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# X-Ray Fluorescence (XRF) Analyzer - Theory, Utility, and QA/QC for Environmental and Commercial Product Samples in Cambodia

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# X-Ray Fluorescence (XRF) Analyzer – Theory, Utility, and QA/QC for Environmental and Commercial Product Samples in Cambodia

by

Sereyrath Lim

An Abstract of a Thesis
in
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Submitted in Partial Fulfillment
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# ABSTRACT OF THESIS

## X-Ray Fluorescence (XRF) Analyzer – Theory, Utility, and QA/QC for Environmental and Commercial Product Samples in Cambodia

Laboratory facilities in developed countries provide a variety of options for analysis of environmental samples and commercial commodities that could impact human health. The same is not true in developing countries and there is a great need to identify technologies that could be used to provide robust, accurate, cost-effective analysis that minimizes the need for extensive technical training. An X-ray Fluorescence (XRF) analyzer seems to be an analytical technique that could be such a tool for developing countries. Therefore, the objective of this thesis was to assess the performance and utility of a handheld, portable XRF unit in analyzing different types of environmental and commercial commodity samples in Cambodia. Because a number of different materials were analyzed, this thesis has a slightly different format than typical. Each of the following three chapters has its own methodology, results and discussion sections. This approach was taken because the materials analyzed and methods for sampling the materials were so different, it was clearer to separate the analyses into separate, individual chapters. This abstract provides a brief overview of each chapter.

**1. Chapter One**

The need to have a more robust, cost effective and less time-consuming form for environmental samples in the field where samples could not be brought in for the laboratory analysis led to the manufacture of a first X-ray fluorescence (XRF) analyzer. This first chapter outlines the theory of the XRF, its advantages and limitations, and provides some QA/QC of a

handheld XRF (XL3t 900, Billerica, MA) on skin whiteners, which were purchased and donated by university students for mercury levels.

The results showed that up to 98 samples (16%) of creams analyzed contained mercury higher than 20 ppm, and 64 concoctions out of 192 samples were contaminated with more than 20 ppm mercury. Although there were suppressions (20%) of mercury at concentrations near 15,000 ppm (i.e. an under-estimation), the XRF proved to be an excellent tool capable of detecting metals; particularly mercury in semi-solid solutions.

## 2. Chapter Two

Phnom Penh, the capital city of Cambodia, is home to some 1.4 million people and undergoing urbanization. In spite of its urbanization, Phnom Penh has yet to have a primary wastewater treatment plant and adequate sewage drainage system in place. There are two main interceptor sewer channels that drain wastewater and storm water from the southern part of the city into a natural wetland, Boeung Cheung Ek. These two sewer channels are the Tum Pun Sewer System and the Meanchey Sewer System. These are open sewer systems which collect all types of industrial, hospital, institutional and household wastes, and in turn discharge into the wetland. In Cambodia data related to metals contamination in sediment and street dust are very limited. So, this chapter of the thesis seeks to determine metal concentrations, spatial patterns and sources in sewer, wetland and street dust samples. Metals levels also are compared with United States Environmental Protection Agency (USEPA), New York State Department of Environmental Conservation (NYSDEC), and Provincial Sediment Quality (PSQ), Ontario, Canada guidelines.

The results showed that although there are elevated metal concentrations in the sewer and wetland sediments and street dust samples, they are still lower than those reported elsewhere such as in Hong Kong, Greece, China, Korea, the US, and Malaysia. One sewer site (M1) had significantly higher metals levels than any other site of the two sewer systems, because it is geographically surrounded by industries and factories. The metal concentrations, especially Pb, Zn, and Cu, decreased with distance from this site. The levels of Pb in street dust appeared higher in high-density traffic areas and decreased with distance from the busy traffic streets. Although leaded gasoline can be a source of lead in street dust and sediments, Cambodia apparently complies with the EU guideline on the level of lead use in gasoline. In addition to leaded gasoline, diesel fuel can also contain metals but the levels are subject to further analysis. Other sources of metals in street dust include tire abrasion, brake lining and transmission oil. To reduce the levels of metals, the two sewer systems should be dredged periodically. The dredging also would increase channel flow capacity during storm events. Source tracking of metals should be conducted in more detail to inform management strategies. For the management of street dust, street sweeping and washing may be effective means to allay the metal toxicity levels.

## 3. Chapter Three

Lead (Pb), which is a potentially hazardous toxicant, can be an additive agent of jewelry items and children's toys. It is added to polyvinylchloride (PVC) pipes, so that it would provide rigidity, lower manufacturing costs and resistance to sunlight. Lead also has been a paint additive and this is of great concern in North America. Cambodia imports most of its consumer goods from other countries, but the regulatory inspection on imported products is not strictly enforced due to the lack of customs inspection tools, facilities and trained professionals. The purpose of this chapter is to assess jewelry items, children’s toys and paints for potential metal contamination from various markets in Phnom Penh, Cambodia and Bangkok, Thailand by means of the handheld X-ray fluorescence (XRF) analyzer.

The results indicated that significant levels of Pb were used in the products (up to 43% in jewelry items and 4.3% in paints). These findings suggested that more restrictive regulations on the sales and use of toxic products should be imposed, so that health risks can be minimized.

The XRF was manufactured, and over the years, has been re-engineered to provide the features necessary to operate in the field where laboratory-based assays not are suited. The XRF has some limitations for some elements like Cr and Hg in soils, the analyses of which necessitate laboratory-based verification such as an AAS or ICP. It also does not have the capacity to assess the degree of dermal and oral absorption of metals, although these aspects are still evolving. Nonetheless, the XRF would be an ideal tool for on-site and in situ investigation in Cambodia; particularly for customs officers, environmental researchers and engineers.

State University of New York
College at Buffalo

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# Chapter 1: X-Ray Fluorescence (XRF) – Theory, Utility, and QA/QC for Commercial Product Samples in Cambodia

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# 1. INTRODUCTION

## 1.1 Background

The world's growing environmental and public health concerns have prompted researchers and professionals to seek alternative forms of analytical tools, which are more robust, portable, cost effective and easy to operate with minimal sample preparation. The conventional methods for metals analysis such as the atomic absorption spectrometry (AAS), inductively coupled plasma atomic emission spectroscopy (ICP-AES), and inductively coupled plasmas optical emission spectrometry (ICP-OES) through sequential digestion, often require lengthy sample preparation time, and take a number of days to obtain results. In some instances, validated data are needed to reflect on-site decision making and the number of samples to be analyzed. The X-ray fluorescence analyzer is a well suited alternative for a variety of analytical applications.

X-ray fluorescence spectrometry (XRF) is an analytical screening tool that was first used to analyze lead (Pb) in paint in the 1970s during abatement and exposure studies (Kalnicky and Singhvi 2001), and has since been used in environmental testing of alloys, geological materials, sediments, glasses, with very minimal sample preparation and treatment (Sitko 2009; Lawryk et al. 2009). Over the years, the XRF has gained acceptance from the environmental research community as a viable analytical tool because of the efficiency of the radioisotope source excitation coupled with extremely sensitive detectors and other electronics, hence offering multi-element analysis capability, economy, high speed and simplistic operation, where its advantages and limitations are well comprehended.

## 1.2 Chapter Objectives

The objectives of this study are to provide the basic concepts of the XRF and assess the performance of a handheld XRF, Niton XL3t 900 Series (Thermo Fisher Scientific, Waltham, MA), on various consumer products in Cambodia.

## 1.3 Theory of the XRF

The basics of the XRF lie in the atoms of the receiving sample emitting different energies when they are excited by X-rays. The excited photons enable the qualitative and quantitative analysis of most elements in a given sample (Kalnicky and Singhvi 2001). First the X-rays dislodge an atom from the inner shell. The atom from an outer shell fills the inner shell (K or L). The excited atom releases energy in the X-ray region of the wavelength as it returns to the ground state. The released photons with energy are equivalent to the difference between the two different shells. For instance, the transition from the L-shell to the K-shell results in a spectral line, which is designated Kα, while the transition from the M-shell to the K-shell provides a spectral line, which is designated Kβ (Figure 2). Thus, each element possesses different characteristic lines in the spectrum because each type of orbital transition produces a distinct X-ray. Clark et al. (1999) showed that when certain atoms are excited, they release energy in the form of fluorescence as they return to the unexcited state. The photons emitted are then detected by the instrument. Figure 1 provides an overview of the basics in theory of the XRF.

# Mechanism of XRF

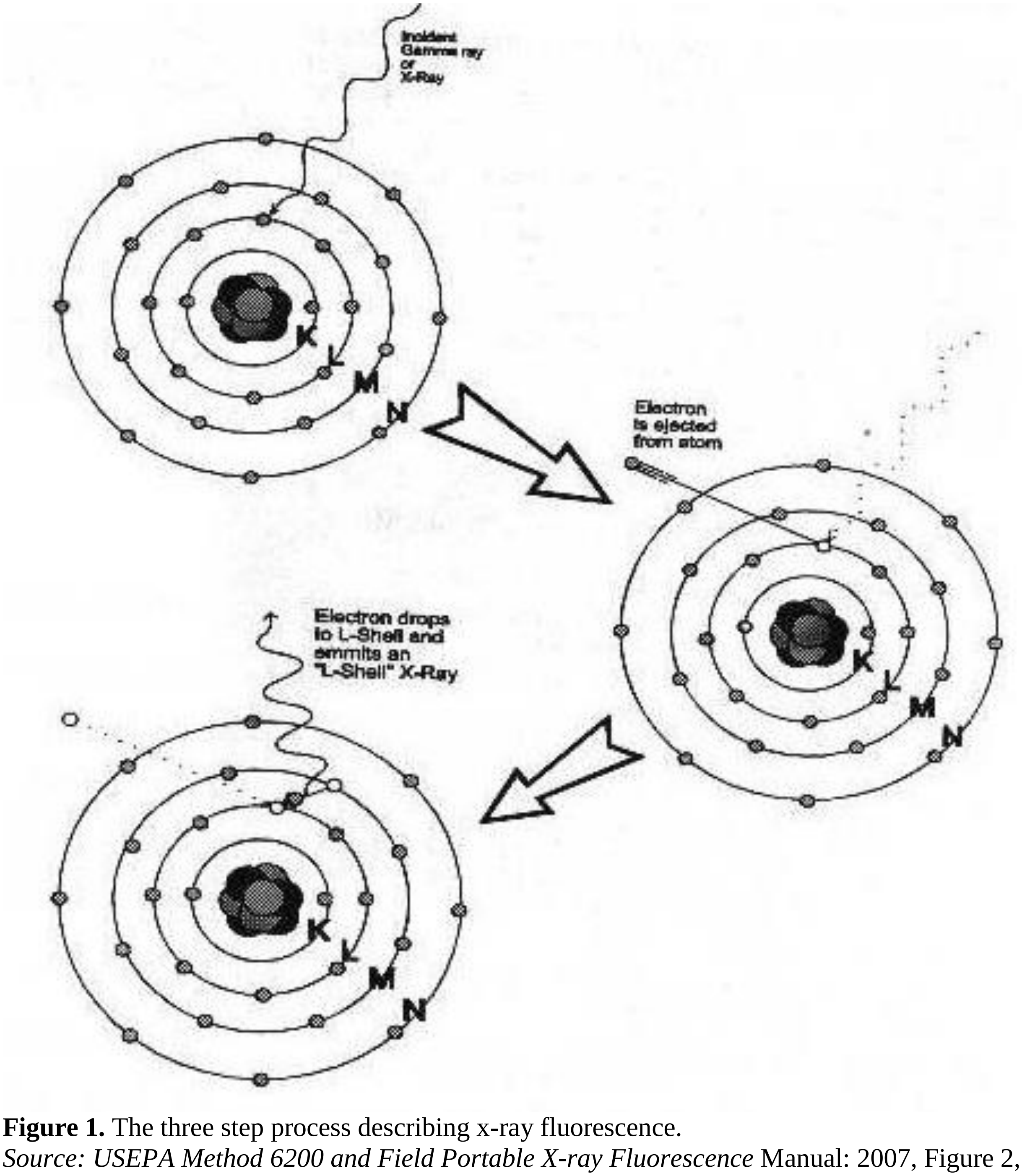

**Figure 1.** The three step process describing x-ray fluorescence.
*Source: USEPA Method 6200 and Field Portable X-ray Fluorescence* Manual: 2007, Figure 2, p. 3.

**Transitional Steps of Atoms**

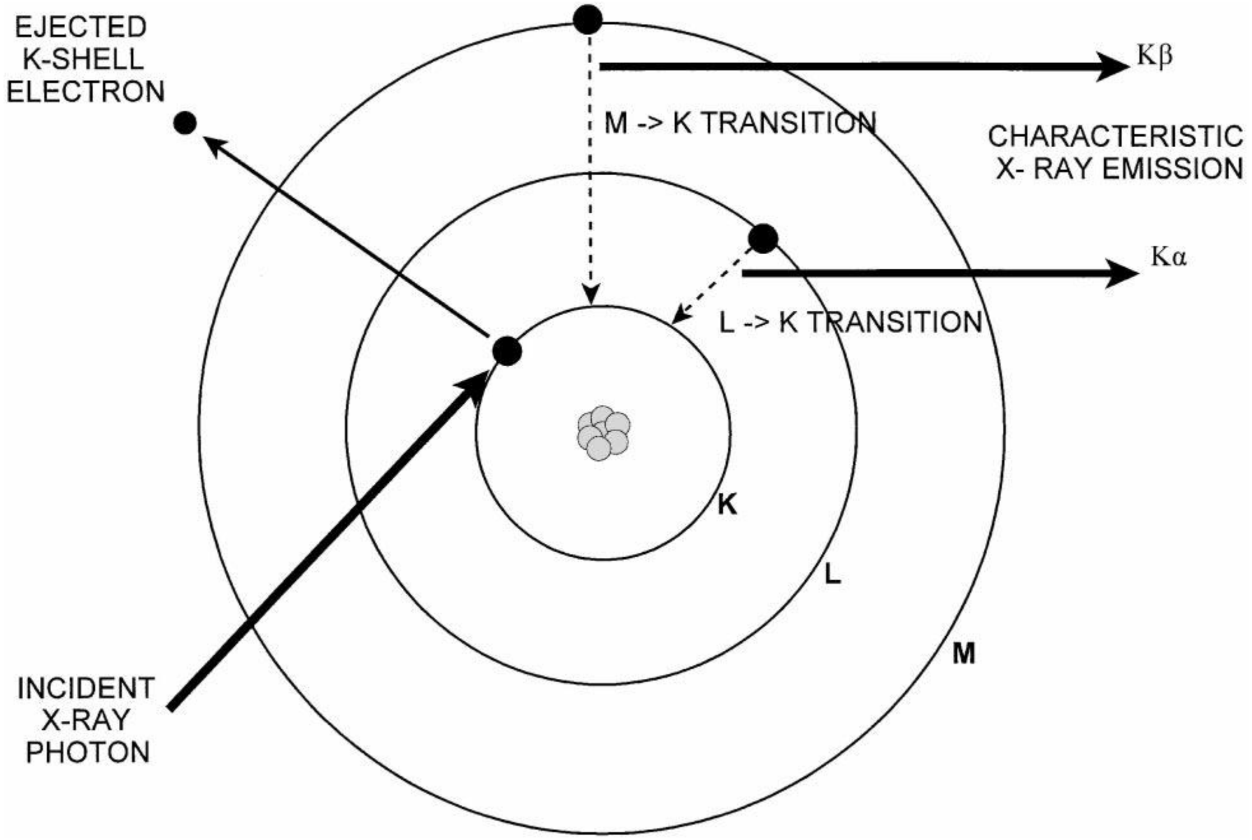

**Figure 2.** Mechanism of X-ray fluorescence of an atom.

1.3.1 Selectivity

The XRF can be used to detect most of the elements in the periodic table ranging from Na to U and even higher atomic number (Z) elements, although the detection of low Z elements requires the use of a vacuum or helium purge gas (Palmer et al. 2009). Modern field portable XRF instruments, however, have improved solid state detectors with sufficient energy resolution for multi-element analysis with few spectral interference problems, and they do not require liquid nitrogen cooling. Many models have been developed and marketed for specific applications such as the analysis of Pb in paint (Dost 1996). Under normal circumstances, a positive detection of a sample is confirmed by multiple fluorescence lines with different energy that can be expanded to show limited resolution of the analyzer (Figure 3). However, the interpretation of the XRF spectra containing multiple fluorescence line overlaps can be very complicated due to the fundamental limitations of the detector in distinguishing photons with similar energies.

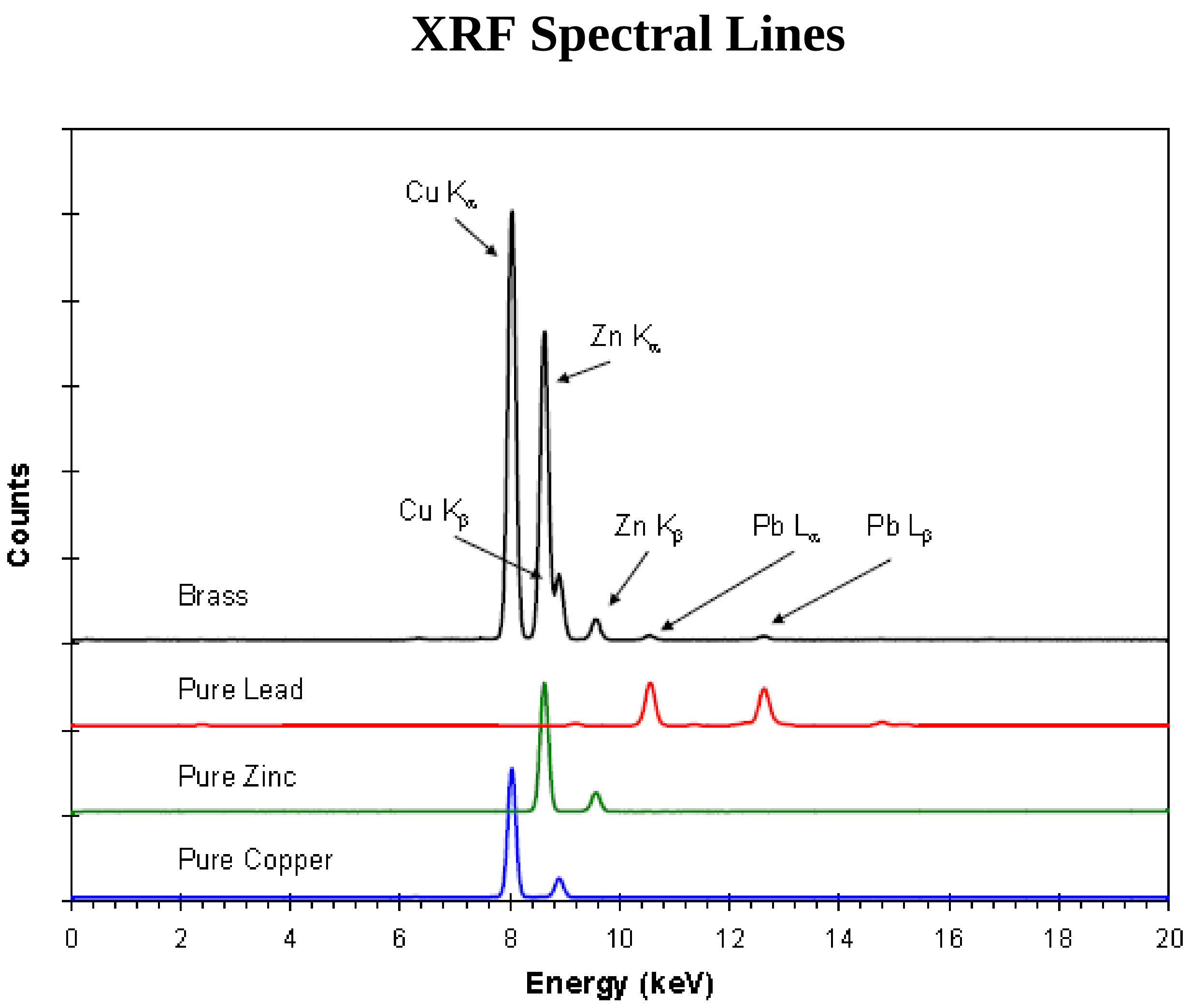

**Figure 3.** Comparison of three pure element spectra and a spectrum taken from a brass sample.

## 1.4 XRF Sources

### 1.4.1 Radioisotope Sources

A variety of excitation sources may be used to irradiate a sample. Various radioisotope sources such as Fe-55, Co-57, Cd-109, and Am-241 have been used, giving off radiation at a specific energy level. Because no single excitation source can efficiently excite the entire range of elements with different atomic numbers, two or three excitation sources can be used to maximize the efficiency of the XRF detection on a wide range of concerned elements (Bertin 1975)

The analyzer emits primary radiation through which the sample being analyzed determines the intensity of the secondary (scattered) radiation. Based on its composition, thickness and density, the sample may absorb more or less of the primary-beam radiation. If the sample is small, thin, and low in density, it would allow much more of the radiation beam to escape, and the escaping radiation is known as the secondary (scattered) radiation (Thermo Fisher Scientific 2010). There should always be a sample in contact with the measurement window when the x-ray tube is on. Individuals should never place any part of the body in the primary beam path as this may potentially lead to cancer. Therefore, caution should be taken when analyzing samples that are small and low in density.

