2010. **25**: p. 180-187.
36. Latchman, D., *Transcription Factors: An Overview* Int. J. Biochem. Cell. Biol., 1997. **29**: p. 1305-1312.
37. Denison, M., et al, *Ligand Binding and Activation of the Ah Receptor*. Chemico-Biological Interactions, 2002. **141**: p. 3-24.
38. Johnsen, S., et al, *Formation of Chlorinated PAH- A Possible Health Hazard From Water Chlorination*. The Science of the Total Environment, 1989. **81/82**: p. 231-238.
39. Ohura, T., et al, *Aryl Hydrocarbon Receptor- Mediated Effects of Chlorinated Polycyclic Aromatic Hydrocarbons*. Chem. Res. Toxicol., 2007. **20**: p. 1237-1241.
40. NIH. *IUPAC Glossary of Terms Used in Toxicology*. 2007 11 March 2009 [cited 2010 10/12]; Available from:  
<http://sis.nlm.nih.gov/enviro/iupacglossary/glossarym.html>.
41. EPA, U.S. *TRI Dioxin and Dioxin-like Compounds Toxic Equivalency (TEQ) Information Rule*. 2008.
42. Blankenship, A., et al, *Relative potencies of Individual Polychlorinated Napthalenes and Halowax Mixtures to Induce Ah Receptor-Mediated Responses*. Environ. Sci. Technol., 2000. **34**: p. 3153-3158.

## CHAPTER 2

**Trace Analysis of Halogenated Polycyclic Aromatic Hydrocarbons from an Electronic Waste Recycling Area and Guangzhou, China**

Leah R. Gonzales<sup>1</sup>, Shejun Chen<sup>2</sup>, Wang Jing<sup>2</sup>, Takeshi Ohura<sup>3</sup>, and Staci Simonich<sup>1,4\*</sup>

<sup>1</sup>Department of Chemistry, Oregon State University, 153 Gilbert, Corvallis Oregon 97331

<sup>2</sup>Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, 511 Kehua Street, Wushan, Tianhe District, Guangzhou, GD 510640

<sup>3</sup>Institute for Environmental Sciences, University of Shizuoka, 52-1 Yada, Shizuoka 422-8526, Japan

<sup>4</sup>Department of Environmental and Molecular Toxicology, Oregon State University, 1007 ALS, Corvallis Oregon 97331

\*Corresponding Author

Prepared for submission to: Environmental Toxicology and Chemistry  
Society of Environmental Toxicology and Chemistry North America  
1010 North 12<sup>th</sup> Avenue  
Pensacola, FL 32501

## Abstract

Halogenated Polycyclic Aromatic Hydrocarbons (X-PAHs) are ubiquitous contaminants that are thought to be generated by processes such as chemical industries and incomplete combustion, including waste incineration and electronic waste (e-waste) burning. X-PAHs are a concern for environmental and human health because they are toxic, mutagenic, and are expected to be more lipophilic than the parent compounds. To study these compounds in the environment, an analytical method was developed, utilizing large-volume injection via a programmable temperature vaporizing (PTV) inlet, using environmental samples from an e-waste area and in Guangzhou, China. The concentrations of 26 X-PAHs were measured in atmospheric particulate matter (PM), house dust (HD), and sediment. In general, the X-PAH concentrations in PM were low, with concentrations ranging from  $<0.078$  to  $41.81$   $\text{pg}/\text{m}^3$ . There was no significant difference in X-PAH concentrations between the e-waste area and Guangzhou. These concentrations are of the same order of magnitude as previous studies of X-PAHs in PM. These data suggest that e-waste activities are not a significant source of X-PAHs in atmospheric PM. The concentrations of X-PAHs in HD samples ranged from  $<0.0372$  to  $3575$   $\text{pg}/\text{g}$  dry weight. In general, there was no significant difference between E-waste and Guangzhou HD concentrations. The profiles of X-PAHs in PM and HD were different, suggesting that there are additional sources for X-PAHs inside homes other



than outdoor air. The concentrations of X-PAHs in sediment samples from an e-waste site ranged from <104 to 2890 pg/g dry weight.

## **Introduction**

PAHs are ubiquitous environmental contaminants, produced by both natural and anthropogenic sources [43]. Multi-substituted PAHs (including halogenated PAHs (X-PAHs)) are also produced. X-PAHs are produced primarily from incomplete combustion, and are emitted from a variety of sources including chemical industries [3], waste incinerators (especially older, fixed grate-type incinerators) [2, 4, 5], leaded gasoline automobile exhaust [6], water chlorination facilities [7], and Kraft Mills [8, 9]. Previous studies suggest that the incineration of electronic waste (e-waste) during the e-waste recycling process (e-cycling) is also a source of X-PAHs [3]. E-cycling emissions are of concern due to the magnitude and composition of the waste involved and the conditions under which the workers labor.

The world generates between 22 to 55 million tons of e-waste each year, and the volume of e-waste increases approximately 4% annually [11]. The United States alone generated 3.16 million tons of e-waste in 2008 [15]. This waste is disposed of by being buried in landfills, or by e-cycling. However, not American-generated all e-waste collected for recycling is actually e-cycled in the U.S. (using modern equipment and appropriate regulations). Approximately 50-80% of e-waste collected in the U.S.

is exported (sometimes illegally) to developing countries to be e-cycled there [11, 16-19]. China is the world's largest importer and recycler of e-waste [20].

E-waste is a mixture of hundreds of compounds, many of them toxic. Some of these compounds are metals such as mercury, lead, cadmium, and chromium. Other compounds, such as polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), PAHs, and flame retardants such as polybrominated biphenyls (PBBs) and polybrominated diphenyl ethers (PBDEs) are also present in e-waste [3, 11-14].

The e-cycling process is not recycling in the conventional sense of turning a useless item into a useful one; but entails only the removal of the valuable metal components (i.e.: gold, silver, palladium, aluminum, and copper) for resale, and the subsequent disposal of the remaining materials [10, 14, 44]. Using proper equipment and precautions, e-cycling is safe. However, this is often not the case when the e-cycling occurs in a developing country, where there are lax or unenforced environmental regulations and health protocols [10, 11, 14].

E-cycling workers first dismantle and sort the electronic equipment. Next, the metals are salvaged using techniques such as the dry roasting of circuit boards, the use of open acid baths, and the burning of cables. The resulting waste is disposed of by shredding, melting and burning plastic materials in open air and disposing (dumping) of the waste in nearby fields and riverbanks [10, 14]. As e-waste recycling is often a household business, the recovery and disposal processes are carried out in

the homes and yards of the workers. Not only do the workers perform these tasks without adequate personal protection equipment, in some cases cooking pots and utensils are used to process the waste [10, 14, 44].

These conditions have devastating consequences for the environment. The e-waste recycling village of Guiyu in Guangdong, China, has the highest documented values of PCDD/Fs abundances in ambient air in the world [13]. Local streams and lakes (sources of fresh water) are so polluted that fresh water must be shipped in from nearby villages, at great expense [19].

## **Materials and Methods**

### Sampling

The X-PAHs were measured in particulate matter (PM) and house dust (HD) from the city of Guangzhou in South-East China, and in several villages in Qingyuan city, an e-waste area located approximately 60 km NW of Guangzhou. X-PAH concentrations were also measured in sediment collected from the e-waste area. The samples were collected January 16 through January 29, 2010. The atmospheric particulate matter samples were collected on quartz fiber filters (Tisch Environmental Inc, OH). The filters were prepared for sampling by baking for four hours at 450 °C. After cooling, the filters were weighed, then wrapped in aluminum foil and stored in polyethylene bags until use. After sampling, the filters were returned to the foil and

plastic bag and stored at -20°C until extraction. The house dust (HD) samples were collected using solvent cleaned brushes from the surface of furniture, tables, windowsills, and floors of the bedroom and living room areas. The samples were wrapped in foil and stored in polyethylene bags at -20°C until extraction [45]. The sediment samples were collected using a stainless steel grab sampler. The top five cm of sediment were freeze-dried, ground, and homogenized by sieving through a 0.05mm stainless steel mesh, and stored at -20°C until extraction. There were 16 samples collected in total: seven PM samples (four from Guangzhou, and three from the e-waste area), seven HD samples (two from Guangzhou, and five from the e-waste area) and two sediment samples (both from the e-waste area). A map of the sampling locations is shown in Fig 2.1 [46].