### 1.4.2 X-Ray Tube Source

High-power X-ray tubes are another alternative source of the XRF, and are often associated with laboratory XRF instrumentation, which results in a higher sensitivity (Figure 4).The handheld XRF spectrometry system needs to be confirmed by the laboratory analysis because the laboratory-based XRF requires sequential extraction of heterogeneity of the sample and higher energy source. Low-power X-ray tubes (1-50W) are sometimes considered to be a qualitative tool (Parsons et al. 2012) but it depends upon the analysis and calibration whether the analysis is qualitative or quantitative. In spite of a number of advantages aforementioned, the short half-life of the XRF sources may have implications for the instrument's sensitivity. Thus, the sources needed to be replaced when the sensitivity is reduced.  Calibration standards are thus mandatory and units may require servicing after two years.

## Laboratory XRF Analyzer

**Figure 4.** Laboratory-based Oxford instrument MDX1080+ MDXRF analyzer.

# Handheld XRF Analyzer

**Figure 5.** Handheld Thermo Scientific Niton XL3t XRF analyzer.

### 1.5 Factors Affecting XRF Calibration

Especially for quantitative analysis, XRF methods require calibration of the XRF analyzer with standards of known concentrations. The calibration simply compares the X-ray intensity of the elements of interest to the certified, known concentrations of a type of sample (e.g. solids, liquids, and films). During a calibration procedure the following factors, which may influence the accuracy and precision of the method, should be considered: 1). detector resolution and relationship to the spectral inferences; 2). sample matrixes; 3). accuracy and suitability of standards; and 4). sample morphology (i.e. uniformity, water content, particle size distribution and surface condition) and sample measurement geometry (Kalnicky and Singhvi 2001).

These limiting factors can be addressed so that an appropriate and meaningful calibration can be done. Different detectors have different efficiency to resolve overlapped X-ray spectral lines. For example, overlapping lines between As-K and Pb-L might not be well separated by certain detectors, resulting in analytical error. Matrix effects occur when other elements interfere with the target element, and this interference can have an impact on the measured X-ray intensity of the target element. These effects produce a non-liner intensity response versus target element concentration, and they appear as either X-ray absorption or enhancement phenomena. These effects can be corrected when the XRF analyzers are calibrated (Parsons et al. 2012). Moreover, the standard concentrations should have accurate concentrations of those elements of interest to be analyzed with a suggested time measurement. Also, the standard should exhibit the same texture as the sample to be analyzed in order to have an accurate calibration method. It is well documented that the sensitivity of the XRF decreases as the distance between the sample being analyzed and the excitation source increases. This discrepancy can be reduced by maintaining the same measurement geometry between all calibration standards and sample measurements. For best results, the window of the probe should be in direct contact with the sample.

## 1.6 Interferences

### 1.6.1 Effects of Particle Size

The XRF analytical method has been demonstrated on different chemical composition of all kinds of materials. The materials can be in solid, liquid, powder, filtered or other form.

However, particle size in solid samples can influence the XRF accuracy. For example, Criss (1976) reported that the sensitivity of an XRF measurement goes down as the sizes and densities of the particles increase, because the X-ray absorption losses increase. Similarly, Maruyama et al. (2008) found that particle size effect in XRF showed a clear decrease in the XRF intensities when these were observed with larger particle size. Both studies reported that correction can be made.

In regard to metal distribution at different particle size fractionations, it is well documented that finer particles tend to preferentially adsorb metals and be associated with higher metals concentrations (Forstner and Whitman 1983). For example, Luo et al. (2011) reported an enrichment of Pb, Cu and Zn in soils <100 um in an urbanized area in Hong Kong which was strongly influenced by anthropogenic activities and vehicular emissions. Clark et al. (1999) found soil samples that were sieved to <125 um had a higher Pb content than those sieved to <250 um. German and Svensson (2002) ascertained metals are a function of particle diameter and proportional to the inverse of the particle diameter, i.e. the highest metal concentrations are associated with finest fractions.

### 1.6.2 Moisture Interference

Sample moisture can affect the accuracy of the analysis. It was reported that sample moisture as much as 20% can affect the analysis (Kalnicky and Singhvi 2001). So, soil and sediment samples should be routinely dried to remove all matric moisture when the water content exceeds 20%. Limiting factors that affect the XRF performance capability include sensitivity of instrumental techniques; low concentration of element of interest; interference of other elements in the matrix; and using large volume of water as representative samples (Kalnicky and Singhvi 2001).

### 1.6.3 Elemental Interference

The XRF is sensitive to chemical matrix effects, and these effects occur as either spectral interferences (peak overlaps), or as X-ray absorption and enhancement phenomena. Both of these effects are common in contaminated soils. The most common interference for As is Pb between the emissions at 10.54 KeV and 10.55 KeV, respectively. To overcome this inference, an inbuilt auto-correction was employed using the Pb Lβ emission line at 12.61 KeV to estimate the intensity of the Pb Lα emission (Model XLt 700 series) (Palmer et al. 2009). For instance, Parsons et al. (2012) reported that in soils, Pb interferes with As while a high Fe content produces a high background for Mn and Cu. As examples of absorption and enhancement effects, Fe tends to absorb Cu X-rays, reducing the intensity of the Cu measured by the detector, while Cr will be enhanced at the expense of Fe because the absorption edge of Cr is a little bit lower in energy than the fluorescent peak of Fe. These effects can be mathematically corrected and compensated for.

## 1.7 Detection Limit

The detection limit (DL), which is defined as three times the calculated standard deviation, is influenced by variations in the physical matrix of the sample, radioisotopes and the elements of analysis. It also has been reported that the detection limits are influenced by the duration of analysis – the longer the analysis is, the lower the DLs tend to be. In a paper published by Schramm et al. (1999), they argued that long measurement times will result in a low detection limits and high precision. It should also be noted that, the use of one X-ray tube in a specific excitation arrangement cannot give optimal excitation conditions for light and heavy elements. So, the duration to obtain a DL of an element of interest can be different from that of another.

Parsons et al. (2012) showed that time of analysis can determine whether the data collected are quantitative or qualitative based on the USEPA quality criteria (Table 1). The authors found in their previous research that a suitable compromise between measurement time and precision for a variety of metals is 120s while others use shorter measurement times, e.g. 45s such as in Kilbride et al. (2006). However, the optimal time required or considered adequate in resulting in quantitative data reflects the type, homogeneity and elements of interest of the sample. For instance, the authors reported that the XRF gave qualitative data for Cu when the count time was for 60 s (%RSD=20.2). However, when the analysis time was 120s (%RSD=10.9), the XRF analyzer produced quantitative data for Cu. There are three types of quantitative data (Definitive 1, Quantitative 2, and Quantitative 3). Different elements may require different analysis (longer or shorter) durations.

They suggested that As at low concentrations (<30mg/kg) exhibited no significant difference when the analysis exceeded 100s. Manganese at 500 mg/kg and Zn at 100 mg/kg showed no significant difference after the analysis of 300s and 50s, respectively, but showed differences at a shorter time of analysis. However, not only are detection limits influenced by physical matrix effects and the elements of analysis, but they are also affected by high analyte concentrations (USEPA 2008). It is, therefore, recommended that only analyte concentrations closer to the minimum detection limit should be used. Despite the USEPA’s (2008) recommendation on the use of low analyte concentration that may affect the sensitivity of the

XRF, Murphy et al. (2012) found a strong linear regression with an $r^2$ value of .999 for skin creams spiked with DMSO (Dimethylsulfoxide) up to 30,000 ppm. So, the DL of the XRF really depends on the type of the instrument and the type of sample media.

# 2. LITERATURE REVIEW

## 2.1 Analysis of Sediments

Contamination of metals in soil has been well documented in recent years and more numerous studies are being carried out in different parts of the world (Powell and Alexander 2003; Mendil and Uluozlu 2007; Wuana and Oklelmen 2011). The analysis of potentially contaminated soil via conventional methods such as the atomic absorption spectrometry (AAS) often takes weeks due to sample preparation and can be expensive. For management, instant analysis of contaminated soil, sediments or geoprospecting may be required to guide further analysis and mapping of the area. The evolution of the XRF application has been reengineered to improve the sensitivity in a more accurate and precise analysis.

The advantages of using the XRF for in situ analysis of soil are the minimal requirement of sample preparation, easy-to-operate instrument and training, and the rapid resultant data at a very low cost. At a mining site in Ireland, 17 soil samples were collected, digested and analyzed using an AAS to determine the levels of Pb, As, Cu and Zn. The results from the AAS were correlated with those produced by the XRF with the $r^2$ being 0.997 for Pb; 0.957 for Cu; and 0.976 for Zn (Radu and Diamond 2009).

Despite using different measurement protocols (sieved, ground and mixed) of soil samples that were collected from areas known to have been contaminated with Pb due to deterioration of a Pb-painted house, Clark et al. (2008) observed no differences in their results. The slopes and significance levels of the regression analyses between the XRF and the flame atomic absorption spectrometry (FAAS) showed that all the slopes were near unity, with a range of 0.972 to 1.018. The $r^2$ values showed a high degree of correlation of Pb ranging between 0.96 and 0.99 ($P<0.001$).

## 2.2 Analysis of Street Dust

The amount of anthropogenically derived metals has increased continuously in recent years, and the awareness and concern about associated environmental and health risks have risen sharply. The growing concern over air pollution has received attention from various sectors of government and researchers (Dockery and Pope 1996; Yeung et al. 2003; Zhang and Wang 2009). At the same time, a more robust portable analytical tool is needed to meet short project timeframes with limited budgets, as well as providing accurate data for on-site decision making, as opposed to conventional sequential digestion methods. The innovative refinement of the XRF technology has resulted in the development of smaller, lighter and more versatile field units than their previous predecessors thereby allowing industrial hygienists and occupational safety professionals to carry out monitoring of airborne metals in street dust and workplaces (Lawryk et al. 2009; Melquiades and Appoloni 2004). A study on the toxicity level of metals in street dust associated with motor vehicle traffic, brake and tire wears by Apeagyei et al. (2011) indicated that the handheld XRF analysis (XL3t 900 Series) reported values of a high degree of accuracy and were in good accordance with the certified NIST values for all measurements.

Petrosyan et al. (2004) investigated Pb content in exterior house soil and dust samples collected in the vicinity of mining and smelting area in Armenia. The XRF technique was used and compared with the laboratory-based ICP-OES. The comparison result showed that there was a strong correlation between the two analytical procedures ($r^2=0.95$, $P<0.0001$). The results also suggested that elevated Pb and other metals such as Cu, Fe, Mn, Cr and Zn and As were observed in the smelter town residential area. The source of elevated Pb concentration was attributed to the polymetallic smelter in the area, resulting in contaminated particulate matter being resuspending into the air and potentially increasing human exposure in the area.

## 2.3 Analysis of Jewelry Items and Children's Toys

Metals such as Cd, Hg and Pb have been used in the manufacturing processes of plastic products to reduce the manufacturing cost because lead chromates, for example, are cheaper than organic pigments and provide durable, bright and flexible products. When these substances are added, they are not bound to the molecules of the products, but rather create a suspension in the solid plastic polymer. Over time such chemical additives may be released into the environment or leach into the skin of children that have been in contact with the contaminated products, causing detrimental health and environmental problems. The need to effectively monitor the import and sales of these contaminated products is very crucial. A light, portable, accurate and real-time data generating analytical tool, such as XRF can quickly identify and quantify prohibited elements in plastic products (Piorek 2004).

XRF analyzers have also been utilized to assess metal levels in various consumer products such as low-cost jewelry items and children's toys. One such study was conducted by Greenway and Gerstenberger (2010) who selected 10 day care centers in Las Vegas, and for each of which 50 toy samples were taken to analyze by a portable XRF (XLt 797 2W) for Pb and other metal compositions. Twenty-nine of 535 toy samples (5.4%) from 10 day care centers, contained elevated Pb equal to or higher than the United States Consumer Product Safety Commission guideline (USCPSC) of 600 ppm (former USCPSC guideline) with the highest Pb content being 8,081 ppm. The average concentration of Pb was 2,019 ppm. The authors showed that toys made with PVC plastics are more likely to contain elevated Pb, although more assessment is needed to determine the potential risk exposure to children.

A similar study by Sanders et al. (2013) who investigated Pb levels in toys from seven day care centers using a handheld XRF found that 40 out of 460 items contained elevated Pb

>300 ppm; and 56 were tested >100 ppm. The XRF method provided an indication of the level of Pb in the tested products, but does not replace laboratory assessment as the legal results, which in this case highlighted another potential source of Pb exposure to children in a Pb-based environment. The Commission Regulation of the European Union, for example, is still evaluating procedures to estimate the release of metals in toys via oral exposure, and dermal absorption also is poorly characterized (European Commission 2009).

### 2.4 Analysis of Lead in Paints

The use of the handheld XRF analysis on Pb-based paints was conducted as early as 1975 by the Chicago Board of Health in Illinois in response to the growing concern of Pb poisoning, particularly in children (Kaplan et al. 1975). One of the first studies assessing the efficacy of the XRF for Pb in paint was conducted by Kaplan et al. (1975) using a radioactive source x-rays. The results of their studies which were confirmed by the AAS and indicated that there was no difference in the Pb value of the paint layer containing Pb near the surface or under several layers of unleaded paint ($r^2=0.97$). This preliminary study on the efficiency of the XRF evaluation of Pb content on wall pinpointed the advantages of the instrument for household inspectors and homeowners to make quick decisions. Thereafter, the U.S. EPA and the U.S. Department of Housing and Urban Development integrated the handheld XRF protocols for testing Pb-based paints into their monitoring programs (Clark et al. 2008).

It is important to note that only XRF analyzers with radioactive sources have the power to measure Pb under layers of paint without Pb (In a message to the author on July 23, 2013, Adrian Smith, Thermo’s Regional Sales Director for Asia Pacific stated that “We are using radioactive source for this application.”). The detection of Pb in paint is complicated by the material underlying the paint, the substrate, and how it affects the high-energy rays directed into the paint by the XRF. The gamma and high energy X-rays from the radiation sources that are directed into the paint will bounce back to the instrument’s detector. This event is referred to as backscatter, and it interferes with the detection of the energy emitted from the Pb atom in paint. However, a substrate correction can be applied. For instance, Schmehl et al. (1999) carried out a correction by first calculating the averages, by substrate and by housing unit containing Pb-based paint, of XRF measurements obtained on a National Institute of Standards and Technology (NIST) standard reference material (SRM) film (with a 1.02 mg/cm$^2$ Pb level) placed over bared areas on the template, and subtracting 1.02 mg/cm$^2$. The resulting correction value was then subtracted from all XRF measurements obtained on painted surfaces within the same housing unit that shared the same substrate type. The need for substrate correction was indicated by the presence of bias, and its effectiveness was assessed according to the reduction in bias when substrate correction was performed.

In India, Clark et al. (2005) used an XRF analyzer (XL-700 Series) to evaluate Pb content in painted surfaces around homes and play environments of children with elevated blood lead levels (BLLs) and Pb content in residential areas. Of the children tested, 11 students had BLLs at or above 40μg/dL. The study discovered that the gym equipment in a neighborhood where 1 of the 11 boys, whose BLLs were >40 μg/dL, played daily contained 3.5 mg/cm$^2$ for yellow paint and 2.4 mg/cm$^2$ for orange paint, which was twice as much as the US guideline of 1 mg/cm$^2$ of Pb for residential paint. However, there was no evidence of Pb exposure sources in the school or playground of the government schools. The probable sources of Pb exposure in the children included batteries, ayurvedic pills formulated with heavy metals, and paints.

Using XRF to assess Pb content in paints in residential areas in the U.S., Jacobs et al. (2002) found that 7% (2,031,000 housing units) may have had Pb-based paint, and more than half the XRF measurements indicated concentrations at 1.0 mg/cm$^2$ or greater. Moreover, Chen et al. (2003) found that 14% of the houses observed in the Little India district in Singapore had Pb levels equal to 1.0 mg/cm$^2$ or greater while 63% of the surfaces tested in Singapore's Chinatown were higher than or equal to 1.0 mg/cm$^2$. The aforementioned studies, including the one published as early as 1975, provided an insight on the usefulness of the XRF instrument and its characteristics in regard to Pb-based paint analysis.

### 2.5 Analysis on Skin Whiteners

Mercury (Hg) is a highly toxic metal that, in low concentration, can impair fertility, suppress the immune response and cause damage to the nervous system (Murphy et al. 2009). In aquatic systems, bioaccumulation through the food chain may result in Hg contamination of fish from even very low concentrations of methylmercury (MeHg) in water (Dionysiou et al. 2004). Sources of Hg are mainly related to anthropogenic activities such as mining, deforestation, fuel combustion, and solid waste incineration (Lecce et al. 2007; Murphy et al. 2009). One of the first cases of Hg contamination in Cambodia was associated with an illegal shipment from Taiwan of 2,700 metric tons of industrial wastes containing inorganic Hg (Murphy et al. 2009).

Mercury is used in skin whiteners to block the production of melanin. Mercury has the ability to accumulate and absorb through skin, as demonstrated by Al-Saleh (2004). The adverse health effects of Hg may include kidney malfunction, nervous system impairment, and liver tissues damage. Murphy et al. (2009) collected 41 brands of skin whiteners and analyzed them with a screening kit. Eleven brands were found to be contaminated with more than 2,000 μg/g (ppm) Hg, exceeding Association of Southeast Asian Nations (ASEAN) guidelines for safe cosmetic manufacturing practice limit of 1 μg/g. The most contaminated skin whitener had 12,590 μg/g Hg. The authors also reported that the Hg-containing products were labeled as being produced in Thailand, Taiwan, China, Vietnam and the United States.

A study by Peregrino et al. (2011) reported that 6 (37.5%) of the 16 skin-whitening creams analyzed by the cold vapor technique coupled with atomic absorption spectrometry (CV-ASS) contained Hg levels greater than the recommended level of the U.S. Food and Drug Administration (USFDA) of 1 μg/g (ppm). The Hg content in the 6 samples varied between 878 and 36,000 ppm. Skin whiteners containing Hg are still available and commonly used in Cambodia and many other developing countries, and the metal contents are poorly regulated (Murphy et al. 2009; Peregrino et al. 2011).

# 3. METHODOLOGY

## 3.1 Instrumentation

The Niton Model XL3t 900 Series analyzer is an energy dispersive X-ray fluorescence analyzer that contains an X-ray tube, which emits radiation when the instrument is on. This device is battery-powered and consists of three components: an X-ray source, a detector and a digital pulse processor (Figure 6). The digital processor monitors both the intensity of the X-rays and the number arriving per unit time. The analyzer's microprocessor and software convert this information into a real-time readout of the sample composition (i.e. element presents and concentrations) (Palmer et al. 2009). Normally, the XRF unit has an built-in bulk standard algorithm calibrated by the vendor of the analyzer for the intended analysis.

# Components of XRF Analyzer

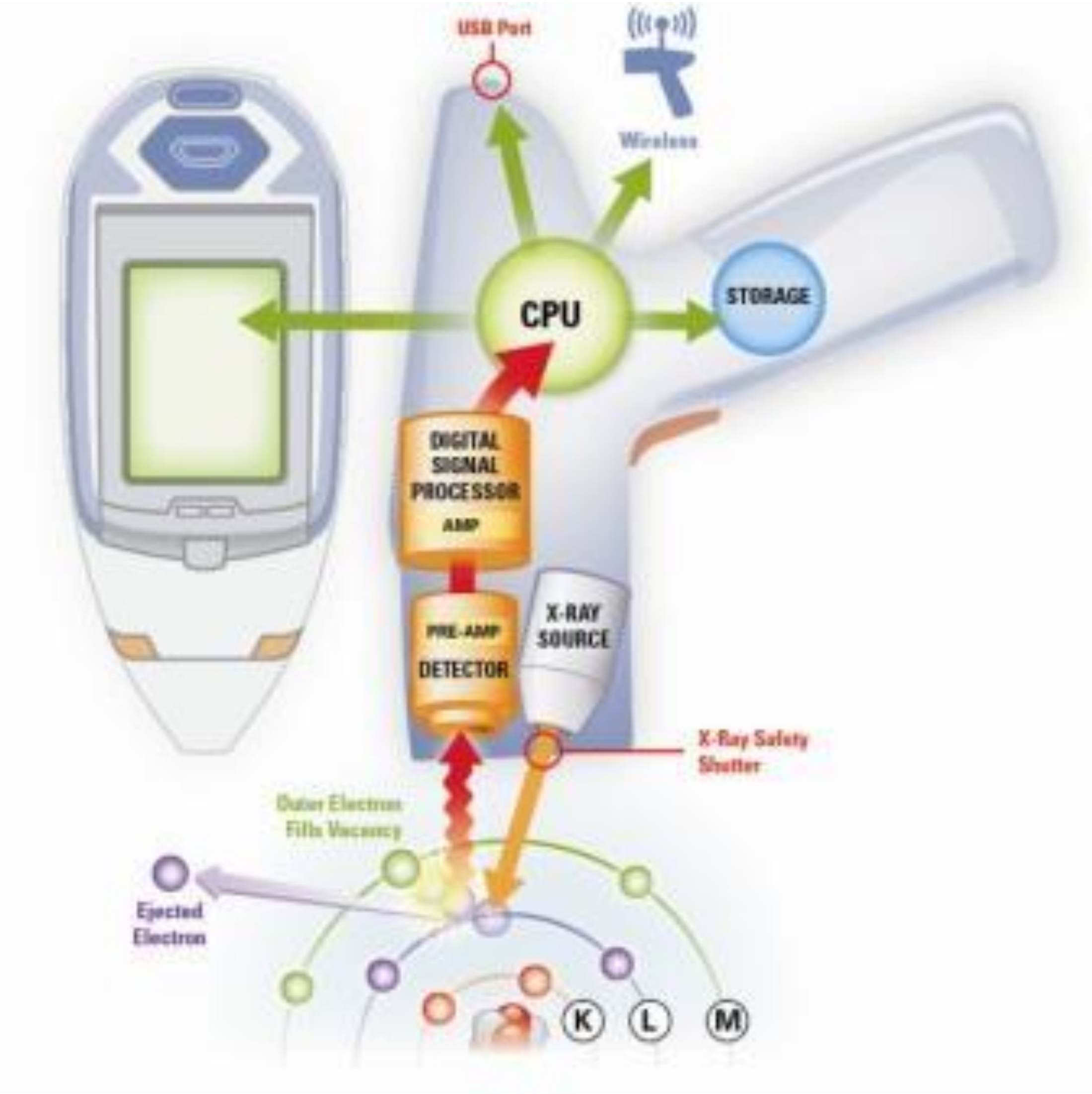

**Figure 6.** Components of a handheld XRF analyzer.

### 3.2 Reducing Radiation Exposure

Three factors are believed to help minimize radiation exposure to the users of the handheld XRF, one of which is *Time.* Thermo Fisher Scientific (2010) suggested the longer an individual is exposed to radiation the longer the radiation is able to interact with the body and the greater the dose he or she receives. By reducing the duration of the analysis, the level of exposure to radiation can be reduced. Another factor is *Distance*. An individual who is much closer to the radiation source during analysis is at a higher risk than another who is farther from the radiation source. Based on geometry, dose increases and decreases vary according to distance. This is a linear relationship. The distance from the window of the analyzer has a dose rate of 0.45 mSv/hr, whereas the distance of 30 cm from the window of the analyzer has a dose rate of 0.03 mSv/hr (Thermo Fisher Scientific 2010). It is recommended that hands and body parts be kept away from the front end of the analyzer when the shutter is open in order to reduce exposure.  Lopez and Solo (2006) recommended no personnel should be located within 1 meter of the front end of the analyzer during testing. *Shielding* is the third factor that helps minimize radiation exposure. Shielding material creates density between the analyzer and the radiation source, and the denser the material, the less radiation is escaped or absorbed by the analyzer. An example of the shielding material is a test stance (Figure 7).