### Chemicals

The 26 X-PAHs were synthesized by Dr. Takeshi Ohura from the University of Shizuoka in Shizuoka, Japan, using published procedures [1, 30]. The chlorinated PAHs are abbreviated as follows: 2-chloroanthracene (2-ClAnt), 9-chloroanthracene (9-ClAnt), 9,10-dichloroanthracene (9,10-Cl<sub>2</sub>Ant), 1,9-dichlorophenanthrene (1,9-Cl<sub>2</sub>Phen), 3,9,10-trichlorophenanthrene (3,9,10-Cl<sub>3</sub>Phen), 3-chlorofluoranthene (3-ClFluor), 8-chlorofluoranthene (8-ClFluor), 3,4-dichlorofluoranthene (3,4-Cl<sub>2</sub>Fluor), 3,8-dichlorofluoranthene (3,8-Cl<sub>2</sub>Fluor), 1,3-dichlorofluoranthene (1,3-Cl<sub>2</sub>Fluor), 1-chloropyrene (1-ClPy), 6,12-dichlorochrysene (6,12-Cl<sub>2</sub>Chr), 7-

chlorobenz[a]anthracene (7-ClBaA), 7,12-dichlorobenz[a]anthracene (7,12-Cl<sub>2</sub>BaA), and 6-chlorobenzo(a)pyrene (6-ClBaP). The brominated PAHs are abbreviated as follows: 2-bromofluorene (2-BrFlu), 9-bromophenanthrene (9-BrPhen), 9-bromoanthracene (9-BrAnt), 9,10-dibromoanthracene (9,10-Br<sub>2</sub>Ant), (1-bromopyrene (1-BrPy), 7-bromobenz[a]anthracene (7-BrBaA), 7,11-dibromobenz[a]anthracene (7,11-Br<sub>2</sub>BaA), 7,12-dibromobenz[a]anthracene (7,12-Br<sub>2</sub>BaA), 4,7-dibromobenz[a]anthracene (4,7-Br<sub>2</sub>BaA), 5,7-dibromobenz[a]anthracene (5,7-Br<sub>2</sub>BaA), and 6-bromobenzo(a)pyrene (6-BrBaP). The structures of these compounds are shown in Fig 2.2 and 2.3. The internal standards (<sup>13</sup>C<sub>6</sub>-1-chloropyrene and <sup>13</sup>C<sub>12</sub>-PCB-138) were purchased from Cambridge Isotope Laboratories (Cambridge, MA). Solvents were optima-grade, and purchased from Fisher Scientific (Fairlawn, NJ).

#### Extraction and Concentration

The samples were extracted by accelerated solvent extraction (ASE 300, Dionex). Each PM filter was placed in a 66 mL ASE cell and spiked with a surrogate (<sup>13</sup>C<sub>6</sub>-1-chloropyrene) before extraction. The sediment and dust samples were ground with baked Na<sub>2</sub>SO<sub>4</sub> prior to spiking the surrogate to remove any residual water and to facilitate extraction. The PM samples were extracted twice using a 1:1 ratio of hexane: acetone. The extraction was performed under the following conditions: the cell temperature was 100°C, the static time was five minutes, the flush volume was 100% of the cell volume and the purge time was 240 seconds [47]. The sediment and

HD samples were extracted under the same conditions as the particulate matter samples, however, the solvent mixture was a 3:1 ratio of hexane: acetone mixture [48]. After extraction, the samples were solvent exchanged to hexane, and concentrated to ~1000  $\mu\text{L}$  using a Turbovap® II (Biotage, Charlotte, NC).

### Clean Up

The samples were purified using solid phase extraction (SPE) with silica as a stationary phase. The pre-packed columns contained 20 g of silica (Varian, Inc). The columns were conditioned using 50 mL each of ethyl acetate (EA), dichloromethane (DCM), and hexane. The samples were loaded on the silica and eluted using 50 mL of the following solvent mixtures: 100% hexane, 90% hexane: 10% DCM (90:10), 80% hexane: 20% DCM, 100% DCM, and 100% EA. The fractions were then solvent exchanged to ethyl acetate, and concentrated to ~400  $\mu\text{L}$ , and then further concentrated under a gentle stream of nitrogen gas to 300 $\mu\text{L}$ . The fractions were then spiked with an internal standard ( $^{13}\text{C}_{12}$ -PCB-138). The X-PAHs and internal standards eluted in the 90:10 fraction.

### Instrument Analysis

The 90:10 fraction from the silica SPE was analyzed on an Agilent 6890 gas chromatograph (GC) coupled to a 5793N mass spectrometer (MS), using a 30 m x 0.25mm x 0.25  $\mu\text{m}$  DB-5MS column (J&W Scientific, Palo Alto, CA). The oven

programming was as follows: initial temperature of 60°C for one minute, a temperature ramp of 25 °C/minute until the oven reached 200°C with no hold, another temperature ramp of 3°C/minute until 300°C, with a hold time of 10 minutes, at 300°C. The names, abbreviations and NCI ions monitored for each of the X-PAHs are shown in Table 2.1., while the structures are shown in Fig. 2.2 and 2.3.

## **Results and Discussion**

### Selection of Ionization Technique

To determine which MS ionization technique was the most sensitive, the X-PAH standard was analyzed using both electron impact (EI) and negative-ion chemical ionization (NCI) ionization modes. To compare the differences in EI and NCI mode, 1 µL of 1000 pg/µL X-PAH standard (1 ng of standard) was injected using a splitless injection. When used in EI mode, all 31 of the X-PAHs in the standard were detected, as shown in Fig 2.4. When used in NCI mode, only 26 of the 31 compounds in the standard were detected, as not all X-PAHs were ionized in NCI mode, as shown in Figure 2.5. The compounds that were not detected in NCI mode are: 9-chlorofluorene, 9-chlorophenanthrene, 3,9-dichlorophenanthrene, 9,10-dichlorophenanthrene, and 6-chlorochrysene. The structures of these compounds are shown in Fig 2.6. Even though fewer compounds were ionized in NCI mode, there was an order of magnitude greater sensitivity for those compounds (Fig 2.6). Therefore, NCI ionization was used to analyze the samples.

### Selection of Injection Method

As previous studies reported low X-PAH concentrations in samples, it was necessary to increase the sensitivity of the analytical method. To do this, a larger volume of extract was injected using a programmable temperature vaporizing (PTV) inlet. Multiple (1  $\mu\text{L}$ ) injections of an extract are held in the PTV inlet while carrier gas (He) flows through the inlet, removing solvent and concentrating the sample. As the X-PAH method was developed before any of the e-waste or Guangzhou samples had been collected, an atmospheric PM sample from Beijing was used as a representative sample to simulate matrix effects. The Beijing PM sample was analyzed using both splitless injection (using a one  $\mu\text{L}$  injection), and a PTV inlet used in solvent vent mode (using several different injection volumes- 1, 2, 3, 4, 5, 7 and 9  $\mu\text{L}$ ) to determine which inlet yielded greater sensitivity.

With PTV injection, it is possible that some of the lower MW X-PAHs are preferentially lost before analysis via the carrier gas. Even though there may be some loss of the more volatile X-PAHs, such as 2-BrFlu, 2-ClAnt, and 9-ClAnt, the larger volume of injected sample makes up for this. This is demonstrated in Fig 2.7 and 2.8, for although there is three times the amount of standard injected in Fig 2.8, there is not a three-fold increase in response for the lower MW compounds.

The ideal injection volume would be large enough to meet the necessary 10:1 signal to noise ratio for quantitation. Several injection volumes are shown in Fig 2.9.



Of the different large volume injections, the five  $\mu\text{L}$  injection had the necessary 10:1 signal to noise ratio for all X-PAHs considered, as shown in Table 2.2. However, the large volume (5  $\mu\text{L}$ ) deposited too much material on the column, resulting in significant noise, significant retention time shifts from the standard, and excessive instrument maintenance. Therefore, the three  $\mu\text{L}$  injection was used, even though some targets did not have a 10:1 signal to noise ratio. This injection volume was not ideal; however, it was a necessary balance between increased signal to noise and excessive instrument maintenance.

#### Analytical Method Validation

A recovery experiment was performed in triplicate to determine the percent loss of X-PAHs during sample preparation. Three blank filters were spiked with 15  $\mu\text{L}$  of 10  $\text{ng}/\mu\text{L}$  of X-PAH standard (resulting in a final concentration of 500  $\text{pg}/\mu\text{L}$ ). The filters were then prepared as actual samples, and spiked with a surrogate and internal standard just prior to analysis.

The average X-PAH recovery was  $60.1 \pm 21.0$  (RSD) % for the entire analytical method. The recoveries of each X-PAH are shown in Table 2.1. The X-PAH recovery percentage increased as the molecular weight (MW) of the X-PAH increased, indicating that the lower MW X-PAHs may have undergone preferential loss during  $\text{N}_2$  blow down.

The X-PAH estimated detection limits for the method were determined using EPA method 8280A [49]. The detection limits were low; most compounds had detection limits lower than 0.50 pg/ $\mu$ L. The detection limits for each compound are shown in Table 2.1.

### Halogenated PAH Measurements

The mean X-PAH concentrations measured in PM are shown in Table 2.3. Generally, the X-PAH concentrations were low; and only seven of the 26 X-PAH measured were detected in both locations. The range of mean X-PAH concentrations in urban air from Guangzhou was 0.262 to 23.09 pg/m<sup>3</sup>, and 0.0779 to 13.43 pg/m<sup>3</sup> from the e-waste area. The mean X-PAH concentrations in PM from these two locations were not statistically different (Table 2.3). In addition, the X-PAH profiles in PM from Guangzhou and the e-waste area were similar and well correlated, as shown in Figs. 2.10 and 2.11. This suggests that the X-PAH sources in Guangzhou and the e-waste area are similar, and that the X-PAH concentrations in the e-waste area are not higher than the X-PAH concentrations in Guangzhou.

The mean X-PAHs concentrations on PM in Guangzhou and in the e-waste area are similar to what has been reported in previous studies (Table 2.4). While there is some variation in concentrations among the different studies, all X-PAH concentrations were the same order of magnitude. As there was no statistical difference between e-waste and Guangzhou X-PAH PM concentrations, and these X-

PAH concentrations are similar to what has been measured elsewhere, it can be concluded that e-waste activities do not contribute significantly to X-PAH concentrations on atmospheric PM. These results are surprising, considering previously reported literature data on e-waste activities [2, 3].

The mean X-PAH concentrations in HD from Guangzhou and the e-waste area are shown in Table 2.5. The X-PAH in highest concentration in HD from Guangzhou and the e-waste area was 1-CIPy, which was measured at 3575pg/g dry weight, and 2103 pg/g dry weight, respectively. The mean X-PAH concentrations in HD from Guangzhou were not statistically different from the e-waste area, except for 1-CIPy (Table 2.5). In fact, the 1-CIPy concentrations were higher in HD from Guangzhou than HD from the e-waste area.

The X-PAH concentrations measured in sediment samples from the e-waste area are shown in Table 2.6. The highest concentrations of X-PAHs detected in sediment was 6-CIBaP, which was measured at 2348.57 pg/g dry weight. Only two sediment samples were collected (from different ponds). However, the mass of sample collected from location #3 was quite small (0.1 grams) in contrast to the mass collected from location #1 (0.7 g). This small sample resulted in a low X-PAH mass. Therefore, only 1-CIPy and 6-CIBaP were measured above the quantification limit in the sample from location #3.

The X-PAH profiles in PM, HD, and sediment from the e-waste site were different, as shown in Fig 2.13. The PM profile was composed of roughly equal amounts of 1-ClPy and 6-ClBaP, with smaller amounts of 3-ClFluor, 8-ClFluor, and 7-ClBaA. In contrast, the HD profile was primarily made up of 3-ClFluor and 1-ClPy, and a smaller amount of 8-ClFluor. There was no correlation between the X-PAH profile in PM and HD from the e-waste area as shown in Fig 2.14. Several X-PAHs (3-ClFluor, 8-ClFluor and 6,12-Cl<sub>2</sub>Chr) made up a higher percentage in HD than in PM. This suggests that the X-PAHs in HD come from additional sources from inside the home, including heating and cooking. The X-PAH profile of sediment more closely resembled that of PM.

The X-PAH profiles in PM and HD from Guangzhou were also different (Fig 2.10). The Guangzhou PM profile was primarily composed of 6-ClBaP and to a smaller extent, 1-ClPy. In contrast, the Guangzhou HD profile was mostly 1-ClPy, with a much smaller amount of 3-ClFluor. There was no significant correlation between PM and HD from Guangzhou, as shown in Fig 2.15, which also implies that there are additional X-PAH sources inside the homes in Guangzhou.

## Conclusion

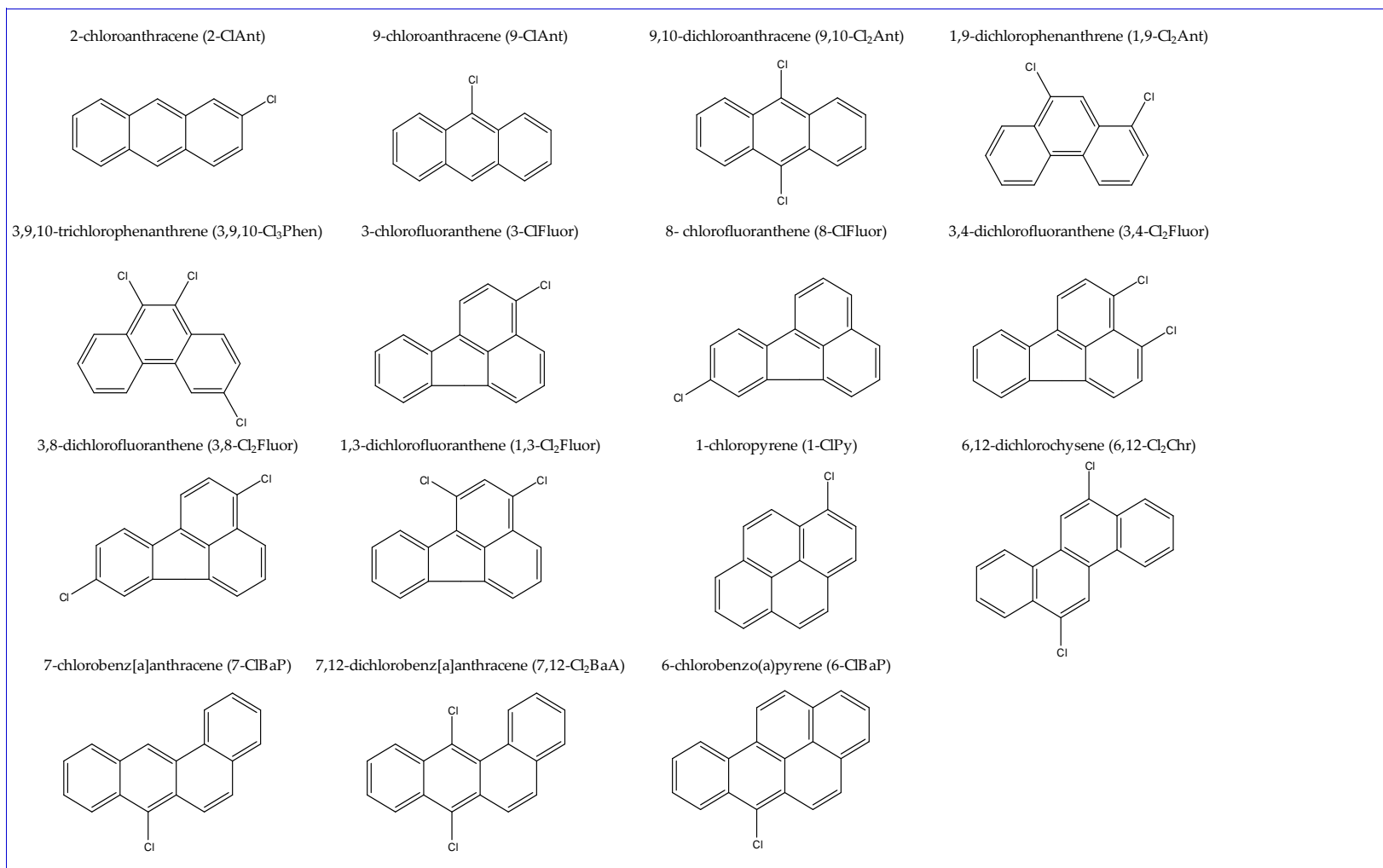
The X-PAH concentrations in PM and HD were compared in Guangzhou, China and a nearby e-waste area to understand if e-waste burning is a significant source of X-PAHs. There was no statistical difference in the X-PAH concentrations in PM and HD from Guangzhou and the e-waste area. The X-PAH PM profiles of the two locations were similar. In addition, the X-PAH PM concentrations were on the same order of magnitude as previous X-PAH PM measurements. These data imply that e-waste activities are not a major source of X-PAHs to atmospheric PM.

In addition, the X-PAH profiles in PM and HD in Guangzhou and the e-waste area were different. This suggests that there are additional X-PAH sources inside the Guangzhou and E-waste area homes. The X-PAH profile for sediment from the e-waste area more closely resembled that of PM.