# X-Ray Shielding Stance

**Figure 7.** A desktop stance of an XLi XRF analyzer.

### 3.2.1. Monitoring Radiation Exposure

Individuals can be monitored for the radiation dose they receive by use of radiation dosimetry devices (dosimeters). These devices can be used to monitor improper and proper use of the analyzer. The dosimeter is required when the user is expected to receive in excess of 10% of the annual dose limit. The most common kinds of dosimeters are whole-body badges and ring badges. The former is often clipped to the collar, shirt pocket or waist, whereas the latter is worn on a finger. When worn, the specific location of the dosimeter should be that part of the body that is expected to absorb the highest dose of radiation (Thermo Fisher Scientific 2010).

### 3.3 Mercury Contamination in Skin Whiteners

The Hg in skin creams study, which was approved by the Ethical Review Committee of the Cambodian Ministry of Health, took place in 2011 at the University of Health Science, two coffee shops near the factories, a bar and massage parlor in Phnom Penh. A questionnaire was given out to the participants to provide information about their socio-economic background; the frequency use of the cream; and the origin and price of the product. In total, 610 skin creams were tested including an additional 66 creams that were purchased from three local markets in Phnom Penh.

The Niton XL3t unit (Thermo Fisher Scientific, Waltham, MA) was used in the study with the 30 second analysis benchmark for each sample. The analytical procedure of the XRF required very minimal sample preparation and produced results within minutes. A spatula was used to scoop 3 to 5 ml from the top 5mm layer of the cream and placed on a piece of Mylar film (6 μm in thickness) that was then folded (Murphy et al. 2012). The unit was adjusted to Plastics Mode algorithm and the internal calibration was done by the manufacturer at Thermo Fisher Scientific, Billerica, MA, USA. The detector was placed directly against the film. It was important to reduce the distance between the unit’s window and the sample because the signal weakened as the distance between the two points increased (Murphy et al. 2012).

# 4. RESULTS

## 4.1 Illustration of QA/QC – Skin Whitening Creams

Due to concerns of potential inference from substances such as Pb or water, it is important to validate the results of the XRF unit with methods such as the atomic absorption spectroscopy (AAS) and inductively coupled plasma atomic absorption spectroscopy (ICP-AES) (Murphy et al. 2012). A set of 12 skin whiteners were purchased in Phnom Penh, and analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES) at the National University of Singapore (NUS). The results were then compared with those of the XRF from Thermo Scientific (Figure 8).

Eight samples containing less than 1,000 ppm of Hg in duplicate were spiked with additional Hg to a final concentration of 2,000 ppm, and the samples containing less than 2,000 ppm were spiked to the final concentration of 4,000 ppm. The analytical procedure of the ICP-OES was followed as outlined in Murphy et al. (2009).

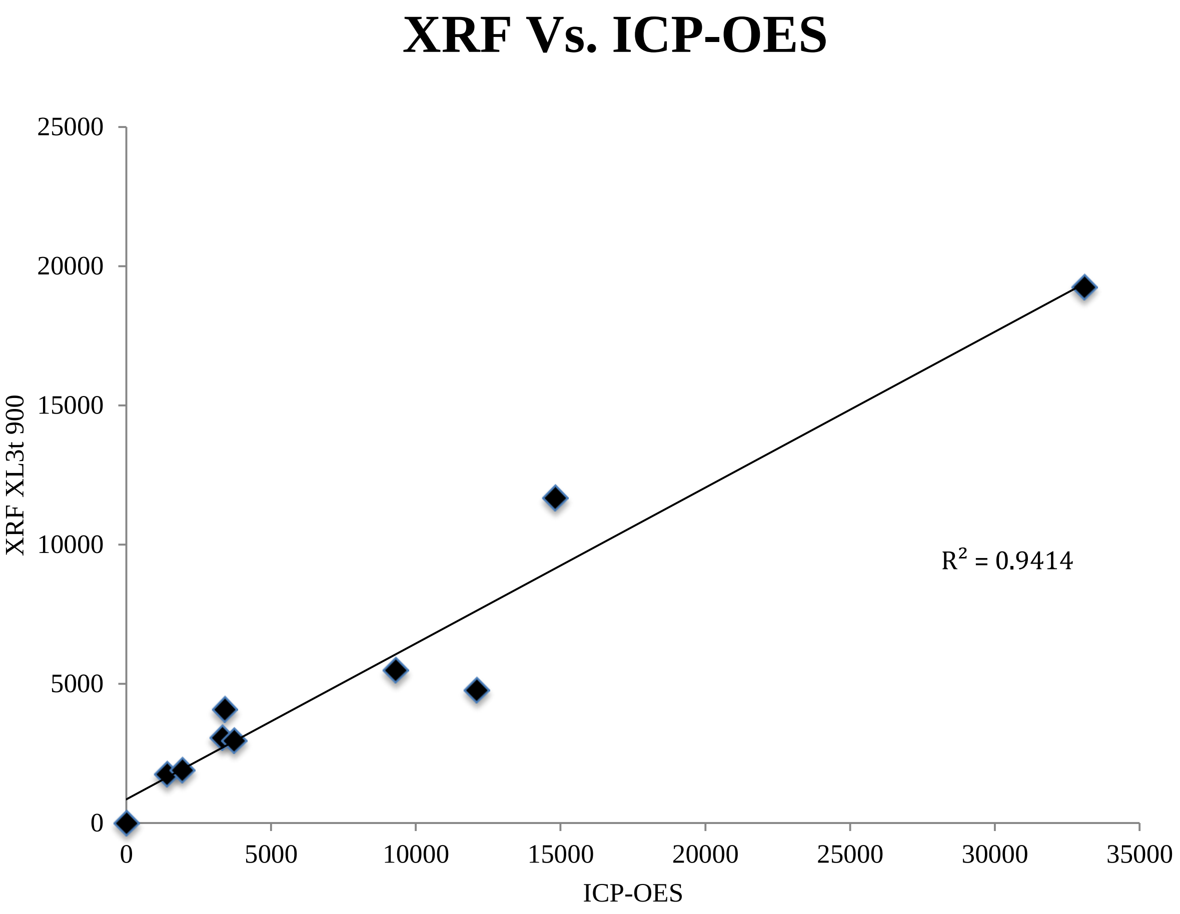

**Figure 8.** Comparison between XRF XL3t and ICP-OES Hg analysis.

At UHS another test was carried out to verify the accuracy of the XRF. A set of nine samples in duplicate were spiked with dimethylsulfoxide (DMSO) due to the desire to analyze high Hg concentrations as part of the QA/QC process. DMOS dissolves mercuric chloride ($HgCl_2$) better than water. Another reason that DMSO was used was because it would take too much of a volume of aqueous Hg to produce a 3% spiked cream (Murphy et al. 2012). Also, Hg is 4 times more stable in DMSO than in water (Murphy et al. 2012). In addition, the certified reference supplied by Thermo Fisher Scientific was used before and after analyses to confirm the analyzer's standard error within range of 5% of the manufacturer's specification. To be considered quantitative data – that is two data sets are statistically similar, the linear regression analysis between the XRF and the ICP-OES must result in a coefficient of determination ($r^2$) at or greater than 0.85 of the USEPA quality criteria (Table 1) (Parsons et al. 2012).

**Table 1.** Definition of USEPA validation quality criteria when comparing handheld XRF data with an alternative analytical technique, e.g. ICP-MS

| Data quality level | Statistical requirement |
|---|---|
| Definitive Q3 | $r^2$=0.85-1. Relative standard deviation (RSD) ≤10%. Inferential statistics (test for gradient of line=1 and y-intercept=0) must indicate the two data sets are statistically similar (at the 95% confidence level), i.e. relationship y=x accepted. |
| Quantitative screening Q2 | $r^2$=0.70-1. Relative standard deviation (RSD) ≤ 20%. Inferential statistics indicate the two data sets are statistically different, i.e. relationships y=mx or y=mx + c accepted. |
| Quantitative screening Q1 | $r^2$= less than 0.70. Relative standard deviation (RSD)≥ 20%. Inferential statistics indicate two data sets are statistically different. |

**Table 2.** XRF measurement of spiked Hg with dimethylsulfoxide (DMSO)

| Mercury Added | Mercury Detected | % of Recovery | % of Suppression |
|---|---|---|---|
| 74 | 64 | 87 | -13 |
| 74 | 72 | 98 | -2 |
| 147 | 157 | 107 | +7 |
| 147 | 124 | 84 | -16 |
| 221 | 200 | 90 | -10 |
| 221 | 211 | 95 | -5 |
| 295 | 295 | 100 | 0 |
| 295 | 301 | 102 | +2 |
| 923 | 811 | 88 | -12 |
| 923 | 838 | 91 | -9 |
| 1,846 | 1,620 | 88 | -12 |
| 1,846 | 1,735 | 94 | -6 |
| 3,693 | 3,045 | 82 | -18 |
| 3,693 | 3,182 | 86 | -14 |
| 7,388 | 6,099 | 83 | -17 |
| 7,388 | 6,035 | 82 | -18 |
| 14,775 | 11,600 | 79 | -21 |
| 14,775 | 11,000 | 74 | -26 |

*Note:* All values are in parts per million (ppm)

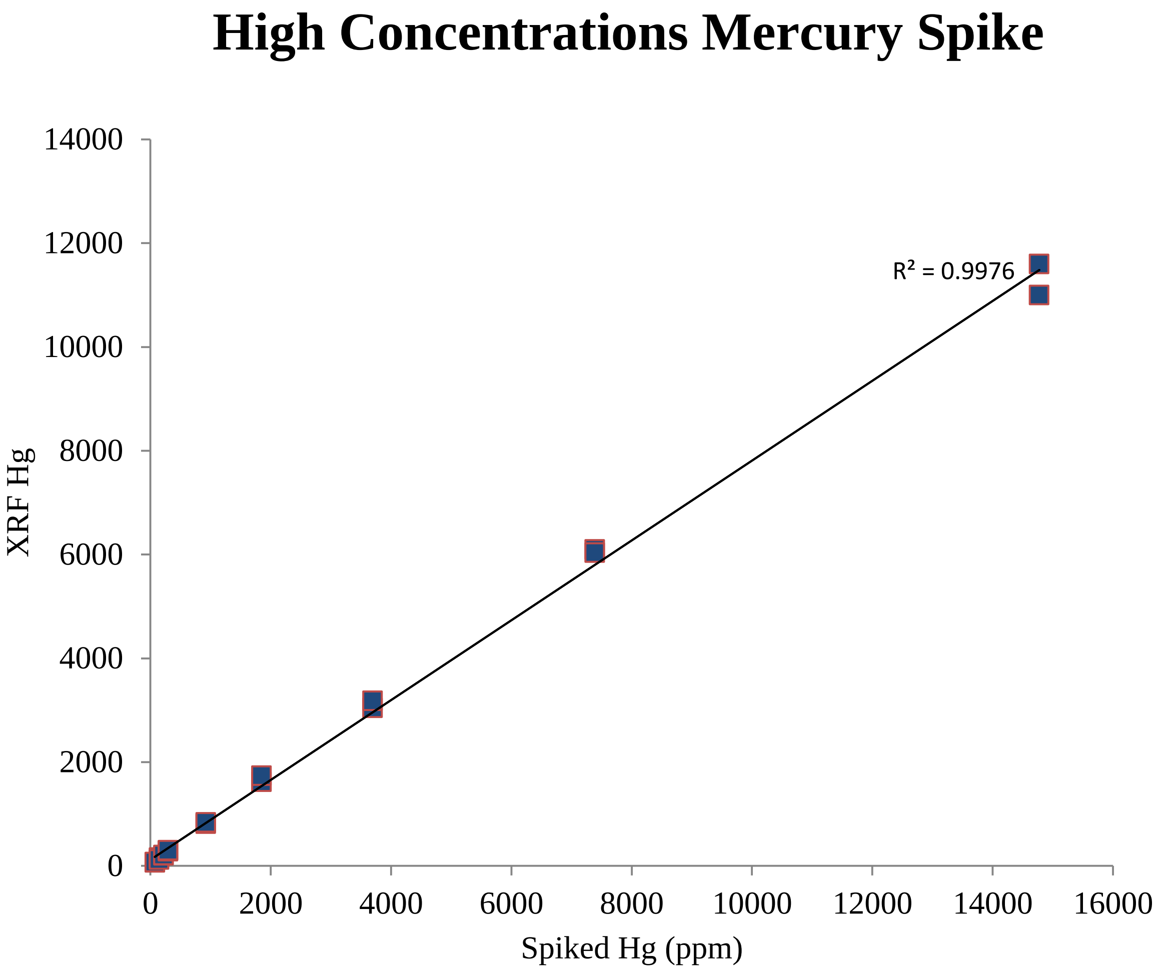

**Figure 9.** XRF measurement of high range spike Hg.

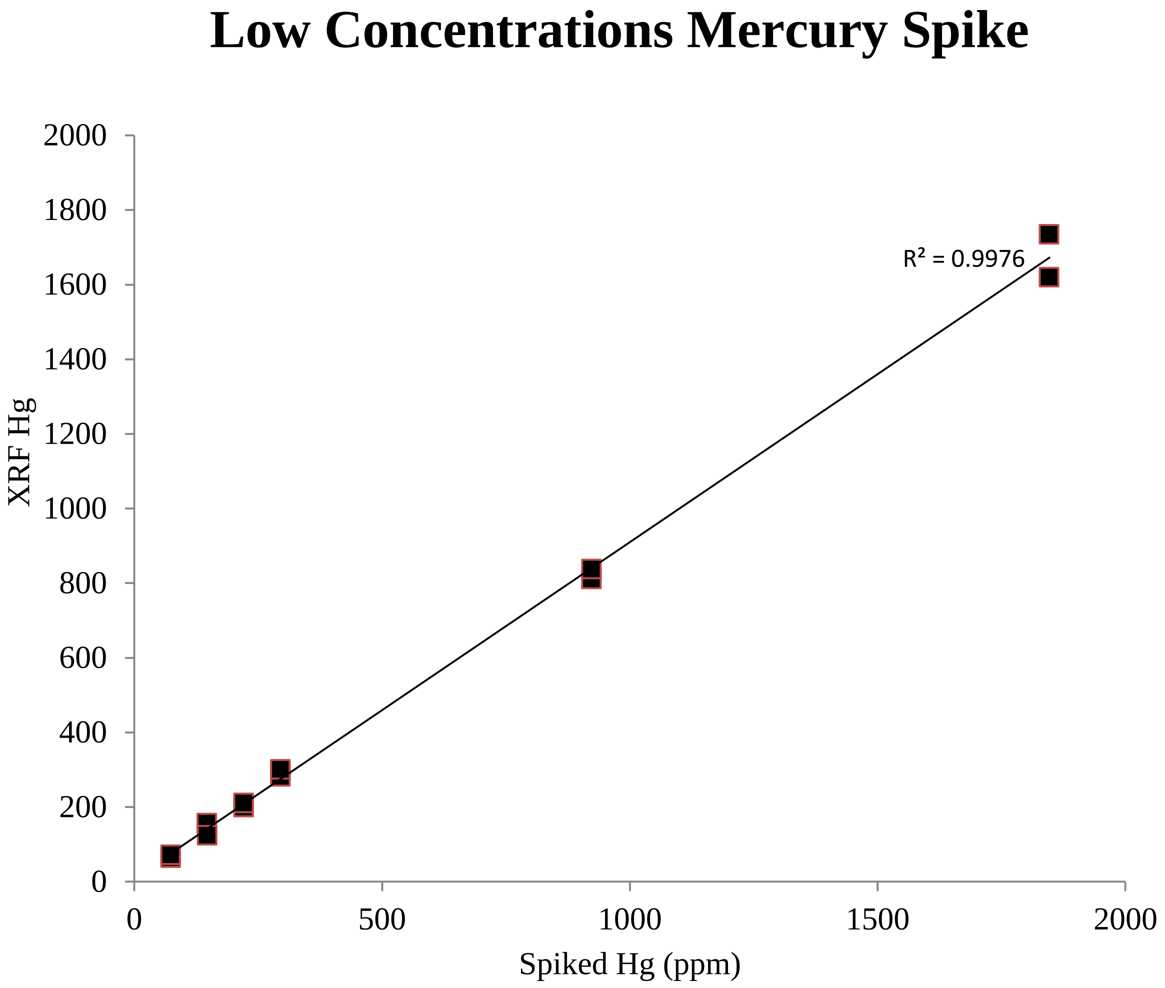

**Figure 10**. XRF measurement of low-range spiked Hg.

Four samples that were brought in by the students were reshot in replicates to assess the consistency of the XRF unit within a 5-10% standard deviation (Table 3). Each cream sample (5-10 ml) was taken and placed on a Mylar film. The detector was placed against the film for the duration of 30 seconds on Plastic Mode.

**Table 3.** XRF replicability measurement of Hg in market skin-whitening creams

| Products | Sun Block | Britney Care | Face Cream | Chinese Whitener |
|---|---|---|---|---|
| First Shot | 693 | 1,964 | 6,733 | 14,500 |
| Second Shot | 658 | 1,943 | 5,947 | 15,400 |
| Third Shot | 641 | 1,940 | 6,584 | 15,100 |
| Mean | 664 | 1,949 | 6,421 | 417 |
| Std | 27 | 13 | 417 | 458 |
| RSD% | 3.9 | 0.6 | 6.5 | 3.0 |

*Note:* All values are in parts per million (ppm).

### 4.2 Analysis of Skin Whiteners

A linear regression analysis showed that the relationship of the results produced by the XRF and the ICP-OES had an $r^2$ value of 0.94. It appeared that skin creams containing less than 5,000 ppm Hg had a more distinct relationship with the ICP-OES than those that had Hg concentrations higher than 5,000 ppm (Figure 8). About 82% (81 samples) of the skin creams had less than 5,000 ppm Hg.

Spiked Hg at a low-range set of concentrations (74-1,846 ppm) had a mean recovery of 93.6% and a standard deviation of 6.6% (n=12) (Figure 10). The spiked Hg at a high-range concentration (923-14,775 ppm) had a mean recovery of 84.7% and a standard deviation of 5.6% (n=10) (Figure 9). The highest percentage of suppression at the high range set of concentrations was 22% compared with a 12% suppression at a low-range set of concentrations. The spiking experiment with DMSO resulted in less variability than in the ICP-OES analysis (Table 2).

Out of 610 skin creams, which were brought in for analysis by 279 young women and 4 men, about 16% (98 samples) contained Hg higher than 20 ppm, which is the XRF limit of detection in this study. The mean of the 16% samples containing detectable Hg was 2,831 ppm, and the highest Hg concentration detected was 23,247ppm. Out of 192 concoctions prepared by local beauty shops or market vendors, about a third (64 samples) was found to be contaminated with more than 20 ppm Hg. Other commercial creams analyzed in this study were believed to be originating from various countries such as Thailand, Taiwan, China, the U.S., and Japan. However, since bootlegging is very common and is not strictly monitored, the researchers were not convinced that all of the so-called branded products were genuine. The skin whiteners that were prepared and sold locally in Cambodia appeared to have no proper labeling to provide information on how to use the cream or heavy metals as ingredients.