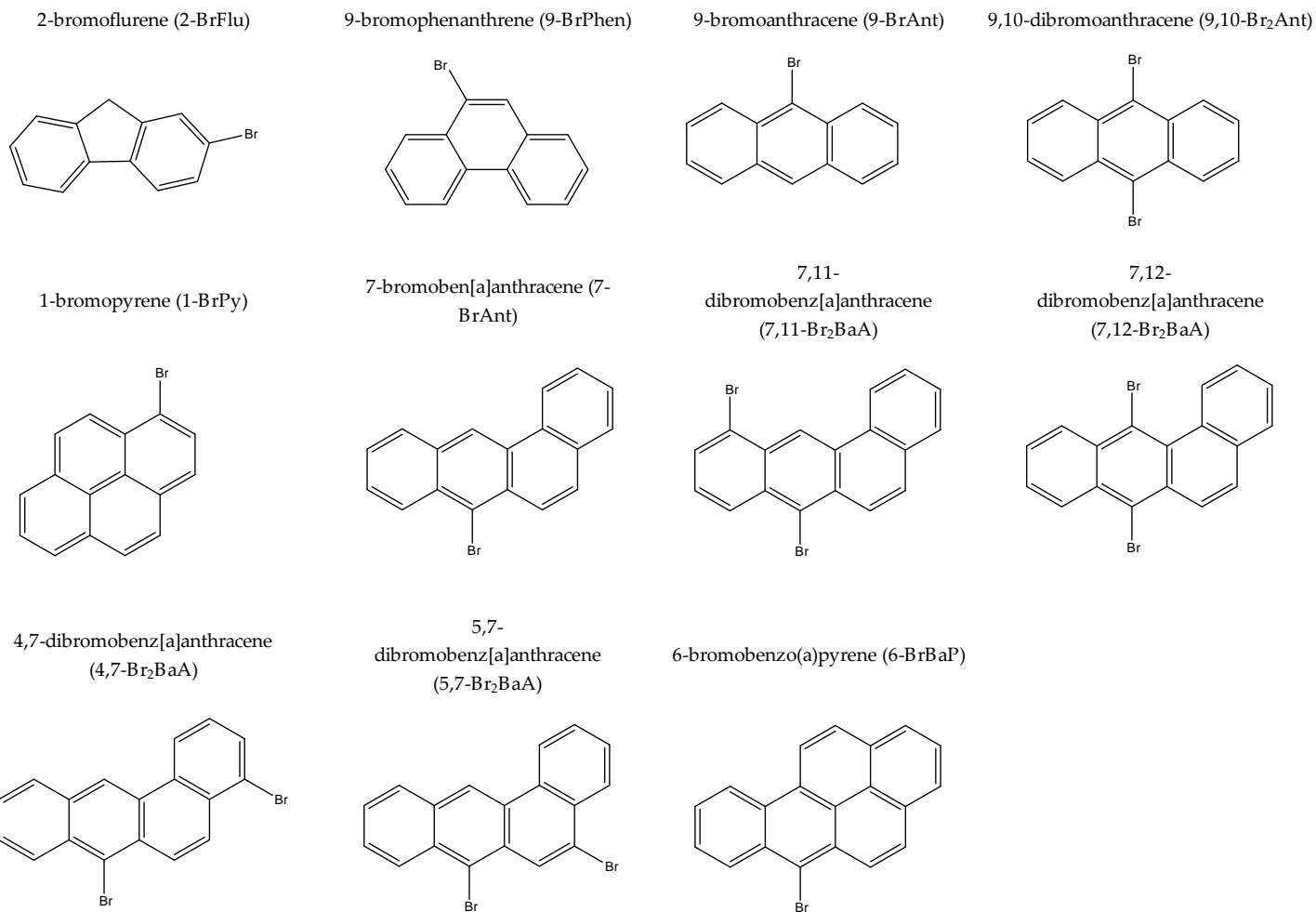
Fig 2.1: Map of Sampling Locations [46].



**Fig 2.2: Structures of Cl-PAHs studied.**

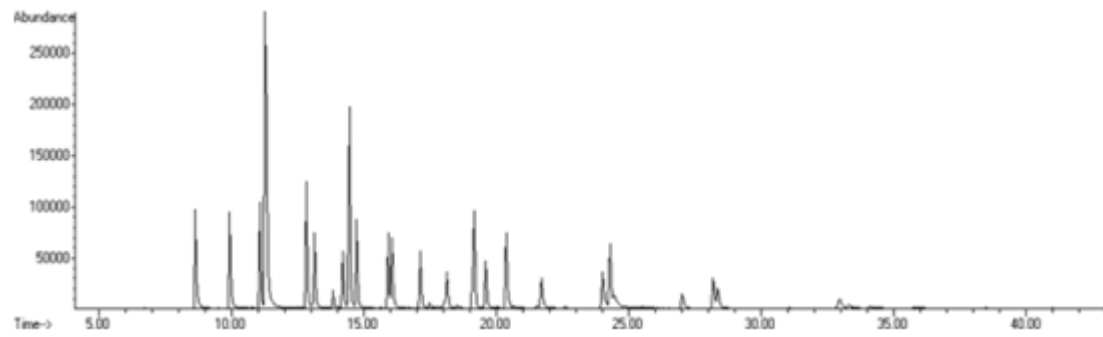


**Fig 2.3: Structures of Br-PAHs studied.**

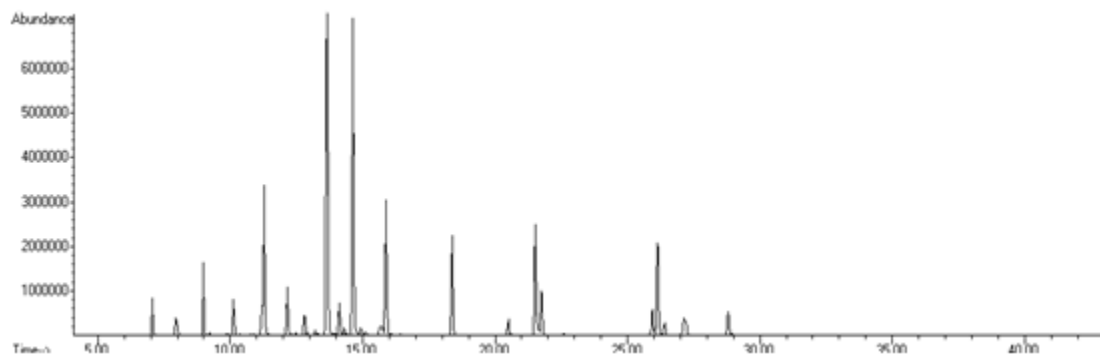




**Fig 2.4: Chromatogram of one  $\mu\text{L}$  splitless injection of X-PAH standard in EI mode (1 ng of X-PAH standard injected).**



**Fig 2.5: Chromatogram of one  $\mu\text{L}$  splitless injection of X-PAH standard in NCI mode (1 ng of X-PAH standard injected).**



**Fig 2.6: Structures of Cl-PAHs not ionized in NCI ionization.**

9-chlorofluorene

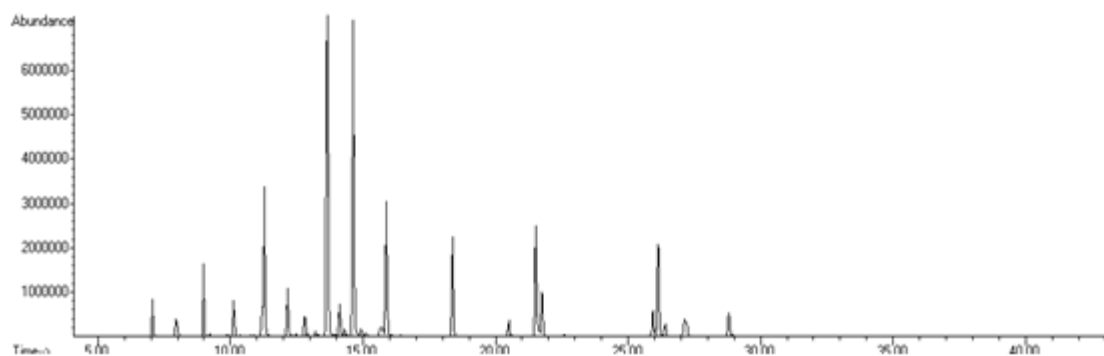
9-chlorophenanthrene

9,10-dichlorophenanthrene

3,9-dichlorophenanthrene

6-chlorochrysene

**Fig 2.7: Chromatogram of X-PAH standard using 1  $\mu$ L splitless injection (and NCI ionization). 1 ng of X-PAH standard injected.**



**Fig 2.8: Chromatogram of X-PAH standard using 3  $\mu$ L solvent vent injection using PTV inlet (and NCI ionization). 3 ng of X-PAH standard injected.**

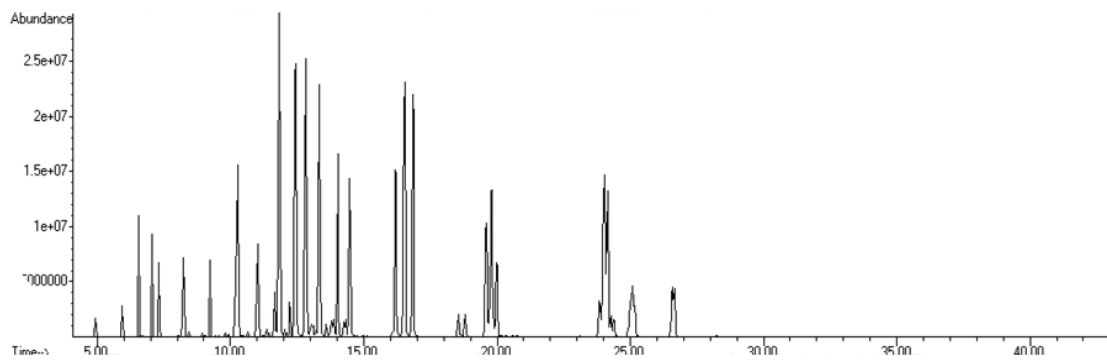
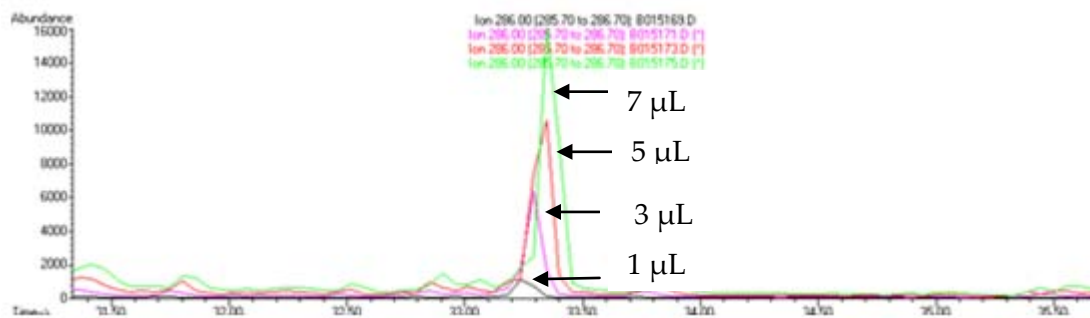


Fig 2.9: Chromatogram of four different PTV injection volumes for  $m/z=286$  for 6-CIBaP (using NCI ionization).