Skin cream product replicates from different markets were also analyzed. There was a high variability of Hg content in the replicates, which reflected different batches containing other different whitening reagents such as retinoic acid or hydroquinone with inconsistent chemistry and formulations (Murphy et al. 2012). It appeared that the mean concentration of Hg is higher in concoctions (736 ppm) than commercial products (391 ppm). The statistics also suggested that it would be more frequent to find a concoction (33.3%) containing higher than 20 ppm Hg than in a commercial cream (8.1%). Concoctions are prepared by beauty shop employees or market vendors with no proper formulation and knowledge of Hg. Hg content variability reflected different amounts of reagents used and formulations as reported by Murphy et al. (2012). Sixty-four (34%) of the concoctions analyzed had Hg concentration higher than the ASEAN and U.S. Food and Drug Administration (USFDA) guidelines of Hg in cosmetic products of 1 ppm (USFDA 2008). Thirty-four (8.1%) samples of the cosmetic products exceeded both the ASEAN and Canadian guideline of 1 ppm.

**Table 4**. XRF measurement of Hg level in skin whitening creams from the Educational Clinics

| | Number of Samples | Mean | Min with XRF | Max with XRF | % of Hg, >20ug/g |
|---|---|---|---|---|---|
| Commercial | 418 | 336 | 22 | 23,247 | 8.1 |
| Concoction | 192 | 712 | 21 | 18,350 | 33.3 |
| Total | 610 | 55 | 21 | 23,247 | 16.0 |

# 5. DISCUSSION

## 5.1 Mercury in Skin Whiteners

About 16% of bleaching creams analyzed contained more than 20 μg/g (ppm), the XRF limit of detection in the study (Murphy et al. 2012). The U.S. and ASEAN guideline of Hg in skin cream is 1 μg/g. The potential adverse health effects of using such creams may result in neurological impairment or poisoning from a skin whitening cream with 6-8% Hg (Weldon et al. 2000). Moreover, Sah (2012) reported that effects after exposure to Hg contained in skin lightening soaps and creams include kidney damage, skin rashes, skin discoloration and scarring, as well as a reduction in the skin's resistance to bacterial and fungal infections. Confirmatory laboratory analysis with the ICP-OES suggested that the XRF used in this study proved to be an excellent tool to measure Hg in skin whitening creams, although information related to dermal absorption has yet to be well resolved. Nonetheless, such a tool proves to be beneficial for on-site, quick preliminary screening with no sample extraction or preparation. The XRF is relatively inexpensive and requires little technical background.

# 6. CONCLUSION

The utility of the XRF is accompanied with strengths and limitations. The XRF is an excellent tool when used for commercial products such as skin creams (and other commercial and environmental products discussed in subsequent chapters of this thesis) analysis. In the skin cream study, the XRF has enough sensitivity to detect skin cream samples containing Hg higher than the EU guideline (70 ug/g), but is not sensitive enough to provide result below 20 ppm. The Hg standard is not enforced in most parts of the world. The fact that the technical and legal aspects of dermal absorption of metals are still poorly characterized in the EU (European Commission 2009) reflects a need of an additional XRF function that will soon be capable of assessing the level of toxicity this way.

Thorough on-site investigation should be followed up by accredited laboratory analysis. Because of high cost associated with laboratory analysis, using the XRF reduces such costs and provides guidance for on-site decision making and identifying contaminated areas or products. Far more sensitive instrumentations such as the AAS and ICP are ideal for providing accurate results, yet they are slow and laborious, as well as expensive. The analysis via the XRF is cheap and allows rapid mapping of contaminated areas where semi-quantitative data can be generated within minutes.

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# Chapter 2: Spatial Characterization of Metals Levels in Urban Sediment: Across the Street Dust, Sewer Treatment Wetland, Continuum, Phnom Penh, Cambodia

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# 1. INTRODUCTION

## 1.1 Background

Phnom Penh is the capital city of Cambodia, a country of about 14 million people (National Institute of Statistics 2010); approximately 1.4 million people reside in the capital. The increase in job market in Phnom Penh has caused people to migrate from rural areas to the city to find employment, higher education pursuits, vocational trainings and better health care (Walton 2010). Research on rural-urban migration in Cambodia suggested a phenomenon observed in several developing Southeast Asian countries; that the garment sector is the main pull factor in providing, over the last decade, more than 250,000 jobs, mostly for young female migrants coming from the provinces surrounding Phnom Penh (Abella 2005). The resulting increase in population has placed an environmental strain on the city, including increased amount of generated waste and wastewater discharges to the sewer system.

From a science and engineering perspective, Phnom Penh lags in development of basic urban infrastructure and services, as well as proper wastewater discharge regulation with deteriorated drainage systems. Only in the past 10-15 years or so did the municipality enhance the water supply systems. The sewer system in Phnom Penh is simple and aging, and usually is made up of 0.5 to 1 meter diameter polyvinyl chloride (PVC) and concrete pipes above and below ground.

The main focus of this chapter is on two interceptor sewers receiving wastes from industries, hospitals, households, institutions and agricultural fields before these wastes are pumped at the Tumpun and Meanchey stations into the Boeung Cheung Ek treatment wetland. Subsequently, the treated flow discharges into the Mekong Bassac, and Tonle Sap Rivers.

Boeung Cheung Ek, which is a natural wetland, has a total surface area of 1,300 hectares in the dry season and 2,000 hectares in the wet season (Irvine and Koottatep 2010), and it plays a very important role in providing both natural and economic benefits to the area and the peri-urban community.

The development of satellite cities in and around the capital has triggered development in the wetland likewise, increasing wastewater discharge into the sewer system and the wetland (Irvine 2007). Currently, certain portions of the wetland are being filled in for the construction of high-rise condominiums, supermarkets and a highway (Khouth et al. 2012). Any large-scale development in the wetland will inevitably pose socioeconomic, biological and ecological impacts on the nearby community and its natural resources.

In addition to sewer sediment that is discharged into the wetland, street dusts can also be used to indicate the extent of chemical toxicity in the environment. Metals levels in street dust can reflect both lithogenic processes and anthropogenic activities. As mentioned above, the development and the increase in construction, garment factories and automobiles has been taking place at an unprecedented rate and the emission from such sources contribute to the existence of particulate matter in the atmosphere. Metals associated with these emissions have the ability to accumulate and adhere to dust particles. Chemical contaminants bound to dust particles will deposit on urban surfaces and can be washed off during storm events into the sewer system and eventually into the receiving water body such as a creek, wetland or a river. Therefore, it is imperative that street dust monitoring be carried out in order to understand the level of its toxicity and the potential impacts on other parts of the urban and peri-urban ecosystem.

## 1.2 Chapter Objectives

The aims of this chapter are, therefore, to: (1) establish the spatial distribution of trace metal levels in street dust samples, sewer sediment samples and Boeung Cheung Ek Wetland samples; (2) and compare the findings with various international sediment quality guidelines such as the United States Environmental Protection Agency (USEPA), the New York State Department of Environmental Conservation (NYSDEC), and the Provincial Sediment Quality Guidelines of the Ministry of Environment, Ontario, Canada (PSQG); and 3) based on the metals levels and size distribution of the sediment develop an understanding of the hydraulic sorting, fate, and transport of particle-associated metals through the urban continuum of street dust, sewer sediment, and treatment wetland sediment.

## 1.3 Chapter Structure

The body of this chapter is presented in eight parts, including the Introduction as Part One. The Literature Review, which is in Part Two, discusses pertinent research on the sewer system and past related findings from wetlands with respect to chemical contamination. Also, there is a review on the contamination of urban road-deposited sediments and the likely sources of the metal contaminants in urban dust samples. Part Three is a description of the methods used to conduct this study. In Part Four the sample calculations and the data analyses are presented. Part Five is the summary and the interpretation of the results; and Part Six is the discussion of the experimental results as compared with other relevant studies. The conclusions are discussed in Part Seven, and Part Eight is the list of the references cited in this thesis chapter.

# 2. LITERATURE REVIEW

## 2.1 Definitions of Metals

Metals can be defined as dense inorganic metallic elements that at times are chemical hazards. Examples include lead (Pb), chromium (Cr), arsenic (As), Zinc (Zn), cadmium (Cd), copper (Cu), mercury (Hg) and nickel (Ni) that are most commonly found in contaminated sites as a result of land application of pesticides, leaded gasoline, paints, mine tailings, industrial wastes, sewage sludge, spillage of petrochemical and coal combustion residues (Wuana and Okieimen 2011). According to Forstner and Wittman (1983), metal contaminants are chemical pollutants that can be regarded as being resistant to environmental biodegradation, potentially toxic, and having the ability to be integrated into the food chain. Because heavy metals are resistant to biodegradation and can inhibit biodegradation of organic pollutants, contaminated soil can pose risks to ecosystems and humans, who are subject to direct and indirect exposure of pollutant sources.

## 2.2 Sediment as Toxicity Indicator

It is well documented that sediment samples are a good indication of environmental concern with respect to metal contamination of anthropogenic activities and natural geological processes (Banerjee 2003). Anthropogenic sources such as agriculture; mining and urban systems can transport chemical pollutants in to waterways and sewer systems, which in turn discharge into natural waterways. Due to less variability with respect to spatial and temporal scale than water, sediment samples provide a reliable, consistent indication of toxicity and also can concentrate chemical contaminants up to several orders of magnitude (Beiras et al. 2003).

Chemical toxicity accumulates over a long temporal scale and is not self-purified by water, and can enter biological food chains (Loska and Wiechula 2003).

## 2.3 Boeung Cheung Ek Wetland

Boeung Cheung Ek wetland is one of the natural wetlands in Phnom Penh that drains runoff and sedimentary flow from the southern part of the city before the wastewater enters the Mekong and Bassac River system. Living around the wetland are approximately 2,000 families who plant and harvest vegetables and other foodstuffs, and there are about 3,000 industrial firms situated around the wetland which also discharge waste into the wetland (Muong 2004). This number of firms; however, may have changed over the years due to development in the area. It is very likely that the number of migrant families has declined, but no data has yet been released as it is still an ongoing investigation. Therefore, wastewater that possibly contains a concentration of heavy metals such as Pb, As, Zn, Cd, Cu, Mn or Cr greater than the acceptable guideline not only pollutes the sediment in the water body, but it will also deteriorate the water quality and the livelihood of the residential communities.

## 2.4 Treatment Characteristics and Use Risks of the Wetland

Phnom Penh has no primary sewage treatment plant. As a result, all wastewater generated in the city and the surrounding areas gets discharged into the Boeung Cheung Ek wetland without abatement. Although there have been a few studies which focused on the consequences of effluent discharges into the Boeung Cheung Ek wetland on foodstuffs and water quality, there are limited data available in relation to sediment contamination with metals resulting from anthropogenic activities in Cambodia (Yim et al. 2008; Tiev et al. 2010; Marcussen et al. 2008).

One of such studies which evaluated the toxicity level of sediment in the wetland was that of Chak et al. (2010), who analyzed four composite sediment samples from the wetland to determine the concentrations of polychlorinated biphenyl (PCBs) and dichlorodiphenyl-trichloroethane (DDTs) using High-Performance Liquid Chromatography (HPLC) analyzer. The PCB and DDT levels were highest where the wastewater enters the wetland and the concentrations of the contaminants decreased gradually through the wetland; eventually becoming within the permissible range by the time flow left the wetland and entered the rivers.

It can be implied that the wetland serves as a natural treatment system in reducing the concentrated toxicity in the wastewater before being discharged into the Mekong and the Bassac Rivers. Vuong et al. (2007), who observed fecal and protozoan parasite contamination of water spinach harvested from the wetland, found that there was a 2-3 log reduction in the number of colonies of thermotolerant coliforms (ThC) between the entry and the exist points of the wetland. Tiev et al. (2010) also found reductions in detergents, $NO_3$, Cu, Zn, Cr, total phosphorus, and *E.* coli between the inlet and outlet sampling sites of the wetland.

According to a study by Ngoen-klan et al. (2010), residential communities that are living around the Boeung Cheung Ek wetland, and those who consume fish caught from the wetland can be potentially infected with liver flukes. Ngoen-klan et al. (2010) found that the fish species of *Henicerhychus Sp.* or Trey Riel and apple snails of the wetlands contained liver fluke cysts. Because Trey Riel is commonly used as a seasonal, fermented fish paste, there is a high likelihood that the parasites encysted within the fish tissues develop into larvae. Unless proper cooking is taken into account, consumers of fish from both peri-urban and urban areas may become a vector for these and other parasites. The main objective of Ngoen-klan's findings was to address the possibility of liver fluke infection among the peri-urban population and what types of fish were the most common vectors (fish and snails) for the parasites, in addition to a potential of sediment contamination. Chea et al. (2010) investigated food stuffs that were harvested from the wetland for metals levels and their potential for bioaccumulation. Although a simple risk calculation showed that consumption of the food stuffs generally did not pose any adverse health effects for adults, it was found that Cr in snails posed a slightly elevated risk for children.

## 2.5 Adverse Effects of Exposure to Metals

A metal such as Pb is used in many different ways in the production of batteries, pipes, gasoline, paints and household products. The long-term exposure effects to Pb may include decreased performance of the nervous system, weakness in fingers, ankles and anemia (Martin and Griswold 2009). Likewise, exposure to As may result in abnormal heart rhythm, decreased production of red blood cells, nausea and, if at a concentration as much as 200 μg/day, possible bladder cancer (Steinmaus et al. 2003). Elemental Zn and Cu are not as toxic as Pb, As, Hg or Cd. Only low concentrations of As, Hg or Pb can cause severe damage to the nervous and the renal system because these are cofactors, promoters and initiators in many diseases and cancer (Dockery and Pope 1996).

Contamination in soil by metals is of major concern because they can impair productivity and soil structure. Friedlova (2010) reported that metals in sediment reduce microbial enzymatic activity in soil, which in turn influences vegetation growth and production, as well as the microflora community. Metals that are deposited in soil as described in a study carried out by Ristic et al. (2004) in the Danube River, Montenegro can bioaccumulate in living tissues of biota, and thus influence the distribution of density of the organisms and their community.

Although there are no data available regarding the adverse physiological effects on the residents living around the Boeung Cheung Ek wetland, there is scientifically valid evidence suggesting that consumption of highly contaminated food stuffs and elevated exposure to such metals can potentially have adverse health effects. There are general agreements and evidence that suggest inorganic metals bioaccumulation in vegetables and fish could cause damage to the central nervous system (CNS) and reproductive fertility, thereby affecting the development, behavioral, and reproduction characteristics, particularly in children (Clarkson 1987; Da Silva et al. 2005; Miller 2004; Walsh and Tilson 1984). Moreover, a metal like Pb is a potent inhibitor of heme synthesis, which is necessary for the function of red blood cells, and methylmercury, an organic form of Hg, has been well documented in cases of the central nervous system deterioration due to the damage of the microtubules (Sager et al. 1983; Vogel et al. 1985).

### 2.6 Street Dust Indicators

There have been a number of studies on mapping and determining temporal characteristics of airborne particulates in Phnom Penh, Cambodia (Vermette et al. 2011; Bernosky and Vermette 2012), but none determined the concentrations of metals in the road-sediment deposits. Like sediment samples, the significance of study on metals bound to street dust particles illustrates the potential of chemical toxicity on humans via contaminated media such as the atmosphere (particle resuspension), water, vegetables, fish and other living organisms which are consumed by humans.

Street dust receives inputs from both natural atmospheric transport and anthropogenic activities. Natural pollutant material may include those deposited from surrounding soils, and biological materials from vegetation. Vermette et al. (1987) reported that cultivated land of the rural surroundings in Hamilton, Canada is the source of particulate matter to both atmosphere and runoff. Anthropogenic activities that are associated with the contribution of pollutant materials to the natural environment include industrial processes, vehicular exhaust emissions, components and abrasion, power plants and tires and road surface wearing (Sutherland and Tolosa 2000; Vermette et al. 1987). The metal deposits in street dust have the ability to bind to fine dust particles (Kelly et al. 1996). The higher the concentration of the metals accumulating in street dust, the higher the risk to their health people become exposed to.

People can become exposed to metal contaminants via a number of means such as fish consumption from metal-contaminated areas. The consumption of contaminated food can release the toxic chemicals into the bloodstream and other living tissues such as the nervous and the renal systems. Due to the fact that street dust is freely inhaled by those residing and traversing within the proximity of the streets, the more dust on the streets contaminated with heavy metals, the higher the concentration of metals people are exposed to (Christoforidis and Stamatis 2009; Irvine et al. 2009).

## 2.7 Sources of Street Dust Contamination

There are air quality regulation guidelines in Cambodia, which were created after 2004 by the Blacksmith Institute in conjunction with Department of Pollution Control, Ministry of Environment in Cambodia, but the regulatory guidelines are not strictly enforced while the city itself has been undergoing rapid development and subsequent population and industrial growth (Blacksmith Institute 2004). Unpaved streets in the city, improper transport of sand, cement and soil lead to the spillage of the materials on the street when being transported to the construction site. When spilled construction materials bind with chemical contaminants generated by commercial and industrial firms, as well as by transportation, the integrated street dust could become contaminated, and are then inhaled by the public. The level of metal contamination varies, and is determined by anthropogenic activities, rainfall and degree of natural sources. Irvine et al. (2009) suggested that street sediment contamination in urban areas is a representation of a repository of various sources, which pose human health risk for prolonged exposure and inhalation.

Tamrakar and Shakya (2011) found high concentrations of Zn and Pb in street dust associated with areas of mechanical workshops. Zn is commonly used in transmission oil, and it suggested that there were possible leakages of the oil during mechanical repair or maintenance of vehicles (Mingkui and Hao 2008). Mingkui and Hao (2008) also indicated possible sources of Pb as being a result of leaded gasoline use, improper disposal of batteries and recycling and coal combustion. Torre et al. (2002) reported that brake linings of vehicles may also contain Pb, Ba, and Sb while Rosselot (2006) found that Cu could also be released from brake lining.

To improve management and minimize potential impacts, spatial characterization of metal concentrations in the sediment and comparisons between these concentrations and certified standards must be evaluated. Understanding the contaminant fate and transport trajectory is a very important step to comprehend the extent of toxicity level and distributive deposition of metals in the sewer systems and the wetland. Therefore, sediment analyses play an important role in the assessment of pollution status and the determination of sources of the trace metals.

# 3. METHODS

## 3.1 Sewer and Wetland Sediment Sampling Sites

A total of 21 samples were obtained from 17 stations - eight sewer samples with a duplicate, and 13 wetland samples with four duplicates and one sample in a duplicate shot. The fieldwork was carried out over two days in June 2011. There are two main sewer canals that drain waste from Phnom Penh – the Tum Pun channel and the Meanchey channel. The samples that were collected from the Tum Pun sewer system are designated in red as T1 and T2P in Figure 3 (done in ArcMap v. 10.1). The T1 site is the head of the open sewer, in a mixed residential/commercial area (and a hospital is nearby); whereas T2P (Figure 1) is the pumping station that drains the untreated wastewater into the wetland. Four sewer samples were obtained from the Meanchey sewer system, and are designated in red as M1, M2, M3 and M4P (Figure 3). M1 is the furthest upstream site (Figure 2) of the sample collection, and M4P is the Meanchey pump station that pumps wastewater from the west section of Phnom Penh into the same wetland (Boeung Cheung Ek). Between the M1 site and the M4P site lie many commercial businesses, industries, hospitals, private clinics, hotels and restaurants that discharge their wastes directly into the canal. Since these two are open sewer canals, other wastes such as plastic bags and drinking bottles can easily enter the waterways.

# Tum Pun Pump Station

**Figure 11.** Squatter housing behind the Tum Pun pump station (T2P).

# Meanchey Sewer Canal

**Figure 12.** First sampling site of the Meanchey sewer canal (M1).

Source: Esri, i-cubed, USDA, USGS, AEX, GeoEye, Getmapping, Aerogrid, IGN, IGP, and the GIS User Community

**Figure 13.** Six sewer samples are designated as T1, T2P, M1, M2, M3, and M4P. Wetland samples are designated as M5W to W8.

### 3.2 Sewer Sample Collection

A sampler was fashioned using a 2.5 meter polyvinyl chloride (PVC) pipe with a small plastic basket attached to one end using a wire, which would collect sewer sediment samples and allow water to drain off, albeit not completely (Figure 4). A plastic spoon was used to scoop the sediment out of the small basket and into a clean polyethylene bag. Clean tissues were used to wipe out any leftover of the previous sample before the next one was collected. This practice ensured that cross contamination of heavy metals concentrations between samples was minimized.

**Figure 14.** Modified sewer and wetland sampling apparatus.

Each of the sewer samples collected was from the top 5cm of the sediment by placing the porous basket into the open sewage system against the flow of the current or within a reaching distance from the bank and scraping along the bottom of the sewer, so that the sediment could be collected. Only the sediment was collected, and plant debris and other materials such as plastic bags and bottles were removed or excluded in the sampling procedure. Each of the samples was properly labeled with the name of the site and the date of the collection. A Garmin eTrex High Sensitivity GPS with an accuracy generally better than 3 m was used to determine each sampling site's coordinates.