**Fig 2.10: X-PAH Profile in particulate matter and house dust from Guangzhou and an E- waste area. The error bars represent the standard deviation.**

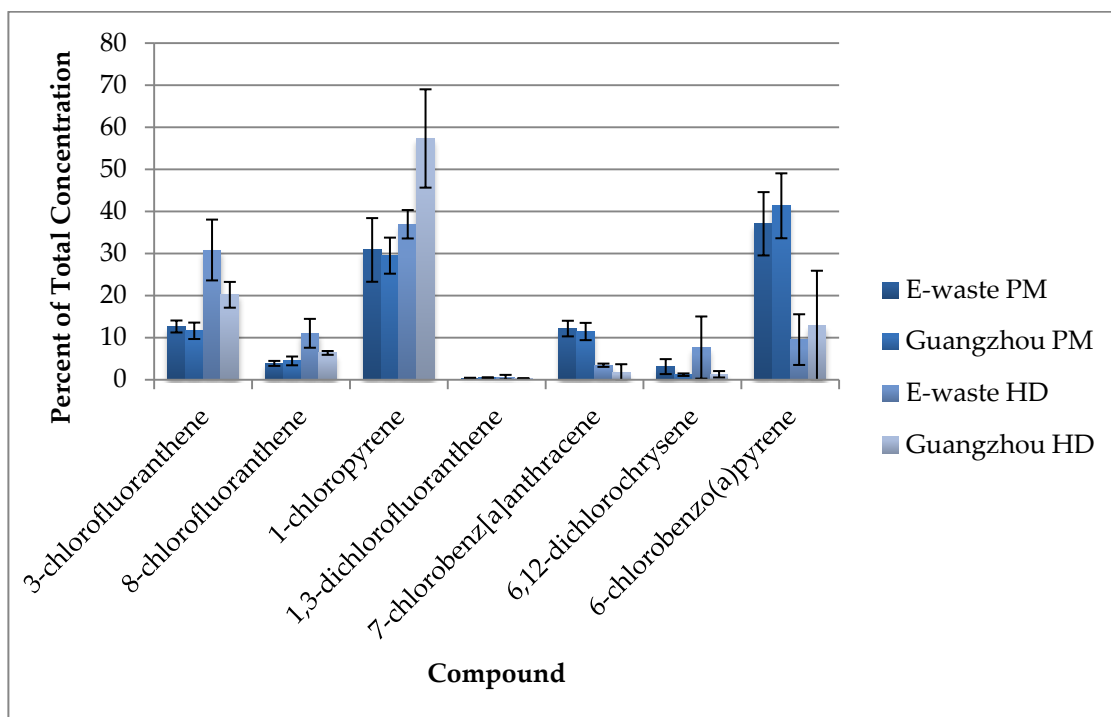
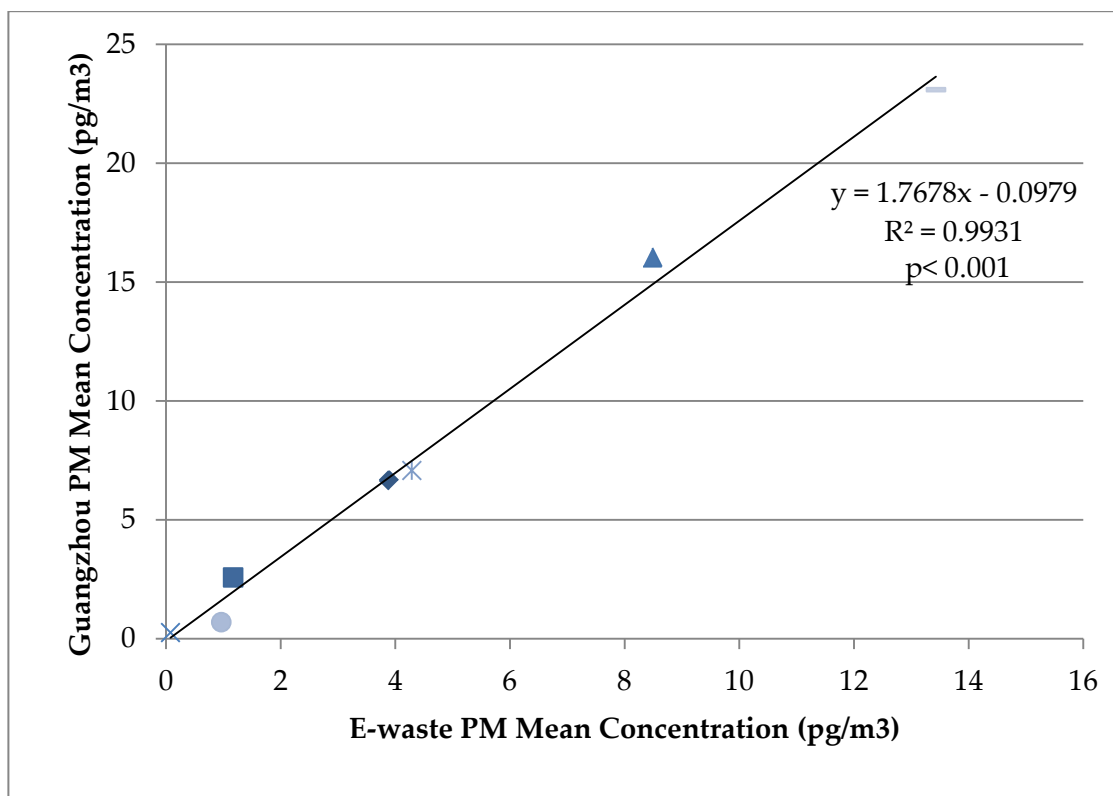


Fig 2.11: Relationship between X-PAH concentrations in particulate matter from an E-waste site and Guangzhou, China (correlation of E-waste and Guangzhou PM Concentrations is statistically significant when  $p < 0.05$ ).





**Fig 2.12: Relationship between X-PAH concentrations in house dust from an E-waste site and Guangzhou, China (correlation of E-waste and Guangzhou house dust concentrations is statistically significant when  $p < 0.05$ ).**

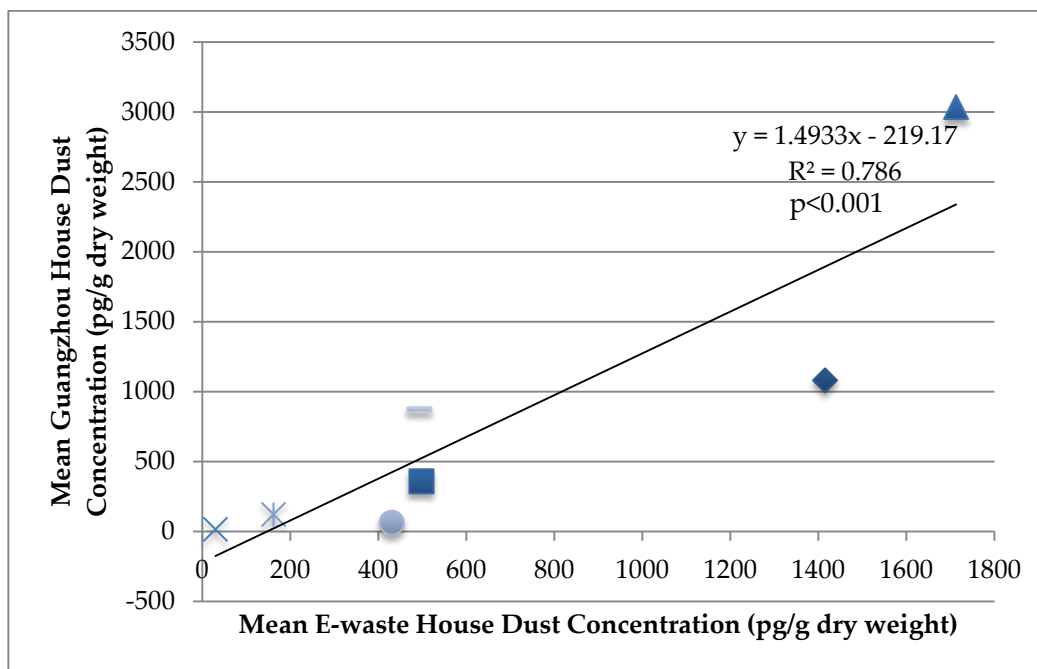


Fig 2.13: X-PAH profile for particulate matter, house dust, and sediment from an E-waste area. The error bars represent the standard deviation.

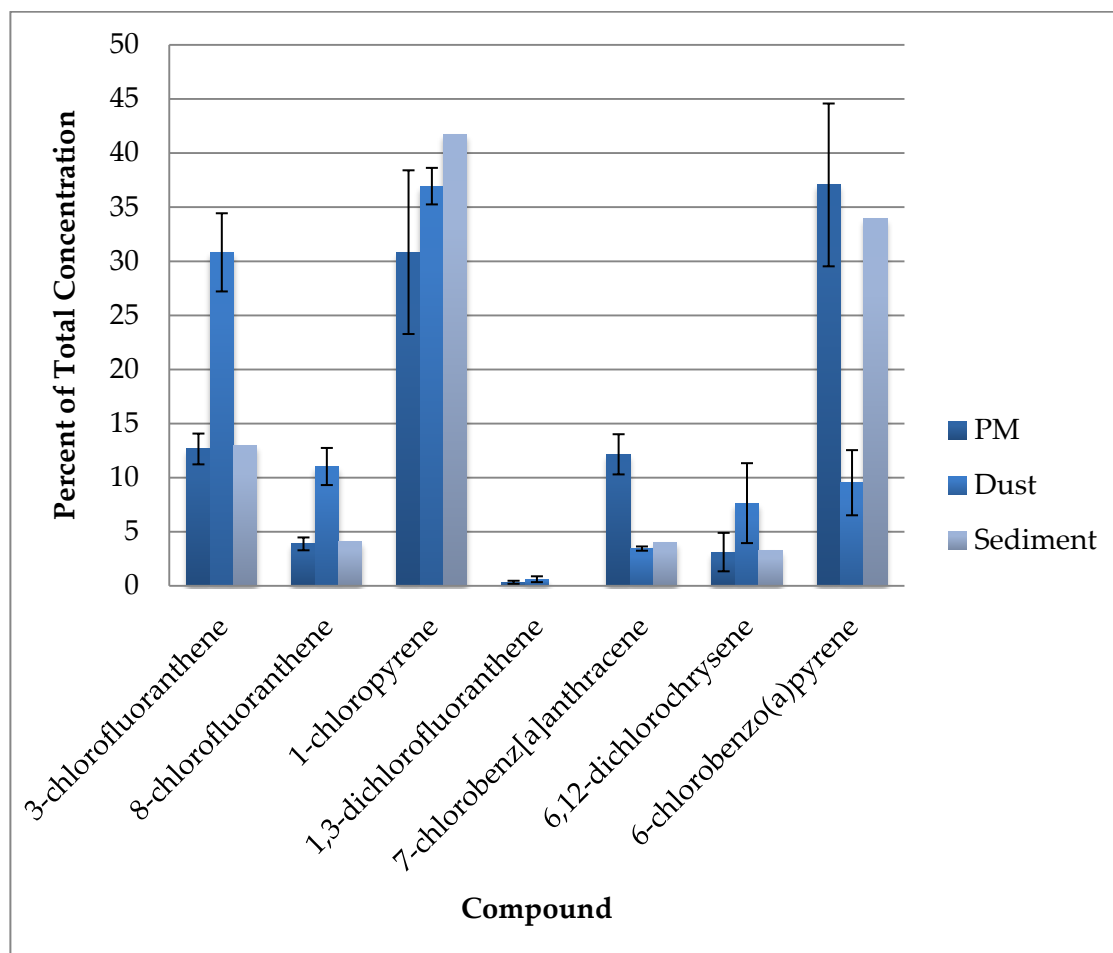


Fig 2.14: Relationship between mean X-PAH concentrations in dust and particulate matter from an E-waste area (correlation of dust and PM concentrations is statistically significant when  $p < 0.05$ ).

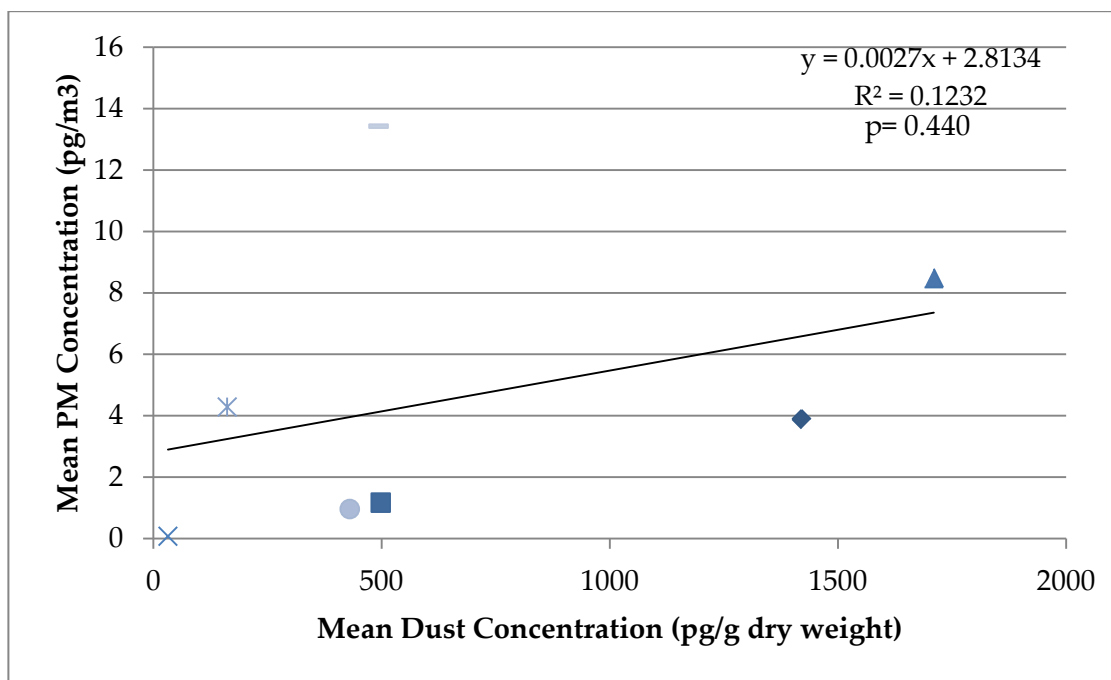
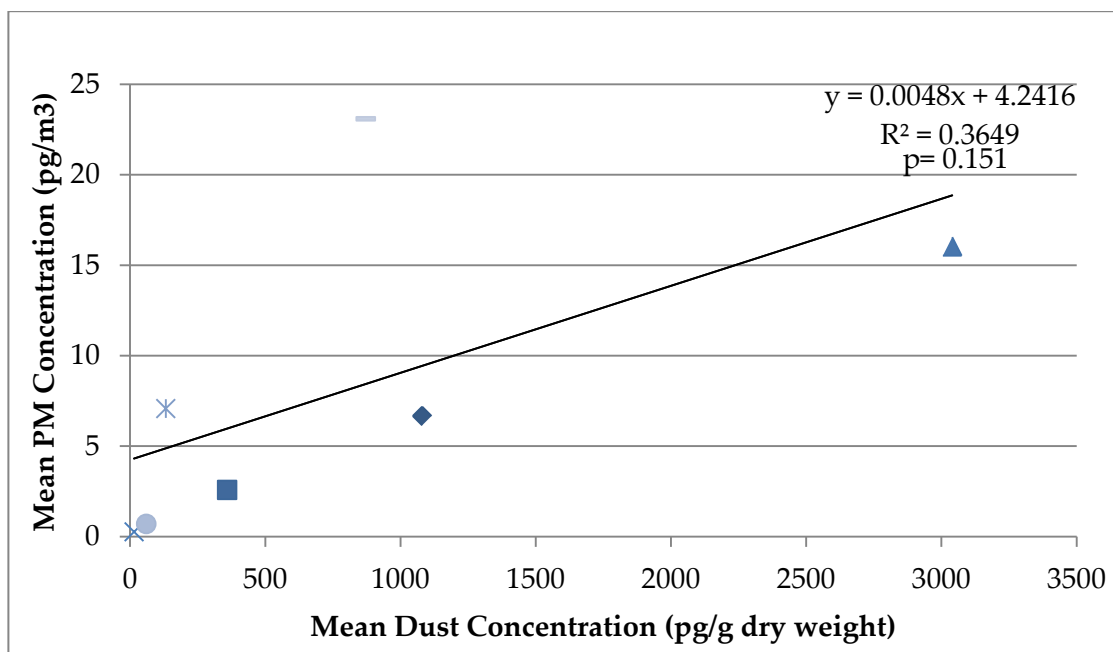


Fig 2.15: Relationship between mean X-PAH concentrations in house dust and particulate matter for Guangzhou, China (correlation of dust and PM concentrations is statistically significant when  $p < 0.05$ ).