### 3.3 Wetland Sediment Sampling Sites

A total of 13wetland samples were collected. The same sewer sediment collection procedure was also used for the wetland sediment collection. The sampling sites are indicated in Figure 3. Sites T3W and M5W are the wetland inlets of Tum Pun and Meanchey respectively. Other samples were collected from areas throughout the wetland that local residents used for planting aquatic vegetables such as morning glory and mimosa. Areas around sites W3, W7 and W8 are undergoing major sand filling for a government-approved highway construction project and high rise condominiums (Figure 5). Two boats were rented to gain access to the wetland open water sites (W4, W5, W7 and W8). Site W6 is one of the wetland outlets that drains the naturally treated wastewater from the wetland into the Mekong and Bassac Rivers.

This sample collection procedure was modified from that of the United States Environmental Protection Agency (USEPA) Chapter 3 of the *Methods for Collection, Storage and Manipulation of Sediment for Chemical and Toxicology Analyses – Contaminated Sediments in Water* to reflect the financial and sampling apparatus availability for the study. Flexibility must be taken into account when fieldwork is carried out in developing countries when all condition cannot be fully satisfied.

# Development in Wetland

**Figure 15.** Sand filling in the wetland near site W8 for a development project.

## 3.4 Street Dust Sampling

### 3.4.1 <u>First Round of Sampling</u>

The first round of street dust samples were collected in January 2012 in Phnom Penh, Cambodia. The particular interest was to focus on heavy traffic areas such as at the intersections of major streets, industrial and commercial areas. Although almost all streets in the city have been paved over the past decade, regular maintenance of the conditions of the streets is yet to be fully implemented. Some of the major streets, not all, are maintained by means of daily manual sweeping by hand-held sweepers. The locations of the sample sites are given in Figure 6.

#### 3.4.1.1 *Street Dust Sample Collection*

Twenty four street dust samples were collected from heavy traffic intersections, major streets, industrial and commercial areas and from a farmland of the Royal University of Agriculture in Phnom Penh (RUA site). The locations of the samples were determined on a map and later were plotted on Google Earth for the corresponding coordinates. Each of the samples was collected using a plastic dustpan and a 30-centimeter hand-held sweeper. The sweeping covered 1-$m^2$ plot and was done in a striated motion as described by Wei et al. (2009). Each street dust sample weighed between 30.3 and 147.2 g. The street sediment was collected adjacent to the curb and then transferred to a polyethylene plastic bag for subsequent air drying and analysis with the X-ray fluorescence (XRF) XLi housed in the Department of Earth Sciences of Buffalo State, State University of New York.

During the second round of street dust sampling, a dustpan and a handheld sweeper were used to collect the samples. The sampling covered a 1 square meter plot near the curb. Next, the samples were screened through a metallic mesh 1.25 mm. Then, about 2g of each sample was placed onto the Mylar film and shot with the XRF XL3t for 30 seconds on Soil Mode. The XRF had a built-in calibration from the manufacturer, so it was acceptable to carry the analysis.

### 3.4.2 Second Round of Sampling

#### 3.4.2.1 *Possible Sources of Lead and Chromium*

To narrow down the possible sources of Pb and Cr in street dust beside vehicular combustion, and to reaffirm that the elevated Cr levels in snail detected in Chea et al. (2010) could be associated with the level of Cr in street dust and industrial discharge such as tanneries, a second round of street dust sampling was carried out on February 14, 2013. The sampling covered eight locations near garment factories including two landfills (Meanchey and Cheung Ek landfills). Lead is used in the manufacturing of PVC pipes, and the incineration of such pipes at the landfills could also contribute to the amount of Pb in street dust. Two samples were collected near a tannery factory; three were collected en route to the dumpsites; one at the old dumpsite; and two were collected at the new dumpsite.

#### 3.4.2.2 *Zinc in Tires*

Zinc in street dust derives from sources like lubricating oil, animal feed, paint and tires. As such, fourteen tire samples were analyzed with the XRF Xl3t analyzer. Twelve of the tires were manufactured in Thailand while two were manufactured in Korea. The analysis was done by placing the XRF unit against the tires for 60 seconds on Soil Mode.

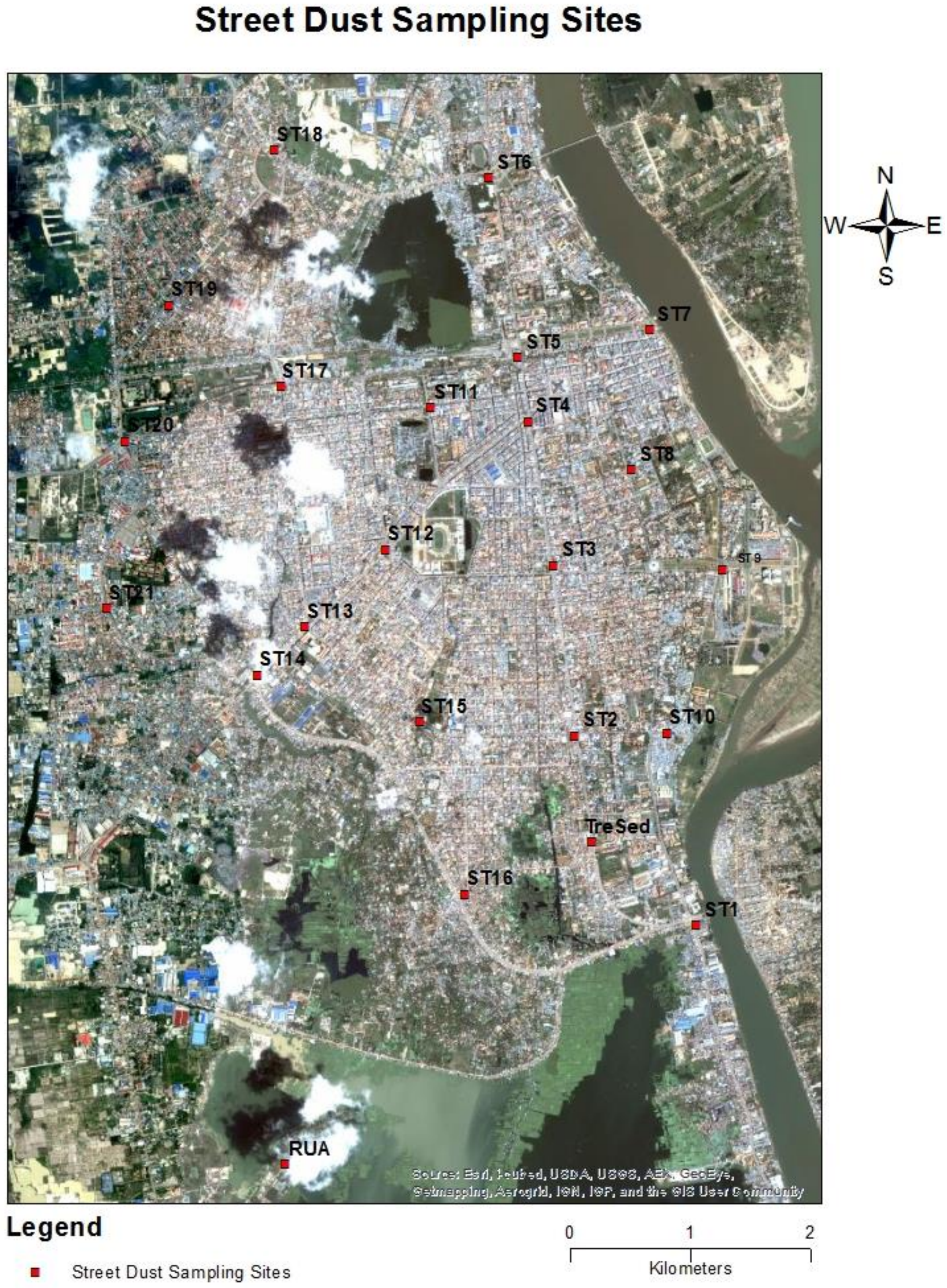

**Figure 16.** Street dust samples designated as ST1 to ST21. TreSed and RUA are the samples from an ongoing construction trench and the Royal University of Agriculture respectively.

# Street Sweeping

**Figure 17.** A routine street sweeping.

## 3.5 Analytical Methods

### 3.5.1 Quality Control and Quality Assurance

To assure the Niton XRF XL3t would be representative in terms of providing data, certified reference sediment from the National Water Research Institute (NWRI) - Canada was used to evaluate the accuracy of the unit. Approximately 2g of the certified reference was placed onto a Mylar film using a pre-washed spatula, folded and shot with the XRF. The unit had been adjusted to the Soil Mode, and the duration of the analysis was 60 seconds using the aforementioned reference material for the calibration. Upon the completion of the analysis, the data were transferred into a software application from which the data were downloaded. The values of the comparison between the certified standard reference and those detected by the XRF XL3t 900 Series are presented in Table 1.

**Table 5.** Comparison of XRF XL3t with certified NWRI

| | Certified Standard | | XRF XL3t | |
|---|---|---|---|---|
| Parameters | Reference Value | Standard Deviation | XRF Reading | Standard Deviation |
| Cu | 82.9 | ±19.0 | 68.3 | ±12.6 |
| Fe | 60,000 | ±4,000 | 48,000 | ±301.4 |
| Mn | 1,264 | ±91.2 | 1,003 | ±65.9 |
| Pb | 243.0 | ±174.3 | 179,7 | ±10.2 |
| Zn | 1,396 | ±107.5 | 1,148 | ±27.6 |
| As | 18.8 | ±1.5 | 28.5 | ±7.6 |

*Note:* All units are in parts per million (ppm).

The concentrations of Pb, Cu, Fe, Mn, As and Zn were detected by the XRF XL3t because they are considered environmentally important to indicate the level of toxicity (Stallard et al. 1995). The metals concentrations were generally lower than those specified by the NWRI reference standard. The variations are in Cu, Fe, Mn, Pb and Zn, and this can be attributed to the experimental sample preparation and the sensor direction of the unit on which the analyses were based (Stallard et al. 1995).

Relatively small differences in metal concentrations between ground and unground sediment samples were observed during the 30 second analysis for 5 different samples with all metal concentrations of the unground samples being higher. The grinding was done by means of using a mortar and pestle. Then, about 2g of sample was placed on the Mylar film and shot with the XRF unit. The mean values of the ground samples for Pb, As, Zn, and Cu were 39.2 ppm ± 0.5, 19.3 ppm ±0.3, 527.5 ppm ±3.2, and 89.3 ppm ±1.2 respectively. The mean values of the unground samples for Pb, As, Zn, and Cu were 47.4 ppm ± 0.4, 23.4 ppm ± 0.3, 666.7 ppm ± 1.4, and 118.2 ppm ± 1.2 respectively. The implication of the results is the XRF chosen for this study is a robust environmental analytical tool that requires minimal sample preparation, and provides results within a short period of time.

### 3.5.2 XRF Side-by-Side Comparison with CCRMP-TILL4

A side-by-side comparison between the Niton XRF XL3t 900 Series and the Niton XRF XLi using two sediment reference standards, CCRMP-TILL4 and NCS73308, was evaluated on August 25, 2012 at the Department of Earth Sciences, Buffalo State, The State University of New York. Each of the XRFs was evaluated with both sediment standards on the built-in Soil Mode for 30 seconds. Although there were variations in the parameters like Pb and Zn, the two XRFs were quite comparable in terms of the results provided, and the 30 second duration analyses between the two XRF analyzers did not seem to significantly affect the metal concentrations detected. The results of the XRF cross reference check are provided below in Table 2.

**Table 6.** Comparison between XRF XL3t and XRF XLi with certified CCRMP-TILL4

| Certified CCRMP-TILL4 | | | XRF XL3t | | XRF XLi | |
|---|---|---|---|---|---|---|
| Parameters | Reference Value | Standard Deviation | Reading Value | Standard Deviation | Reading Value | Standard Deviation |
| Cu | 230 | ±13 | 217 | ±16 | 235 | ±15.7 |
| Fe | 32,000 | ±39 | 31,009 | ±234 | 31,230 | ±245 |
| Pb | 56 | ±4.2 | 24 | ±6 | 32 | ±10 |
| Zn | 71 | ±12 | 48 | ±8.1 | 55 | ±6.1 |
| As | 97 | ±5.2 | 101 | ±6.2 | 105 | ±7.2 |

*Note:* All values are in parts per million (ppm).

### 3.5.3 XRF Side-by-Side Comparison with NCS 73308

XRF XL3t and XRF XLi were compared with a sediment reference NCS 73308 for 30 seconds on Soil Mode. The results are shown in Table 3.

**Table 7.** Comparison between XRF XL3t and XRF XLi with certified NCS 73308

| Certified NCS 73308 | | | XRF XL3t | | XRF XLi | |
|---|---|---|---|---|---|---|
| Parameters | Reference Value | Standard Deviation | Reading Value | Standard Deviation | Reading Value | Standard Deviation |
| Cu | ND | ND | 19 | ±9 | 15 | ±7 |
| Fe | 19,800 | ±74.6 | 19,051 | ±167.6 | 19,150 | ±150.5 |
| Pb | 29 | ±3.8 | ND | ±6.3 | 10 | ±4.3 |
| Zn | ND | ND | 24 | ±5.6 | 29.5 | ±10.8 |
| As | 21 | ±0.8 | 20 | ±3.4 | 22.9 | ±2.3 |

*Note:* All values are in parts per million (ppm). Not Detected abbreviated (ND)

### 3.5.4 Analysis of Sewer and Wetland Samples

The sewer and wetland samples were air dried at room temperature to standardize the water content at a laboratory of the University of Health Sciences in Phnom Penh. The Buffalo State sewer sample, which was collected, dried and analyzed with the same XRF unit at Buffalo

State using the same methodological and analytical procedure as the sewer samples from Phnom Penh. The samples collected in Cambodia may have exceeded the standardized dry period of seven days as described by Birge et al. (1998) but this was done due to excessive water content observed during the sample collection process. The samples were dried in porcelain cups pre-washed with deionized water. When the samples were dried, they were ground with a mortar and pestle, so that the samples would be suitable for the analysis with the XRF unit. About 2g of each of the samples were used for the analysis (Birge et al. 1998). A spatula pre-swashed with deionized water was used to transfer the required sample amount of sediment onto a Mylar film, which had a thickness of 0.45 microns. Each of the sewer and wetland sediment samples was analyzed for 30 seconds.

### 3.5.5 Analysis of Street Dust Samples

#### 3.5.5.1 *First Round Sampling*

The street dust samples that were collected in Phnom Penh in January 2012 were taken to Buffalo State, State University of New York for analysis by the handheld XRF XLi analyzer. Each analysis was done by placing the street dust sample inside the polyethylene bag on the XRF unit stand, which has an enclosed chamber to prevent the x-ray scattering during the analysis. A two-minute duration analysis was used for all street dust samples, although a 30 second analysis time also was acceptable (Thermo Fisher Scientific 2009). Because most of these samples are composed of readily suitable sediment particles for analysis, no further grinding was necessary, except for the sample that was collected from a construction site in front of a hotel (TreSed) because there were large clumps of sediment sticking together.

### 3.5.6 Grain Size Analysis of Sewer and Wetland Samples

During the study survey, 21 samples from the sewer systems and the Boeung Cheung Ek wetland were collected to determine the grain size distribution. Due to limited availability of technical analysis in Cambodia, the samples were taken to the School of Environment, Resources and Development (SERD) of the Asian Institute of Technology (AIT), Thailand for analysis. Unfortunately, most of the samples were lost during the record floods in Thailand in 2011. Only three samples had been analyzed for the grain size distribution prior to the flood, namely site T2P, T1 and M1.

The procedure used for the analysis was described by the American Society for Testing and Materials (ASTM) (Wray 1986) and consisted of sieves with seven fractional classes between 4.76 mm and 0.10 mm diameter. Prior to the analysis, the sediment samples were air dried and later ground with a mortar and pestle to disintegrate the clumps. First, the sample was poured into the top of the sieve pan. Then, the sieve pan was shaken manually for 60 seconds to make sure all sediments passed through the sieve pan, except for those particles larger than the designated sieve grids. Next, the sediment in each individual sieve pan was poured into a clean, dry bowl and weighed; and the weights were recorded.

### 3.5.7 Grain Size Analysis of Street Dust

Twenty-four street dust sediments were analyzed for their grain size distribution at the Department of Geography and Planning of Buffalo State, The State University of New York. Prior to the particle size analysis the samples were air dried in the pre-washed porcelain dishes for seven days. Four factional classes between 4 mm and 0.063 mm diameter were used. The procedure was carried out according to the American Society of Testing Materials (ASTM) D422.

All samples weighed between 30.3g and 147.2 g. Each of the samples was poured into the top sieve, which in turn was shaken manually for 60 seconds to make sure that all smaller size particles could pass down onto the next sieve category. The sample that remained on the sieve was poured into a porcelain bowl, and the weighed sample was adjusted based on the standard calculation to find its grain size distribution. Grinding of the sediment samples was not required because of the nature of the fine particles of the street dust. The results of the grain size analysis of the street dust are shown in Table 13.

### 3.5.8 Kriging Analysis

Kriging is an advanced geostatistical estimator that generates an estimated surface from a scattered set of points at unobserved locations and associates the quantification of the uncertainty with the estimator. The value of an unknown location is based on the average of the know values at its neighbors. Kriging assumes that the distance or direction between sample points reflects a spatial correlation that can be used to explain metal concentrations variation in the surface. Correlation is the tendency of two types of variables to be related – that is things closer together tend to be more similar than those that are apart. The rate at which the correlation decays can be expressed as a function of distance. The sampling sites of the street dust were georeferenced with a base map of Phnom Penh, and the metal concentrations, for the visibility purpose, were binned into five categories.

# 4. RESULTS

## 4.1 Metal Concentrations in Sewer and Wetland Samples

Eight sewer samples were collected with a duplicate and 13 wetland samples were collected with four duplicates and one duplicate shot. The metal concentrations of each sample are compared with the USEPA, NYSDEC, and PSQG guidelines. The number of samples exceeding a designated guideline is also indicated. A summary of the metal concentrations detected in the two sewer systems, the wetland, and the street dust is given in Table 4.

**Table 8.** Comparison of mean concentrations of metals in Tum Pun and Meanchey sewer systems, wetland and street dust samples

| Samples | Pb | Std | As | Std | Zn | Std | Cu | Std | Mn | Std | Fe |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Tum Pun | 27.8 | 24.1 | 15.0 | 7.3 | 476.5 | 76.6 | 74.9 | 46.8 | 299.2 | 117.2 | 20,772 |
| Meanchey | 77.4 | 47.9 | 14.9 | 3.4 | 590.5 | 287.8 | 125.1 | 62.4 | 332.9 | 44.6 | 22,476 |
| Wetland | 7.0 | 8.1 | 18.9 | 7.5 | 184.3 | 127.4 | 65.0 | 52.6 | 523.4 | 275.6 | 34,047 |
| Street dust | 39.2 | 12.3 | 8.8 | 10.8 | 176.5 | 84.8 | 61.4 | 21.1 | 224.9 | 75.2 | 15,369 |

Values are in parts per million (ppm).

**Table 9.** Metal concentrations in sewer and wetland samples

| Sites | Pb | As | Zn | Cu | Fe | Mn |
|---|---|---|---|---|---|---|
| T2P | 39.9 | 18.8 | 491.3 | 93.4 | 25,585 | 383.9 |
| T1 | ND | 6.58 | 393.6 | 21.7 | 11,946 | 165.4 |
| T1 Duplicate | ND | ND | 407.3 | 30.1 | 12,121 | 109.9 |
| M1 | 126.6 | 13.4 | 785.6 | 208.3 | 21,708 | 311.5 |
| M2 | 104.6 | 11.7 | 717.5 | 123.4 | 25,864 | 293.7 |
| M3 | 81.3 | 19.6 | 737.3 | 126.1 | 25,053 | 372.9 |
| M4P | 74.4 | 17.2 | 626 | 135.6 | 19,382 | 297.7 |
| M5W | ND | 12.4 | 86 | 32.2 | 20,373 | 388.9 |
| M5W Duplicate | ND | 12.3 | 58.1 | 24.5 | 17,832 | 223.7 |
| W1 | ND | 10.6 | 74.9 | 19.5 | 28,708 | 89.2 |
| W2 | ND | 15.1 | 67.2 | 21.2 | 31,816 | 233.4 |
| T3W | 43.5 | 19.8 | 544.7 | 109.8 | 24,785 | 348.4 |
| W7 | 15.4 | 30.4 | 392.5 | 104.2 | 35,518 | 632.2 |
| W8 | 11.6 | 25.6 | 320.2 | 100 | 34,196 | 556.6 |
| W8 Duplicate | ND | 11.7 | 153.9 | 34.5 | 15,582 | 275.6 |
| W3 | 19.9 | 10.2 | 141.4 | 35.2 | 19,483 | 292.3 |
| W4 | ND | 26.1 | 271.1 | 165.1 | 58,552 | 862.5 |
| W5 | 9.2 | 15.3 | 146.7 | 48.5 | 41,216 | 600.4 |
| W6 | ND | 17.9 | 60.5 | 26.4 | 22,883 | 920.8 |
| W6 Duplicate Shot | ND | 13.7 | 57.5 | 22.9 | 23,591 | 608.7 |
| W6 Duplicate | ND | 14.7 | 45.6 | 17.1 | 23,003 | 559.3 |
| Buffalo State | 209.2 | 24.7 | 1,039 | 182.7 | 24,898 | 228.6 |
| Mean | 32.9 | 16.9 | 366.7 | 85.6 | 27,942 | 421.8 |
| Sigma (δ) | 41.7 | 6.4 | 259.4 | 58.2 | 10,880 | 233.8 |
| USEPA[1] | 35.8 | 9.8 | 121 | 31.6 | 20,000 | 460 |
| NYSDEC[2] | 110 | 33 | 270 | 110 | 20,000 | 460 |
| PSQG[3] | 250 | 33 | 820 | 110 | 40,000 | 1100 |
| USEPA[β] | 7 | 19 | 15 | 14 | 14 | 5 |
| NYSDEC[β] | 2 | 0 | 11 | 6 | 14 | 5 |
| PSQG[β] | 0 | 0 | 1 | 6 | 2 | 0 |

*Note:* All values are in parts per million (ppm). Tum Pun and Meanchey systems abbreviated "T" and "M" respectively. Wetland abbreviated "W". Buffalo State, a sewer sample from the campus.