**Table 2.1: X-PAHs listed in elution order with abbreviations, NCI ions monitored, method recoveries, and estimated detection limits (All X-PAHs were quantified against  $^{13}\text{C}_6$ -1-chloropyrene as the surrogate).**

Compound	Abbreviation	Ions Monitored (m/z)		Recovery (%) n=3 ± Standard Deviation	Estimated Detection Limits (pg/μL)
		Quant	Qual		
2-bromofluorene	2-BrFlu	79	81, 246, 248	34.1 ± 2.97	0.078
2-chloroanthracene	2-ClAnt	212	214	50.3 ± 1.68	*
9-chloroanthracene	9-ClAnt	212	214	50.2 ± 1.68	*
9-bromophenanthrene	9-BrPhen	79	81, 256, 258	42.3 ± 1.38	0.234
9-bromoanthracene	9-BrAnt	79	81, 256, 258	44.0 ± 2.43	11.1
9,10-dichloroanthracene + 1,9-dichlorophenanthrene	9,10-Cl <sub>2</sub> Ant + 1,9-Cl <sub>2</sub> Phen	246	248	49.1 ± 1.03	0.324
3-chlorofluoranthene	3-ClFluor	236	238	55.8 ± 2.38	0.246
8-chlorofluoranthene	8-ClFluor	236	238	55.1 ± 1.85	0.054
1-chloropyrene	1-ClPy	236	238	67.3 ± 1.55	0.272
3,9,10-trichlorophenanthrene	3,9,10-Cl <sub>3</sub> Phen	280	282	61.2 ± 1.45	0.309
9,10-dibromoanthracene	9,10-Br <sub>2</sub> Ant	336	334	53.6 ± 3.57	0.109
1,3-dichlorofluoranthene	1,3-Cl <sub>2</sub> Fluor	270	272	54.0 ± 2.38	0.028
1-bromopyrene	1-BrPy	79	81, 280, 282	55.1 ± 4.23	0.334
3,8-dichlorofluoranthene	3,8-Cl <sub>2</sub> Fluor	270	272	58.5 ± 1.35	0.089
3,4-dichlorofluoranthene	3,4-Cl <sub>2</sub> Fluor	270	272	60.5 ± 1.80	0.285
7-chlorobenz[a]anthracene	7-ClBaA	264	266	70.9 ± 6.51	0.146
7-bromobenz[a]anthracene	7-BrBaA	79	81, 227	62.5 ± 0.653	11.0
6,12-dichlorochrysene	6,12-Cl <sub>2</sub> Chr	296	298	78.7 ± 5.90	0.258
7,12-dichlorobenz[a]anthracene	7,12-Cl <sub>2</sub> BaA	296	298	61.3 ± 6.21	1.39
7,11-dibromobenz[a]anthracene	7,11-Br <sub>2</sub> BaA	386	79, 81	74.6 ± 4.06	1.75
6-chlorobenzo(a)pyrene	6-ClBaP	286	288	73.7 ± 7.52	0.286
7,12-dibromobenz[a]anthracene	7,12-Br <sub>2</sub> BaA	79	81, 307, 309	64.0 ± 4.49	3.77
4,7-dibromobenz[a]anthracene	4,7-Br <sub>2</sub> BaA	386	79, 81	80.6 ± 2.71	5.30
5,7-dibromobenz[a]anthracene	5,7-Br <sub>2</sub> BaA	386	79, 81	79.5 ± 5.47	5.57
6-bromobenzo(a)pyrene	6-BrBaP	332	79, 81	80.0 ± 14.0	2.96

\* These X-PAHs co-elute and were only detected qualitatively. The estimated detection limit was not determined.

**Table 2.2: Signal to noise ratios for different injection volumes of a Beijing atmospheric particulate matter sample.**

<b>Injection Volume (<math>\mu\text{L}</math>)</b>	<b>Approximate S/N ratio</b>
1	3
3	5
5	10
7	15

**Table 2.3: X-PAH concentrations in PM from Guangzhou and an E-waste Area (the X-PAH concentrations are significantly different when  $p < 0.05$ ).**

Compound	Guangzhou (n=4)		E-waste Site (n=3)		Statistical Difference (p-value)
	Mean Concentration (pg/m <sup>3</sup> )	Standard Deviation	Mean Concentration (pg/m <sup>3</sup> )	Standard Deviation	
3 Cl Fluoranthene	6.66	2.99	3.89	1.55	0.208
8 Cl Fluoranthene	2.58	1.29	1.17	0.465	0.137
1 Cl Pyrene	16.04	5.14	8.48	1.20	0.0584
1,3 Cl <sub>2</sub> Fluoranthene	0.262	0.146	0.0779	0.0683	0.103
7 Cl Benz[a]Anthracene	7.08	4.76	4.29	2.80	0.413
6,12 Cl <sub>2</sub> Chrysene	0.697	0.367	0.963	1.33	0.711
6 Cl Benzo[a]Pyrene	23.09	12.75	13.43	9.79	0.327

**Table 2.4: Comparison of literature X-PAH PM concentrations with this study.**

Compound	Mean Concentrations of X-PAHs in PM (pg/m <sup>3</sup> )							
	This Study		Urban Air from Shizuoka, Japan ref #20	Urban Air from Shizuoka, Japan ref #2	Urban Air from Sweeden ref #25	Road Tunnel Air from Sweeden ref 25	Urban Air from Shizuoka, Japan ref 26	Urban Air from Shizuoka, Japan ref 28
	Guangzhou	E-waste						
3 Cl Fluoranthene	6.66	3.89	1.56	3.1	2.6	10	4.5	2
8 Cl Fluoranthene	2.58	1.17	0.35	*	0.7	4.4	*	1.3
1 Cl Pyrene	16.0	8.48	3.99	5.2	4.9	14.7	7.5	3.8
1,3 Cl <sub>2</sub> Fluoranthene	0.262	0.0779	*	*	*	*	*	*
7 Cl Benz[a]Anthracene	7.08	4.29	0.66	3.1	0.4	2.3	2.4	0.86
6,12 Cl <sub>2</sub> Chrysene	0.697	0.963	0.05	*	*	*	*	0.26
6 Cl Benzo[a]Pyrene	23.1	13.4	7.17	15	1.9	6.1	5.6	7.1

\*= Not Analyzed



**Table 2.5: X-PAH concentrations in house dust from Guangzhou and an E-waste Area (X-PAH concentrations are significantly different when  $p < 0.05$ ).**

Compound	Guangzhou (n=2)		E-waste Site (n=5)		Statistical Difference (p-value)
	Mean Concentration (pg/g dry weight)	Standard Deviation	Mean Concentration (pg/g dry weight)	Standard Deviation	
3 Cl Fluoranthene	1080	327	1420	369	0.319
8 Cl Fluoranthene	359	182	498	135	0.304
1 Cl Pyrene	<b>3040</b>	764	<b>1710</b>	386	<b>0.0226</b>
1,3 Cl <sub>2</sub> Fluoranthene	15.9*	9.33*	29.6	29.5	0.566
7 Cl Benz[a]Anthracene	122*	150*	162	48.2	0.574
6,12 Cl <sub>2</sub> Chrysene	62.4*	10.4*	430	472	0.345
6 Cl Benzo[a]Pyrene	871	1040	493	386	0.471

\*= These three compounds were detected in only one of the two samples from this location. The non-detect value was replaced with  $\frac{1}{2}$  EDL.

**Table 2.6: X-PAH concentrations in Lake Sediment from the E-waste Area.**

Compound	Sample Location (n=2)	
	Location #1 (pg/g dry weight)	Location #3 (pg/g dry weight)
3 Cl Fluoranthene	900	< 474*
8 Cl Fluoranthene	283	< 104*
1 Cl Pyrene	2890	930
7 Cl Benz[a]Anthracene	279	< 141*
6,12 Cl <sub>2</sub> Chrysene	223	< 147*
6 Cl Benzo[a]Pyrene	2350	720

\*= These targets were below the detection limit

## References

1. Kitazawa, A., et al., *Temporal Trends and Relationships of Particulate Chlorinated Polycyclic Aromatic Hydrocarbons and Their Parent Compounds in Urban Air*. Environ. Sci. Technol., 2006. **40**: p. 4592-4598.
2. Horii, Y., et al, *Occurance and Profiles of Chlorinated and Brominated Polycyclic Aromatic Hydrocarbons in Waste Incinerators*. Environ. Sci. Technol., 2008. **42**: p. 1904-1909.
3. Ma, J., et al., *Chlorinated and Parent Polycyclic Aromatic Hydrocarbons in Environmental Samples from an Electronic Waste Recycling Facility and a Chemical Industrial Complex in China*. Environ. Sci. Technol., 2009. **43**: p. 643-649.
4. Eklund, G., and Stromberg, B., *Detection of Polychlorinated Polynuclear Aromatics in Flue Gases from Coal Combustion and Refuse Incinerators*. Chemosphere, 1983. **12**: p. 657-660.
5. Samuelson, U.a.L., A., *Chlorinated Compounds in Emissions from Municipal Incineration*. Chemosphere, 1983. **12**: p. 665-668.
6. Haglund, e.a., *Analysis of Halogenated Polycyclic Aromatic Hydrocarbons in Urban Air, Snow, and Automobile Exhaust*. Chemosphere, 1987. **16**: p. 2441-2450.
7. Shiraishi, e.a., *Occurance of Chlorinated Polynuclear Aromatic Hydrocarbons in Tap Water*. Environ. Sci. Technol., 1985. **19**: p. 585-590.
8. Koistinen, J.e.a., *Chlorophenanthrenes, Alkylchlorophenanthrenes, and Alkylchloronaphthalenes in Kraft Pulp Mill Products and Discharges*. Chemosphere, 1994. **28**: p. 1261-1277.
9. Koistinen, J.e.a., *Chlorinated Fluorenes and Alkylfluorenes in Bleached Kraft Pulp and Pulp Mill Discharges*. Chemosphere, 1994. **28**: p. 2139-2150.
10. Wong, M.H., et al, *Export of Toxic Chemicals- A Review of the Case of Uncontrolled Electronic-Waste Recycling*. Environmental Pollution, 2007. **149**: p. 131-140.
11. Schwarzer, S., et al., *Environment Alert Bulletin: E-waste, the Hidden Side of IT Equipment's Manufacturing and Use*, UNEP, Editor. 2005.
12. Yu, X.Z., et al., *Distribution of polycyclic aromatic hydrocarbons in soils at Guiyu area of China, affected by recycling of electronic waste using primitive technologies*. Chemosphere, 2006. **65**: p. 1500-1509.
13. Li, H., et al., *Severe PCDD/F and PBDD/F Pollution in Air around an Electronic Waste Dismantling Area in China*. Environ. Sci. Technol., 2007. **41**: p. 5641-5646.
14. Puckett, J.e.a., *Exporting Harm: The High-Tech Trashing of Asia*, T.B.A. Network, Editor. 2002.
15. EPA, U.S., *Municipal Solid Waste Generation, Recycling, and Disposal in the United States: Detailed Tables and Figures for 2008*. 2009.
16. Dhanda, K., and Peters, A., *Reverse Logistics in the Computer Industry*. International Journal of Computers, Systems, and Signals, 2005. **6**: p. 57-67.