[1] USEPA guidelines
[2] NYSDEC guidelines
[3] Provincial sediment quality guideline, Ontario, Canada (Fletcher et al. 2008)
[β] Number of samples exceeding the guideline

### 4.1.1 <u>Lead, Zinc and Copper Levels</u>

Seven samples (T2P, M1, M2, M3, M4P, T3W, and Buffalo State) contained Pb concentrations higher than the threshold level of the USEPA of 35.8 ppm. M1 site exceeded both the USEPA and NYSDEC threshold levels for Pb. The concentration of Pb is highest at M1 site, which collects wastewater from the northern part of the city and is surrounded by industrial discharges, and its elevated Pb concentration could be because of industrial discharge from the area. The hypothesis that Pb in sediment from M1 originated from Pb composition in gasoline is unlikely true; however, it would be true to say that diesel fuel is a possible source. That being said, this assertion is still not clear and warrants more analysis. If the source of Pb at M1 was only caused by vehicular emission of gasoline or diesel fuel from trucks in northern areas of the city, there would be an even distribution of Pb in the sediments at the wetland inlet of the Meanchey (77.4 ppm) and Tum Pun (27.8 ppm) sewer systems. The level of Pb at M1 deceases downstream to below the detection limit at the inlet of the Meanchey canal. The pump station (T2P) and the wetland inlet of the Tum Pun pump station (T3W) exhibited elevated concentrations of Pb due to depositions of Pb from non-point sources and as a result of hydraulic sorting. Hydraulic sorting involves the partition of particles according to their size, shape and density (Miller et al. 2004). The sorting process involves differential transport, in which smaller particles move farther than larger ones following entrainment.

The highest level of Zn sewer is almost seven times the USEPA guideline of 121 ppm, and four times the NYSDEC guideline of 270 ppm. The concentrations of Cu and Zn decreased as the distance from site M1 increased. Zinc is often released from galvanized steel, brake linings; tire abrasion and vehicular exhaust (De Miguel et al. 1997; Yeung et al. 2003). The mean of Cu in the sewer (100 ppm) is higher than the mean in the wetland (65 ppm). Eighty seven percent (14 samples) exceeded the USEPA guideline for Cu of 31.2 ppm, and 31% (5 samples) exceeded the NYSDEC and PSQG guidelines.

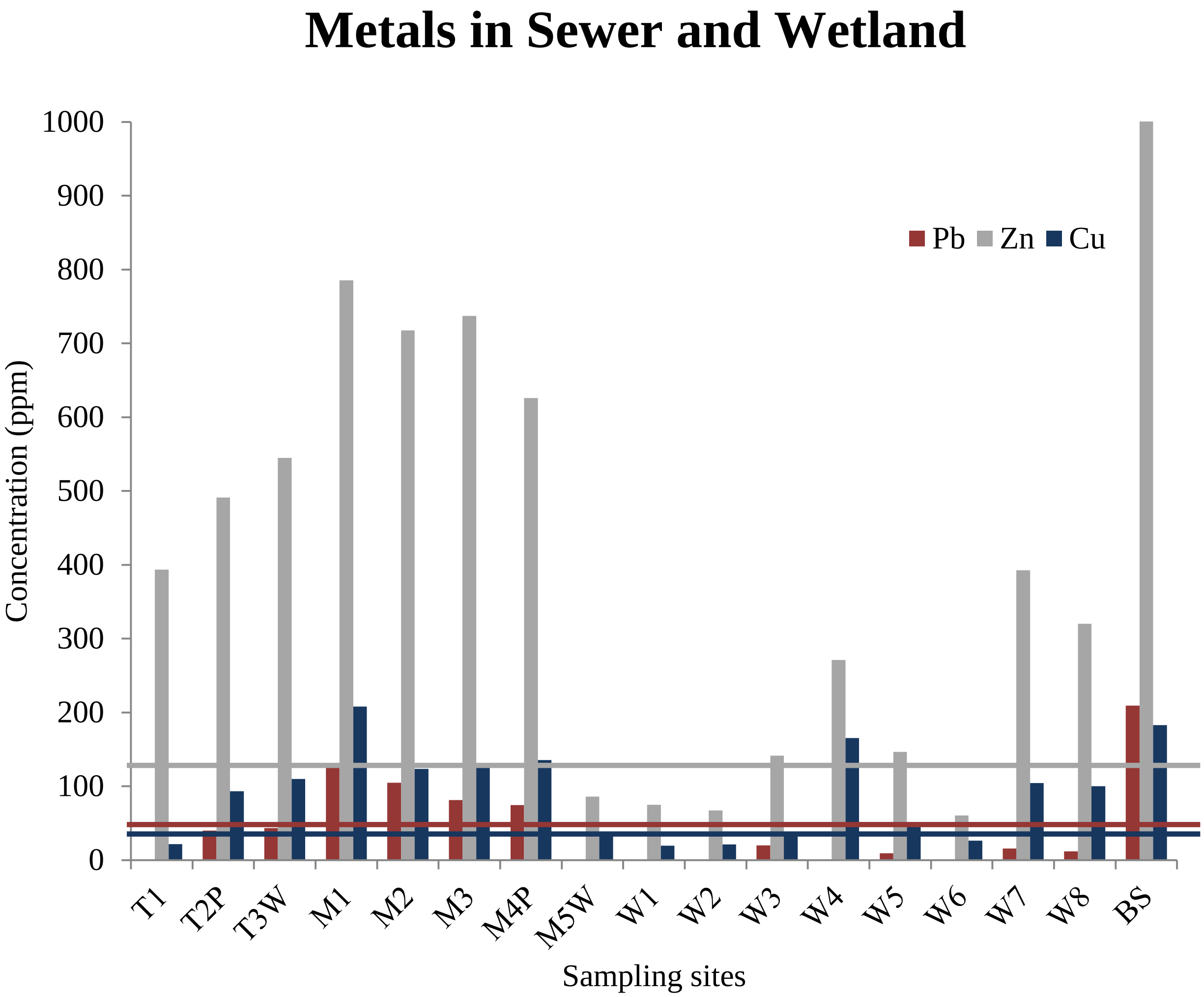

**Figure 18.** Concentrations of Pb, Zn, Cu compared with the USEPA guideline. Buffalo State sewer abbreviated "BS".

# Levels of Lead from Sampling Sites

**Figure 19.** Comparison of Pb concentration in Tum Pun and Meanchey sewer systems and the wetland.

### 4.1.2 Arsenic, Manganese and Iron Levels

The levels of As seemed to fluctuate, and most sites (19 out of 21 samples) exceeded the USEPA guideline of 9.8 ppm. The mean As concentration of the samples is 16.9 ppm. All of the samples exceeded the USEPA guideline for As, except for T1 site. Similar to Pb, Mn level was highest at M1 site and lower at other subsequent downstream sites. Elevated Mn concentrations ($\bar{x}$ = 422ppm) may be a result of vehicular methylcyclopentadienyl manganese tricarbonyl (MMT) (Okonkwo et al. 2009), but further study is needed to determine if such a compound is available in gasoline in Phnom Penh. However, it is highly likely that the high levels of Fe and Mn are naturally occurring elements of soil; particularly tropical soil, as stated by Rieuwerts (2007) and Silveira et al. (2006). The levels of Fe are lower in the sewer than in the wetland. The levels of Fe in the sewer seem to be evenly distributed, but increased in the wetland. As mentioned above Fe is naturally abundant in soil, especially in the tropics as a result of the weathering of Fe-bearing minerals (Lindsay and Schwab 2008; Rieuwerts, 2007). Table 6 provides a comparison between the levels of Fe in the wetland and the levels in the samples from Kien Svay, Kandal Province which are natural soils.

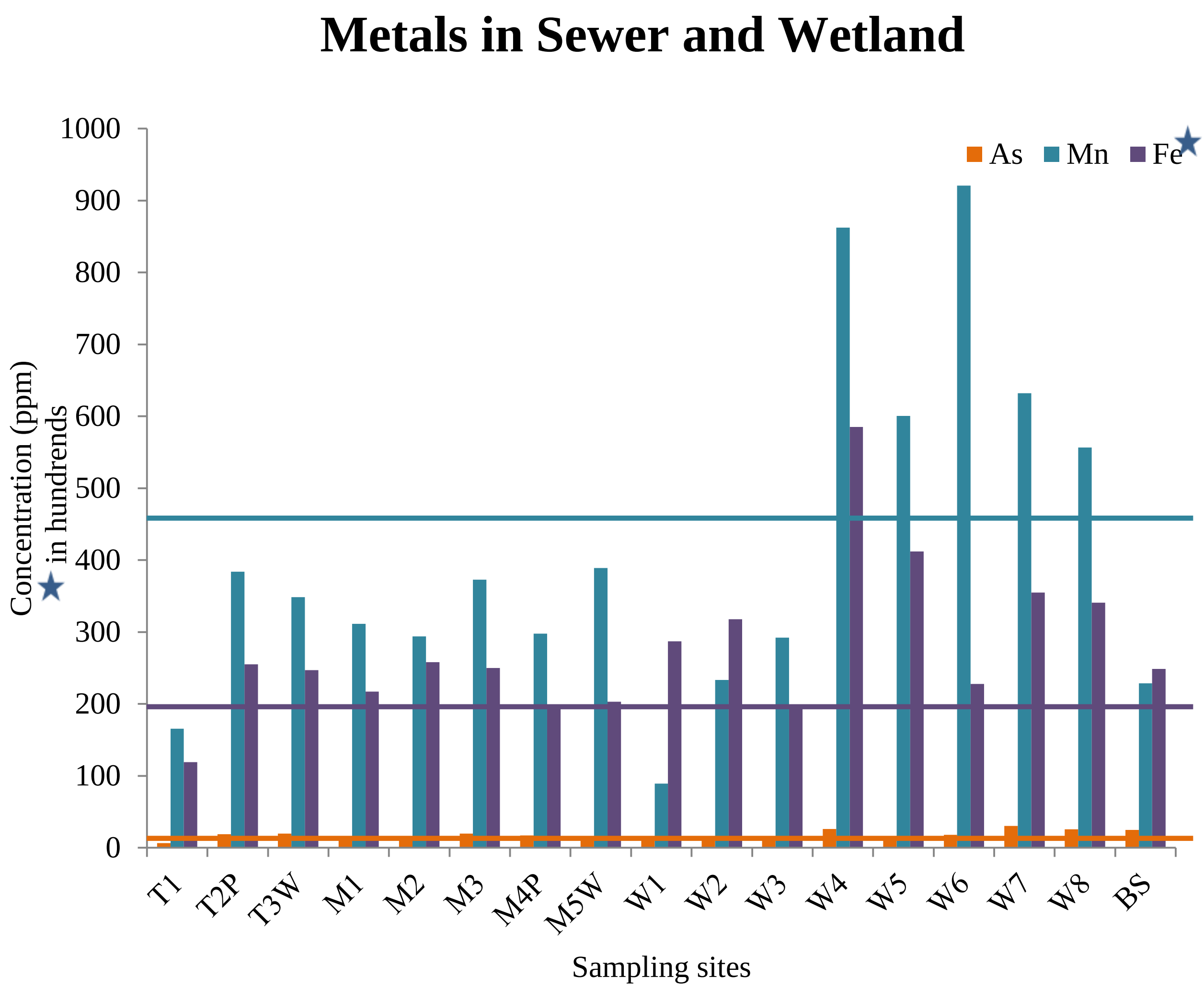

**Figure 20.** Concentrations of As, Mn, Fe in sewer and wetland samples compared with the USEPA guideline. Buffalo State abbreviated "BS".

**Table 10.** Comparison of metal levels between samples in Kien Svay (K) and the wetland (W)

| Wetland Samples | Pb | As | Zn | Cu | Fe | Mn | Cr |
|---|---|---|---|---|---|---|---|
| W1 | 311.5 | 13.4 | 785.6 | 208.2 | 21,708 | 126.6 | ND |
| W2 | ND | 15.1 | 67.2 | 21.2 | 31,816 | 233.4 | ND |
| T3W | 43.5 | 19.8 | 544.7 | 109.8 | 24,785 | 348.4 | ND |
| W7 | 15.4 | 30.4 | 392.5 | 104.2 | 35,518 | 632.2 | ND |
| W8 | 11.6 | 29.6 | 320.2 | 100.0 | 34,196 | 556.6 | ND |
| Mean | 76.4 | 16.1 | 391.2 | 130.5 | 29,605 | 379.1 | ND |
| Std. Dev. | 132.4 | 7.9 | 266.6 | 66.3 | 6,052 | 213.0 | ND |

| Kien Svay | Pb | As | Zn | Cu | Fe | Mn | Cr |
|---|---|---|---|---|---|---|---|
| K1 | 13.3 | 18.6 | 74.8 | 24.2 | 37,553 | 337.7 | ND |
| K2 | ND | 19.0 | 60.4 | 36.2 | 36,118 | 408.4 | ND |
| K3 | ND | 16.8 | 35.9 | 16.8 | 22,613 | 556.0 | ND |
| K4 | ND | 14.4 | 74.4 | 29.1 | 31,808 | 218.6 | ND |
| K5 | ND | 14.1 | 87.4 | 16.9 | 21,366 | 528.9 | ND |
| Mean | 2.6 | 16.5 | 66.5 | 24.6 | 29,892 | 409.4 | ND |
| Std. Dev | 5.9 | 2.2 | 19.6 | 8.2 | 7,530 | 139.1 | ND |

*Note:* All values are in parts per million (ppm).

## 4.2 Metal Concentration in Street Dust

### 4.2.1 Lead, Zinc and Copper Levels

Fourteen street dust samples exceeded Pb permissible guideline of the USEPA of 35.8 ppm. These samples were collected from heavy volume traffic areas and gas stations. Twenty one out of 24 samples exceeded the USEPA guideline of Cu of 31.6 ppm. Nineteen samples exceeded the USEPA guideline of Zn of 121 ppm (Table 8). The results from the second round of sampling indicated that there was a high concentration of Pb (135 ppm) at the new dumpsite (11˚ 28’ 58.71” N; 104˚ 53’ 21.27” E), and the old dump had more Pb (37 ppm) than any other samples collected in the second round. Other sampling sites en route to the old dumpsite had no detectable Pb level. The mean of Pb was still lower than the USEPA guideline of 35.8 ppm.

Twenty samples exceeded the USEPA guideline for Zn of 121 ppm. Also, during the second round of sampling, twelve Thai tires (TT) and two Korean tires (KT) were analyzed with the handheld XRF XL3t. The results showed that Zn has the highest concentrations ($\bar{x}$=27,862 ppm), followed by Cu and Fe (Table 7). The mean value of Zn was more than two times of the value that is normally found in tires in North America (Golding 2008). Levels of Pb and As were low and likely were not a major source of Pb and As in street dust in Phnom Penh.

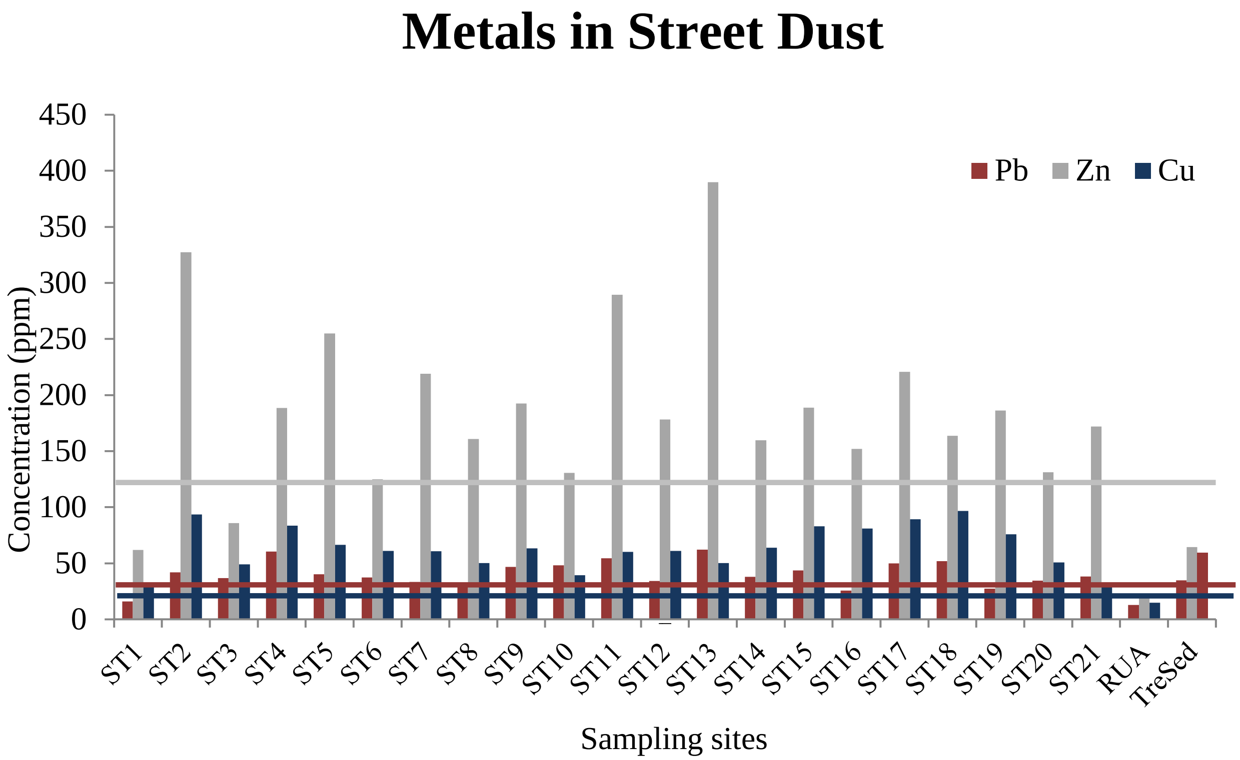

**Figure 21.** Concentrations of Pb, Zn and Cu compared with the USEPA guideline

**Table 11**. Metal concentrations in tires.

| Samples | Pb | As | Zn | Cu | Fe | Mn |
|---|---|---|---|---|---|---|
| TT1 | ND | 137.5 | 27,629 | 41,423 | 616.4 | ND |
| TT2 | 12.5 | ND | 27,490 | 59.5 | 747.8 | ND |
| TT3 | 14.2 | ND | 28,221 | ND | 231.4 | ND |
| TT4 | 5.8 | ND | 26,887 | 20.9 | 1,839 | ND |
| TT5 | ND | ND | 28,534 | ND | 772.3 | ND |
| TT6 | 8.6 | ND | 33,901 | 33.9 | 85.6 | ND |
| TT7 | 25.3 | ND | 29,779 | 36.8 | 94.4 | ND |
| TT8 | 35.4 | ND | 30,582 | 40.7 | 3,945 | ND |
| TT9 | 81.3 | ND | 25,083 | ND | 2,243 | ND |
| TT10 | ND | ND | 14,772 | ND | 1,323 | ND |
| TT11 | 99.8 | ND | 33,040 | 32.7 | 2,937 | ND |
| TT12 | ND | ND | 29,884 | 35.7 | 467.8 | ND |
| KT13 | ND | ND | 25,671 | ND | ND | ND |
| KT14 | 8.3 | ND | 28,587 | 56.7 | 863.5 | ND |
| Mean | 20.8 | 9.8 | 27,862 | 2,981 | 1,155 | ND |
| Std. Dev. | 31.5 | 35.4 | 4,347 | 10,662 | 1,142 | `ND |

*Note:* All values are in parts per million (ppm)

**Table 8.** XRF XLi measurement of street dust samples

| Site | Pb | As | Zn | Cu | Fe | Mn |
|---|---|---|---|---|---|---|
| ST1 | 16.1 | 20.7 | 61.8 | 30.1 | 10,639 | 111.7 |
| ST2 | 41.9 | ND | 327.0 | 93.5 | 17,145 | 221.7 |
| ST3 | 36.7 | ND | 85.9 | 49.1 | 16,710 | 260.3 |
| ST4 | 60.4 | 11.3 | 188.6 | 83.6 | 22,142 | 251.5 |
| ST5 | 40.1 | ND | 254.9 | 66.6 | 18,700 | 226.5 |
| ST6 | 37.2 | ND | 125.0 | 60.9 | 14,888 | 191.7 |
| ST7 | 33.5 | 8.4 | 218.9 | 60.9 | 15,609 | 274.1 |
| ST8 | 31.9 | ND | 160.7 | 50.2 | 13,377 | 158.8 |
| ST9 | 46.8 | ND | 192.6 | 63.4 | 15,668 | 252.0 |
| ST10 | 48.3 | ND | 130.5 | 39.2 | 13,329 | 153.5 |
| ST11 | 54.6 | 54.3 | 289.5 | 60.2 | 14,591 | 240.3 |
| ST12 | 34.2 | ND | 178.1 | 61.0 | 12,519 | 208.9 |
| ST13 | 62.1 | 13.5 | 389.7 | 50.1 | 15,782 | 185.5 |
| ST14 | 38.0 | ND | 159.7 | 64.0 | 13,890 | 274.9 |
| ST15 | 43.7 | ND | 188.6 | 83.1 | 19,218 | 277.3 |
| ST16 | 25.6 | 13.8 | 151.9 | 80.9 | 8,057 | 78.2 |
| ST17 | 50.0 | ND | 220.8 | 89.3 | 20,438 | 324.8 |
| ST18 | 51.9 | ND | 163.6 | 6.6 | 20,600 | 327.5 |
| ST19 | 27.5 | ND | 186.2 | 75.9 | 17,701 | 353.7 |
| ST20 | 34.6 | 8.8 | 131.0 | 50.8 | 16,010 | 226.5 |
| ST21 | 38.1 | 12.4 | 172.0 | 29.2 | 12,768 | 277.8 |
| ST21 1st Duplicate Shot | 32.5 | ND | 169.9 | 56.3 | 13,087 | 202.7 |
| ST21 2nd Duplicate Shot | 33.3 | ND | 167.8 | 57.7 | 13,172 | 184.7 |
| Sand | 16.5 | ND | 26.0 | 33.8 | 11,319 | 172.5 |
| RUA | 13.0 | ND | 18.8 | 15 | 3,929.3 | 60.0 |
| TreSed | 34.8 | 8.2 | 64.4 | 59.1 | 19,776 | 236.8 |
| Mean | 38.2 | 8.6 | 170.3 | 60.3 | 15,200 | 222.8 |
| Sigma(δ) | 25.2 | 10.6 | 88.5 | 21.4 | 4190.3 | 74.36 |
| USEPA[1] | 35.8 | 9.8 | 121 | 31.6 | 20,000 | 460 |
| NYSDEC[2] | 110 | 33 | 270 | 110 | 20,000 | 460 |
| PSQG[3] | 250 | 33 | 820 | 110 | 40,000 | 1100 |
| USEPA[β] | 14 | 6 | 20 | 21 | 4 | 0 |
| NYSDEC[β] | 0 | 1 | 3 | 0 | 4 | 0 |
| PSQG[β] | 0 | 1 | 0 | 0 | 0 | 0 |

*Note:* All values are in parts per million (ppm). Not Detectable abbreviated ND. Trench sediment abbreviated "TreSed"

[1] USEPA guideline

[2] NYSDEC guideline

[3] Provincial sediment guideline, Ontario, Canada (Fletcher et al. 2008)

[β] Number of samples exceeding the guideline

### 4.2.2 Arsenic, Manganese and Iron Levels

Unlike Pb, As concentrations in most areas were still well below the USEPA guideline of 9.8 ppm although some of the areas (6 samples) exceeded the guideline (Table 8). The levels of Mn detected were lower than the USEPA guideline of 460 ppm. Four samples (ST4, ST17, ST18, and RUA) exceeded the USEPA guideline of Fe of 20,000 ppm. The highest concentration of Fe was observed at site ST4, the traffic intersection of Monivong Blvd. and Charles De Gaulle Blvd. The area is locally known as one of the busiest intersections in the city. A similar pattern, but at lower concentrations, was also observed at sites ST17 and ST18.

#### 4.2.2.1 *Chromium Levels*

Only one sample was detected with high Cr (120 ppm) and that was at the old dumpsite. No Cr level was detected at the new dumpsite or the tannery factory (tannery gate). The results indicate that dust at the garment factory sites were not very contaminated with metals (Table 9).

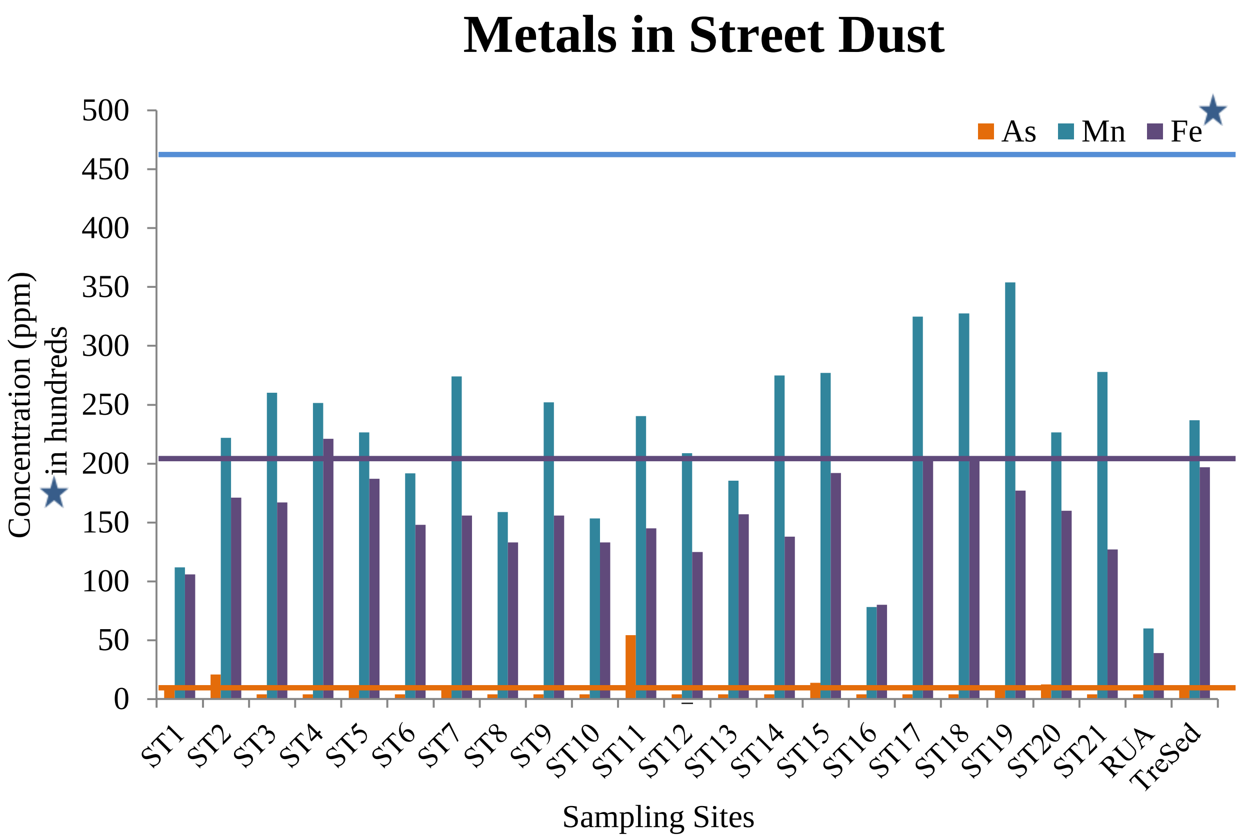

**Figure 22.** Concentration of As, Mn and Fe in the street dust compared with the USEPA guidelines.

### 4.2.3 Regression Analysis

Regression analysis is used to determine that As, Mn and Fe are a common source in soil. The calculated regression lines defined Fe-As and Fe-Mn relationships and provided a statistical estimate of the range of values to be expected from samples taken from the sewer and wetland sediments. Although the levels of Fe and As of the samples from the wetland had a good correlation of coefficient (r=0.65), the coefficient of determination was 0.33 ($r^2$= 0.42). The $r^2$ value of Fe and Mn in the wetland samples was 0.28. However, a stronger Fe-Mn relationship was observed in the sewer samples ($r^2$=0.67). The $r^2$ value of Fe-As was 0.64. Figures 13 and 14 show the relationships of these metals.

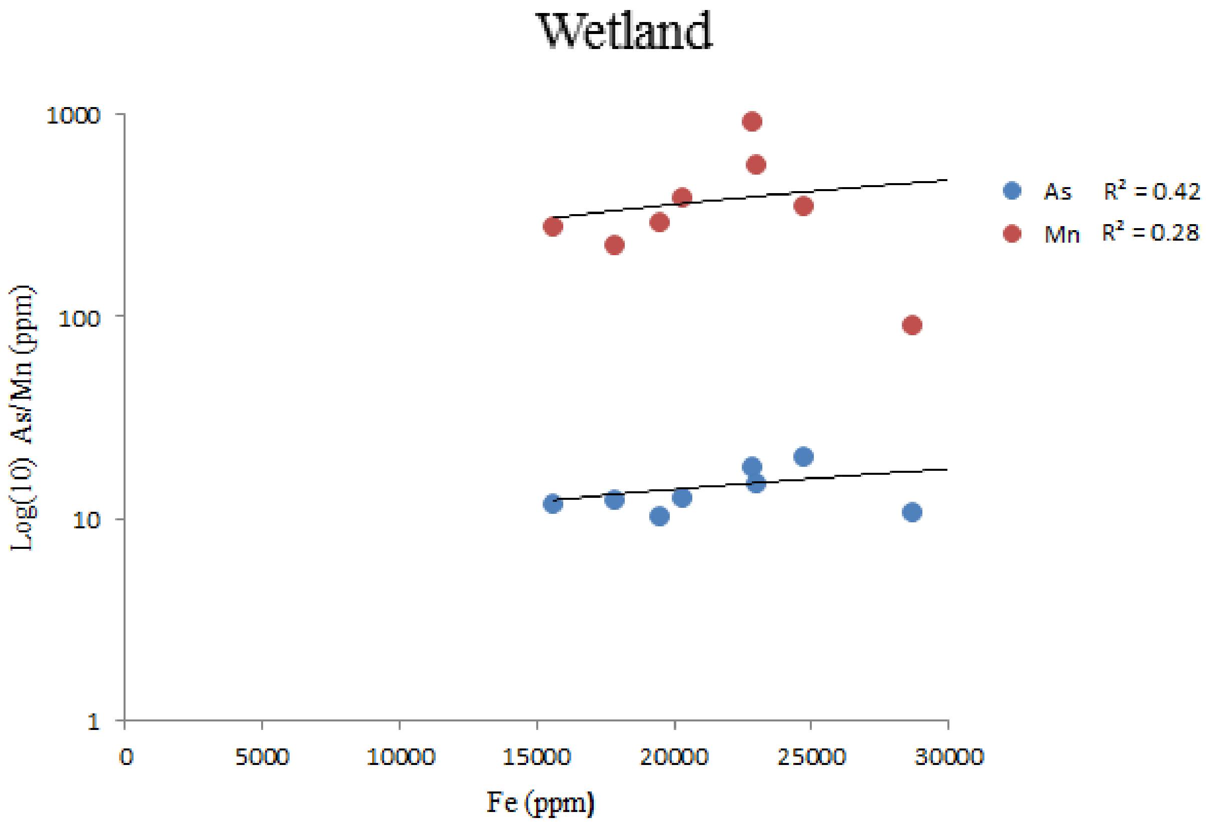

**Figure 23.** Regression between Fe-As and Fe-Mn in wetland samples

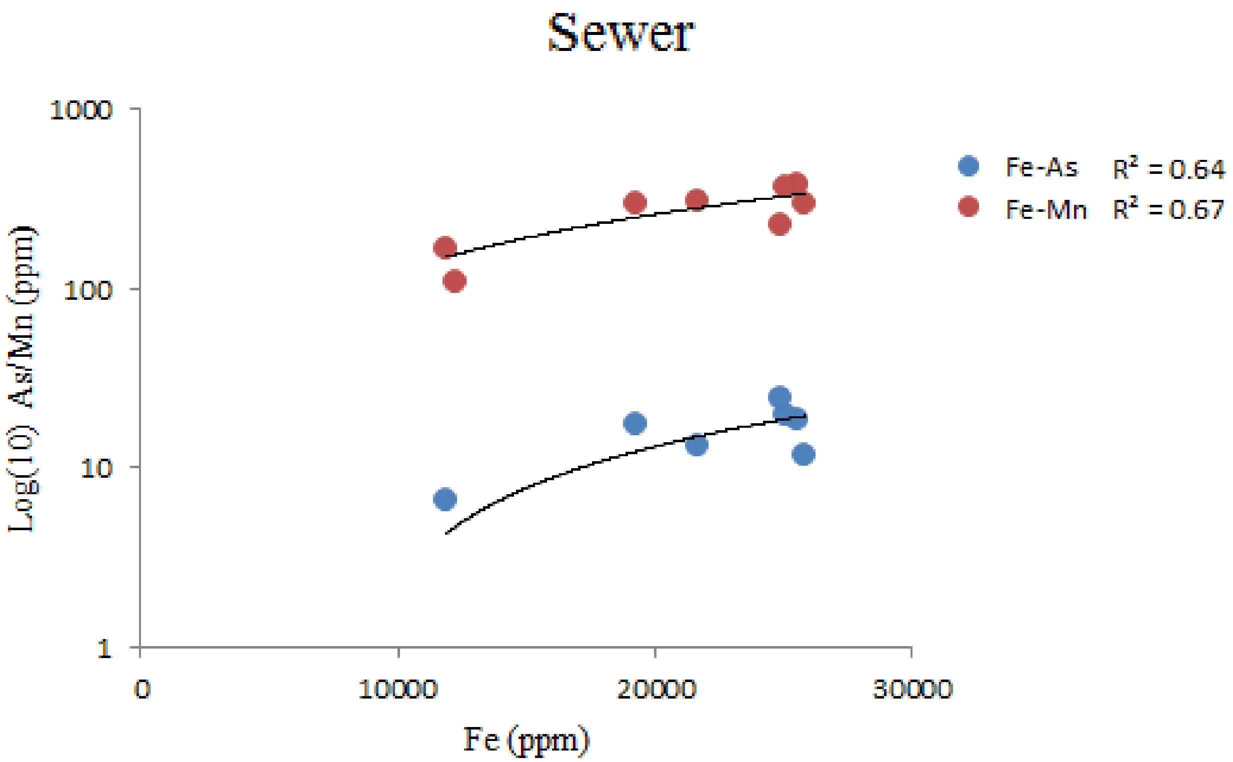

**Figure 24.** Regression between Fe-As and Fe-Mn in sewer samples.

**Table 12.** Metal concentrations in the street dust samples (second round)

| Sample | Pb | As | Zn | Cu | Fe | Mn | Cr |
|---|---|---|---|---|---|---|---|
| Dump 1 | 9.7 | 8.2 | 73.9 | ND | 23,065 | 467.4 | ND |
| Dump 2 | 135.6 | 24.5 | 78.9 | 25.6 | 20,670 | 510.6 | ND |
| Old Dump | 37.2 | 19.8 | 242.2 | 66.7 | 11,298 | 570.4 | 120 |
| Tannery Gate | ND | 6.9 | 120.7 | ND | 10,303 | 168.9 | ND |
| Vattanac Park | ND | 9.7 | 143.5 | 28.9 | 12,996 | 289.8 | ND |
| St. 105K | ND | ND | 15.1 | ND | 4,913 | 119.3 | ND |
| Canadia Factory | 9.9 | ND | 120.9 | ND | 11,223 | 276.1 | ND |
| Universal Apparel | 10.5 | ND | 102.4 | ND | 11,994 | 247.6 | ND |
| Mean | 25.4 | 8.6 | 112.2 | 15.2 | 13,308 | 331.3 | 15.4 |
| Sigma (δ) | 43.2 | 8.6 | 61.3 | 22.6 | 5,467 | 154.5 | 37.9 |

*Note:* All values are in parts per million (ppm). ND = Not Detectable.

## 4.3 Correlation Analysis

### 4.3.1 Metal Correlation in Sewer and Wetland Samples

The Pearson correlation coefficient (r) was applied using SPSS v. 16 to determine whether or not there were significant correlations among the metal contaminants. Strong correlations were observed between Pb and Zn in the sewer ($r=0.96$; $P<0.01$) and wetland samples ($r=0.80$; $P<0.05$). While the correlation between Pb and Fe in the sewer was 0.60 ($r=0.60$), the correlation between Pb and Fe in the wetland was -0.25 ($r= -0.25$). The correlation between Pb and Mn in the sewer was 0.45 ($r=0.45$) whereas the correlation between Pb and Mn in the wetland was -0.18 ($r= -0.18$).

The correlations between Pb and Cu; and Zn and Pb of the sewer sediments were at 0.93 and 0.96 respectively ($\alpha=0.01$). The correlation between Zn and Cu was 0.88 ($\alpha=0.05$). The correlation between the metals decreased in some of the wetland samples. For instance, the Pb-Zn correlation in the sewer was 0.96, while the correlation of the same metals in the wetland was 0.80. The result of the analysis is shown in Table 10.

**Table 13.** Metal correlations in the sewer and wetland samples

| Sewer Sediments | Pb | Fe | Zn | Mn | As | Cu |
|---|---|---|---|---|---|---|
| Pb | 1 | | | | | |
| Fe | 0.60 | 1 | | | | |
| Zn | 0.96** | 0.60 | 1 | | | |
| Mn | 0.45 | 0.88* | 0.48 | 1 | | |
| As | 0.29 | 0.69 | 0.36 | 0.92** | 1 | |
| Cu | 0.93** | 0.52 | 0.88* | 0.52 | 0.41 | 1 |

** and * indicates significant correlation P<0.01 and 0.05 respectively

| Wetland Sediments | Pb | Fe | Zn | Mn | As | Cu |
|---|---|---|---|---|---|---|
| Pb | 1 | | | | | |
| Fe | -0.25 | 1 | | | | |
| Zn | 0.80** | 0.20 | 1 | | | |
| Mn | -0.18 | 0.47 | 0.13 | 1 | | |
| As | 0.16 | 0.57 | 0.67* | 0.61 | 1 | |
| Cu | 0.33 | 0.69* | 0.77** | 0.48 | 0.81** | 1 |

** and * indicates significant correlation P<0.01 and 0.05 respectively.

### 4.3.2 Metal Correlation of Street Dust Samples

The Pearson correlation coefficient (r) was calculated using SPSS v.16 to evaluate correlations between metal contaminants in the street dust collected. The strongest correlation in street dust samples was observed between Fe and Mn at 0.78 ($\alpha$=0.01). Fe and Mn are naturally occurring components of soil, and could not be attributed to anthropogenic activities. The correlation between Cu and Pb is also in an agreement with that of Irvine et al. (2009) who suggested that Cu and Pb are associated with industrial and high volume areas. Similarly, Faiz et al. (2009) found a correlation between Cu and Pb in expressway street dust in Pakistan, and attributed to common human activities. The correlation between Pb and Zn was 0.70 and their coexistence can be associated with anthropogenic activities. The decreasing order of correlation in street dust samples was Fe-Mn>Pb-Zn> Cu-Mn> Pb-Cu. The result is shown in Table 11.

**Table 14.** Metal correlations in street dust samples.

| Street Dust | Pb | Fe | Zn | Mn | As | Cu |
|---|---|---|---|---|---|---|
| Pb | 1 | | | | | |
| Fe | 0.68** | 1 | | | | |
| Zn | 0.70** | 0.41* | 1 | | | |
| Mn | 0.48* | 0.78** | 0.34 | 1 | | |
| As | 0.23 | 0.083 | 0.38 | 0.10 | 1 | |
| Cu | 0.51* | 0.68** | 0.50* | 0.55** | 0.13 | 1 |

** and * indicates significant correlation $P<0.01$ and 0.05 respectively.

## 4.4 Grain Size Analysis

### 4.4.1 Grain Size Analysis of Sewer, Wetland, and Street Dust Samples

There are two types of grain size analyses: mechanical (or sieve) analysis and hydrometer analysis. In this study only the mechanical analysis was used. Mechanical analysis determines the particle sizes and their relative distribution. According to Wray (1986), a soil is said to be *well graded* or *poorly graded* when they fit in the two criteria. The first criterion is the coefficient of curvature (Cc), the value of which must be between 1 and 3. The second criterion is the coefficient of uniformity (Cu), whose value equals to or greater than 4 indicates gravels and equals to or greater than 6 indicates sands. Should one of the criteria fails, the soil is considered *poorly graded.*

Median diameter ($D_{50}$) is the 50th percentile that measures the central tendency of a given sample. The results of the individual particle size $D_{50}$ of the sewer and wetland samples ranged from 0.31 mm to 0.39 mm with the average being 0.35 mm. It also should be noted that only three samples were analyzed and the rest of the samples collected were lost during the flood in 2011. Almost all of the samples were poorly graded. Only one sample (ST4) was categorized as sand. The results of the sewer and wetland grain size analysis are shown in Table 12. Generally, the sediment particles of the sewer and wetland are coarser than those of the street dust samples. The individual median range ($D_{50}$) of the street dust samples varies from 0.10 mm to 0.55 mm with the average being 0.17 mm (Table 13). The dust particles were mostly uniform in size.