17. Arensmann, R., *Ready for Recycling*. Electronic Business, 2000. **26**: p. 108.
18. EPA, U.S., *Municipal Solid Waste Generation, Recycling, and Disposal in the United States: Detailed Tables and Figures for 2008*, U.S.E.O.o.R.C.a. Recovery, Editor. 2009.
19. Greenpeace. (2007) *Toxic tea Party*. Greenpeace.org.
20. Ni, H.-H.a.Z., Eddy, *Law Enforcement and Global Collaboration are the Keys to Containing E-waste Tsunami in China*. Environ. Sci. Technol., 2009. **43**: p. 3991-3994.
21. Carroll, C. (2008) *High-Tech Trash*. National Geographic.
22. Chi, X.e.a., *Informal electronic waste recycling: A sector review with special focus on China*. Waste Management, 2011. **31**: p. 731-742.
23. Ohura, T., et al., *Discovery of Novel Halogenated Polycyclic Aromatic Hydrocarbons in Urban Particulate Matters: Occurrence, Photostability, and AhR Activity*. Environ. Sci. Technol., 2009. **43**: p. 2269-2275.
24. EPA, U.S., *Estimation Programs Interface Suite™ for Microsoft® Windows, v 4.00*. 2010, United States Environmental Protection Agency, Washington DC, USA.
25. Schwarzenbach, R., et al., *Environmental Organic Chemistry*. Second Edition ed. 2003, Hoboken, NJ: Wiley-Interscience.
26. Opresko, D., *Review of Exposure Assessment Guidelines*, S.E.R.a.D. Program, Editor. 1996.
27. Ishaq, R.e.a., *PCBs, PCNs, PCDD/Fs, PAHs and Cl-PAHs in Air and Water Particulate Samples- Patterns and Variations*. Chemosphere, 2003. **50**: p. 1131-1150.
28. Lang, C., et al., *Atmospheric Transport and Outflow of Polycyclic Aromatic Hydrocarbons from China*. Environ. Sci. Technol., 2008. **42**: p. 5196-5201.
29. Nilsson, U.a.O., C., *Chlorinated Polycyclic Aromatic Hydrocarbons: Method of Analysis and Their Occurrence in Urban Air*. Environ. Sci. Technol., 1993. **27**: p. 1826-1831.
30. Ohura, T., et al., *Occurrence, Profiles, and Photostabilities of Chlorinated Polycyclic Aromatic Hydrocarbons Associated with Particulates in Urban Air*. Environ. Sci. Technol., 2005. **39**: p. 85-91.
31. Ohura, T., *Environmental Behavior, Sources, and Effects of Chlorinated Polycyclic Aromatic Hydrocarbons*. TheScientificWorldJOURNAL, 2007. **7**: p. 372-380.
32. Ohura, T., et al., *Chlorinated Polycyclic Aromatic Hydrocarbons in the Atmosphere: Seasonal Levels, Gas-Particle Partitioning, and Origin*. Environ. Sci. Technol., 2008. **42**: p. 3296-3302.
33. EPA, U.S. *Particulate Matter: Health and Environment*. 2010 August 06, 2010 [cited 2010 September, 24]; Available from: <http://www.epa.gov/particles/health.html>.

34. Ohura, T., et al, *Spatial Distributions and Profiles of Atmospheric Polycyclic Aromatic Hydrocarbons in Two Industrial Cities in Japan* Environ. Sci. Technol., 2004. **38**: p. 49-55.
35. Ohura, T., et al, *Differential Action of Chlorinated Polycyclic Aromatic Hydrocarbons on Aryl Hydrocarbon Receptor-Mediated Signaling in Breast Cancer Cells*. Environmental Toxicology, 2010. **25**: p. 180-187.
36. Latchman, D., *Transcription Factors: An Overview* Int. J. Biochem. Cell. Biol., 1997. **29**: p. 1305-1312.
37. Denison, M., et al, *Ligand Binding and Activation of the Ah Receptor*. Chemo-Biological Interactions, 2002. **141**: p. 3-24.
38. Johnsen, S., et al, *Formation of Chlorinated PAH- A Possible Health Hazard From Water Chlorination*. The Science of the Total Environment, 1989. **81/82**: p. 231-238.
39. Ohura, T., et al, *Aryl Hydrocarbon Receptor- Mediated Effects of Chlorinated Polycyclic Aromatic Hydrocarbons*. Chem. Res. Toxicol., 2007. **20**: p. 1237-1241.
40. NIH. *IUPAC Glossary of Terms Used in Toxicology*. 2007 11 March 2009 [cited 2010 10/12]; Available from:  
<http://sis.nlm.nih.gov/enviro/iupacglossary/glossarym.html>.
41. EPA, U.S. *TRI Dioxin and Dioxin-like Compounds Toxic Equivalency (TEQ) Information Rule*. 2008.
42. Blankenship, A., et al, *Relative potencies of Individual Polychlorinated Napthalenes and Halowax Mixtures to Induce Ah Receptor-Mediated Responses*. Environ. Sci. Technol., 2000. **34**: p. 3153-3158.
43. Fan, C.-W., et al., *Characteristics of sedimentary polycyclic aromatic hydrocarbons (PAHs) in the subtropical Feitsui Reservoir*. Journal of Hydrology, 2010. **391**: p. 217-222.
44. Carroll, C., *High-Tech Trash*, in *National Geographic*. January 2008. p. 64-81.
45. Wang, J.e.a., *Brominated Flame Retardants in House Dust from E-waste Recycling and Urban Areas in South China: Implications on Human Exposure*. Environent International, 20010. **36**: p. 535-541.
46. Shi, T., et. al., *Occurrence of brominated flame retardants other than polybrominated diphenyl ethers in environmental and biota samples from southern China*. Chemosphere, 2009. **74**: p. 910-916.
47. Primbs, T., et. al., *Atmospheric Outflow of Anthropogenic Semivolatile Compounds from East Asia in Spring 2004*. Environ. Sci. Technol., 2007. **41**: p. 3551-3558.
48. Genualdi, S., et al., *Enantiomeric Signatures of Organochlorine Pesticides in Asian, Trans-Pacific and Western U.S. Air Masses*. Environ. Sci. Technol., 2009. **43**: p. 2806-2811.

49. EPA, U.S. *The Analysis of Polychlorinated Dibenzo-p-Dioxins and Polychlorinated dibenzofurans by High Resolution Gas Chromatography/ Low Resolution Mass Spectrometry (HRGC/LRMS)*. 1996; Available from:  
[http://www.accustandard.com/asi/pdfs/epa\\_methods/8280a.pdf](http://www.accustandard.com/asi/pdfs/epa_methods/8280a.pdf).

### CHAPTER 3: Conclusions

To investigate halogenated PAHs (X-PAHs) in environmental samples, an analytical method was developed. The method was used to measure the concentrations of 26 X-PAHs in atmospheric particulate matter (PM), house dust (HD), and sediment.

To lower the detection limit, the analytical method included the use of NCI ionization and a large volume injection via a programmable temperature vaporizing (PTV) inlet. The average recoveries for the entire method were  $60.1 \pm 21.0$  (RSD) %.

The X-PAH concentrations in PM and HD were compared in Guangzhou, China and a nearby e-waste area to understand if e-waste burning is a significant source of X-PAHs. The X-PAH concentrations from the two locations were low, and there was no statistical difference in the X-PAH concentrations in PM and HD from Guangzhou and the e-waste area. The X-PAH PM profiles of the two locations were similar. In addition, the X-PAH PM concentrations were on the same order of magnitude as previous X-PAH PM measurements. These data imply that e-waste activities are not a major source of X-PAHs to atmospheric PM.

In addition, the X-PAH profiles in PM and HD in Guangzhou and the e-waste area were different. This suggests that there are additional X-PAH sources inside the Guangzhou and E-waste area homes.