**Table 15.** Grain size distribution of sewer samples.

| Sample No. | Range (mm) | Individual $D_{50}$ Range (mm) | $C_c$ (mm) | $C_u$ (mm) | Condition |
|---|---|---|---|---|---|
| M1 | <0.105 – >4.76 | 0.35 | 0.26 | 4.5 | Poorly graded |
| T1 | <0.105 – >4.76 | 0.39 | 0.15 | 3.4 | Poorly graded |
| T2P | <0.105 – >4.76 | 0.31 | 0.0016 | 0.7 | Poorly graded |
| Average $D_{50}$ | - | 0.35 | - | - | - |

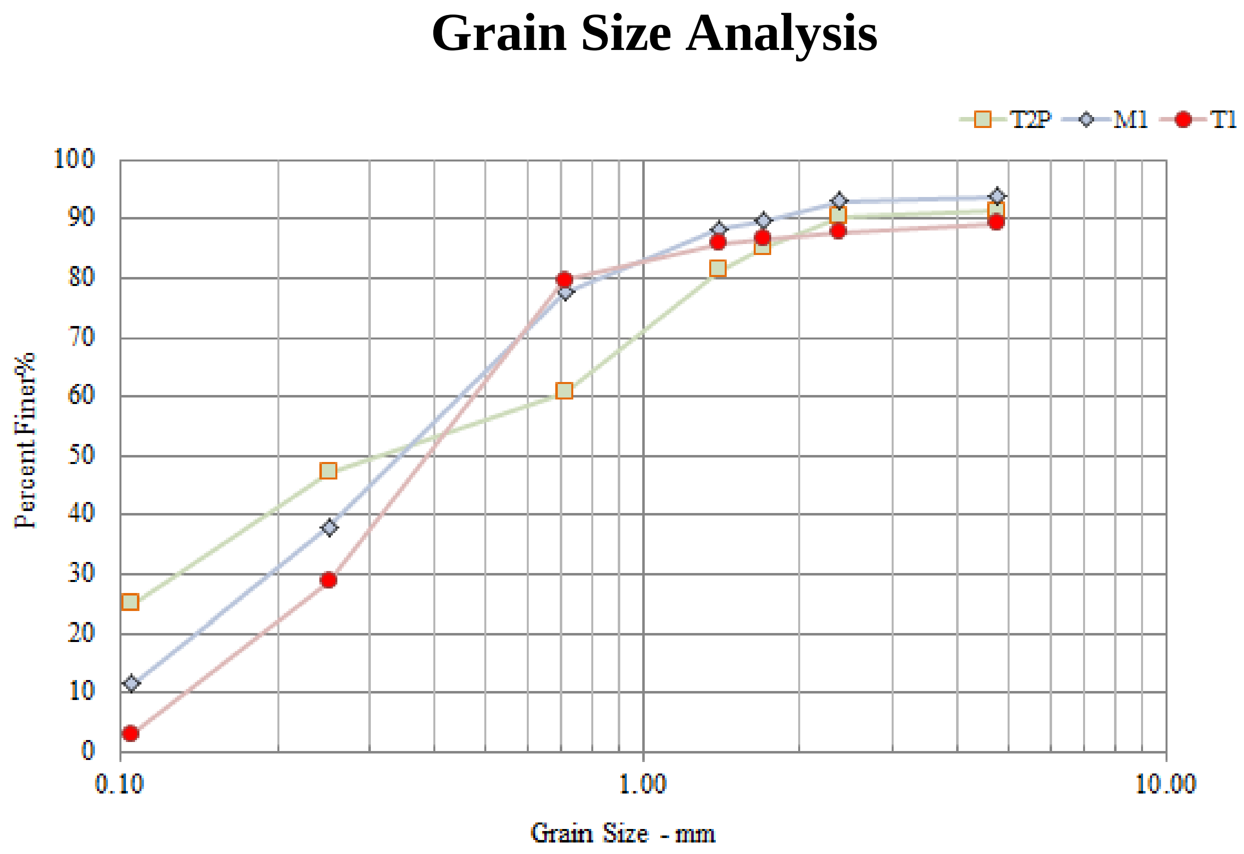

**Figure 25.** Grain size distribution of the sewer sample plotted on a semi-log scale.

**Table 16.** Grain size distribution of street dust samples.

| Sample No. | Range (mm) | Individual $D_{50}$ Range (mm) | $C_c$ (mm) | $C_u$ (mm) | Condition |
|---|---|---|---|---|---|
| ST1 | <0.063 – >4.00 | 0.18 | 0.71 | 2.86 | Poorly graded |
| ST2 | <0.063 – >4.00 | 0.18 | 0.28 | 3.67 | Poorly graded |
| ST3 | <0.063 – >4.00 | 0.14 | 0.89 | 4.5 | Poorly graded |
| ST4 | <0.063 – >4.00 | 0.2 | 1.04 | 10.67 | Sand |
| ST5 | <0.063 – >4.00 | 0.18 | 0.67 | 4.12 | Poorly graded |
| ST6 | <0.063 – >4.00 | 0.16 | 0.83 | 3.34 | Poorly graded |
| ST7 | <0.063 – >4.00 | 0.16 | 0.83 | 3.34 | Poorly graded |
| ST8 | <0.063 – >4.00 | 0.17 | 0.79 | 3.5 | Poorly graded |
| ST9 | <0.063 – >4.00 | 0.19 | 0.77 | 5.2 | Poorly graded |
| ST10 | <0.063 – >4.00 | 0.17 | 0.75 | 2.99 | Poorly graded |
| ST11 | <0.063 – >4.00 | 0.3 | 0.73 | 6.29 | Poorly graded |
| ST12 | <0.063 – >4.00 | 0.45 | 0.72 | 8.75 | Poorly graded |
| ST13 | <0.063 – >4.00 | 0.18 | 0.86 | 3.43 | Poorly graded |
| ST14 | <0.063 – >4.00 | 0.14 | 0.89 | 4.5 | Poorly graded |
| ST15 | <0.063 – >4.00 | 0.11 | 0.82 | 3.75 | Poorly graded |
| ST16 | <0.063 – >4.00 | 0.16 | 0.72 | 2.86 | Poorly graded |
| ST17 | <0.063 – >4.00 | 0.12 | 0.82 | 3.75 | Poorly graded |
| ST18 | <0.063 – >4.00 | 0.13 | 0.8 | 2.29 | Poorly graded |
| ST19 | <0.063 – >4.00 | 0.16 | 0.83 | 3.33 | Poorly graded |
| ST20 | <0.063 – >4.00 | 0.1 | 0.8 | 5 | Poorly graded |
| ST21 | <0.063 – >4.00 | 0.11 | 0.93 | 4.29 | Poorly graded |
| Sand | <0.063 – >4.00 | 0.18 | 0.96 | 2.75 | Poorly graded |
| RUA | <0.063 – >4.00 | 0.17 | 0.81 | 4 | Poorly graded |
| TreSed | <0.063 – >4.00 | 0.55 | 0.63 | 12.86 | Poorly graded |
| Average $D_{50}$ |  | 0.17 |  |  |  |

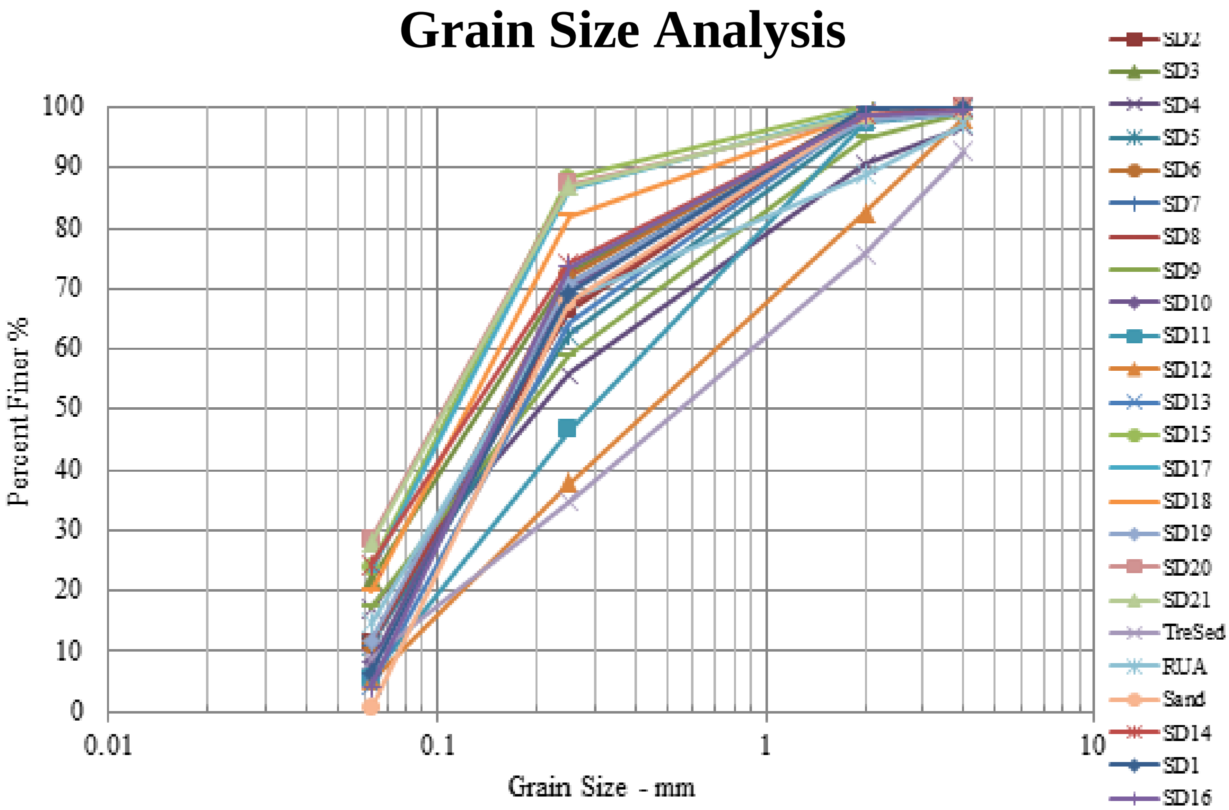

**Figure 26.** The results of the grain size distribution of street dust samples plotted on a semi-log scale.

### 4.5 Kriging Analysis

The results, along with the coordinates located on a Garmin eTrex High Sensitivity GPS, of the street dust samples were entered into ArcMap (ArcGIS v.10.1) for Kriging analysis. Each of the following figures shows the extent of metal levels of a particular element found in the street dust.

# Lead in Street Dust

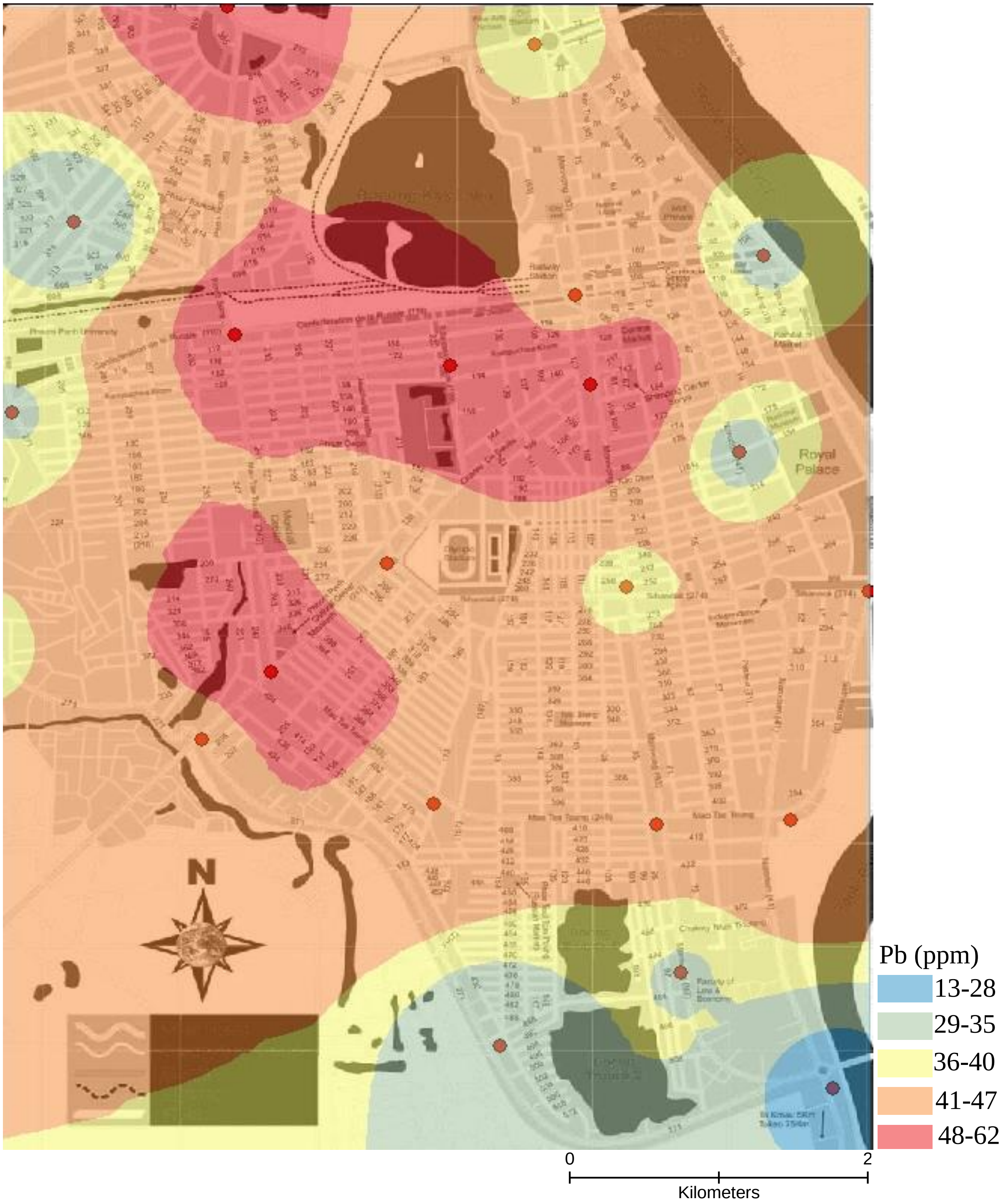

**Figure 27.** Spatial distribution of Pb in street dust.

# Arsenic in Street Dust

**Figure 28.** Spatial distribution of As in street dust.

# Zinc in Street Dust

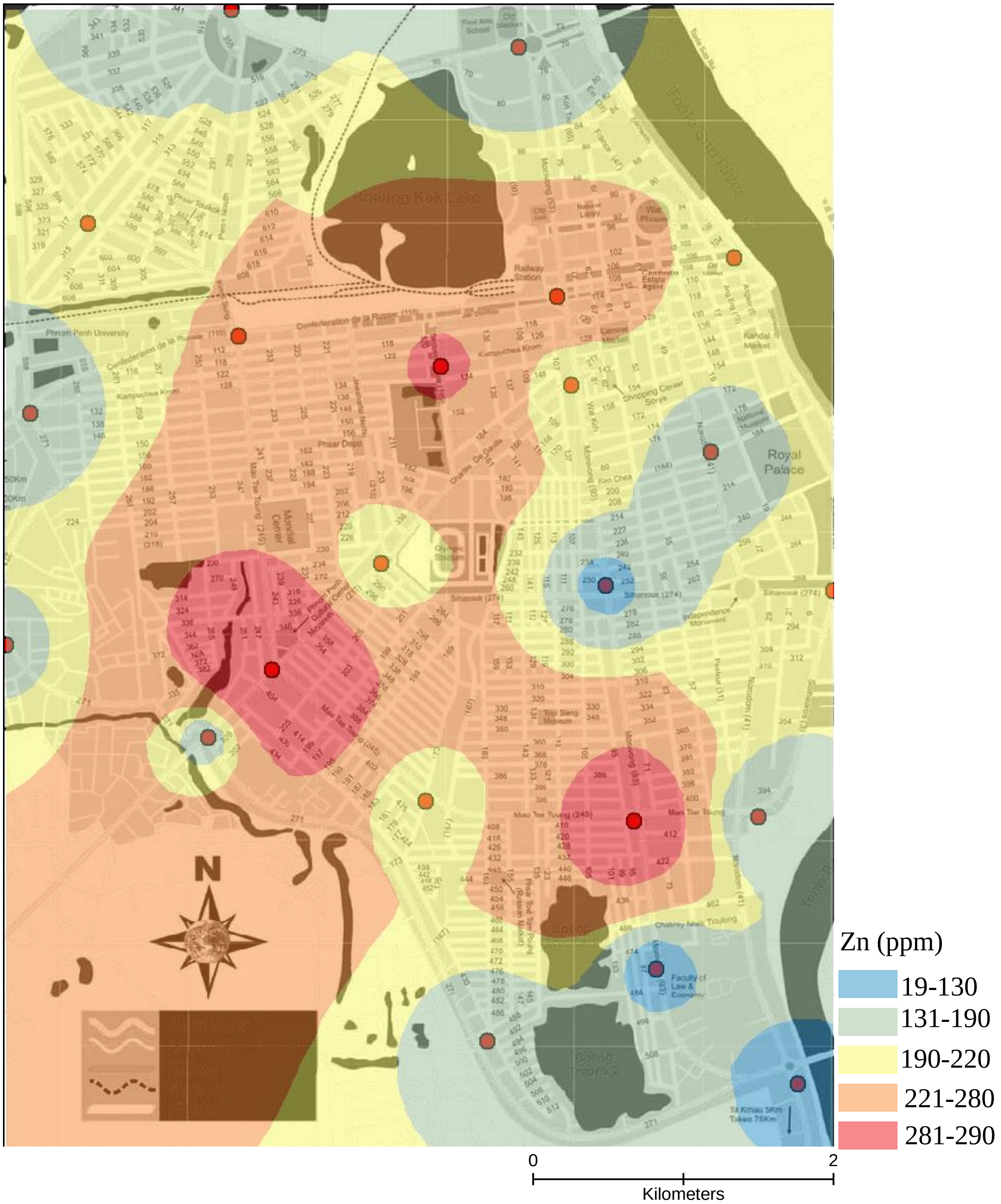

**Figure 29.** Spatial distribution of Zn in street dust.

# Copper in Street Dust

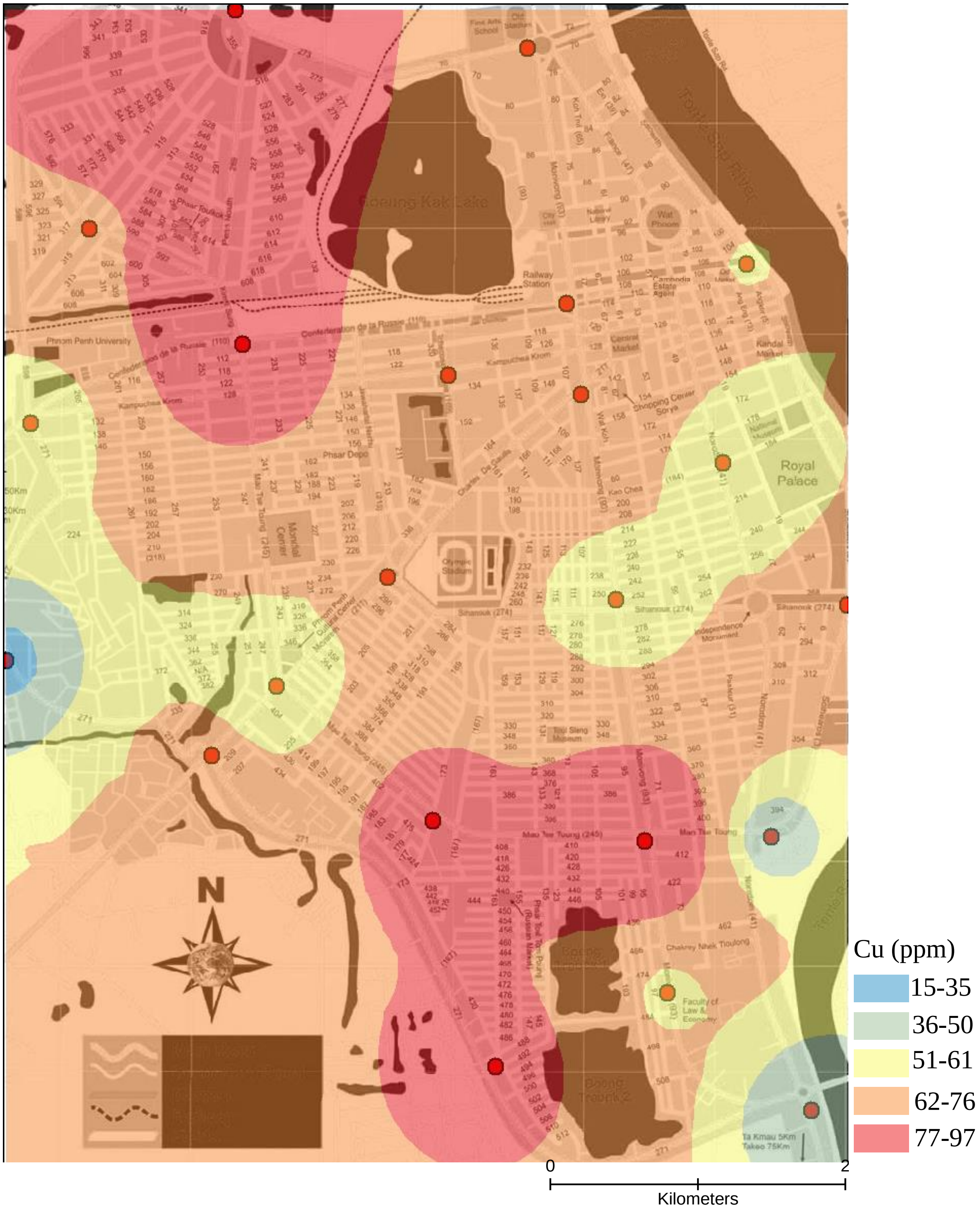

**Figure 30.** Spatial distribution of Cu in street dust.

# Iron in Street Dust

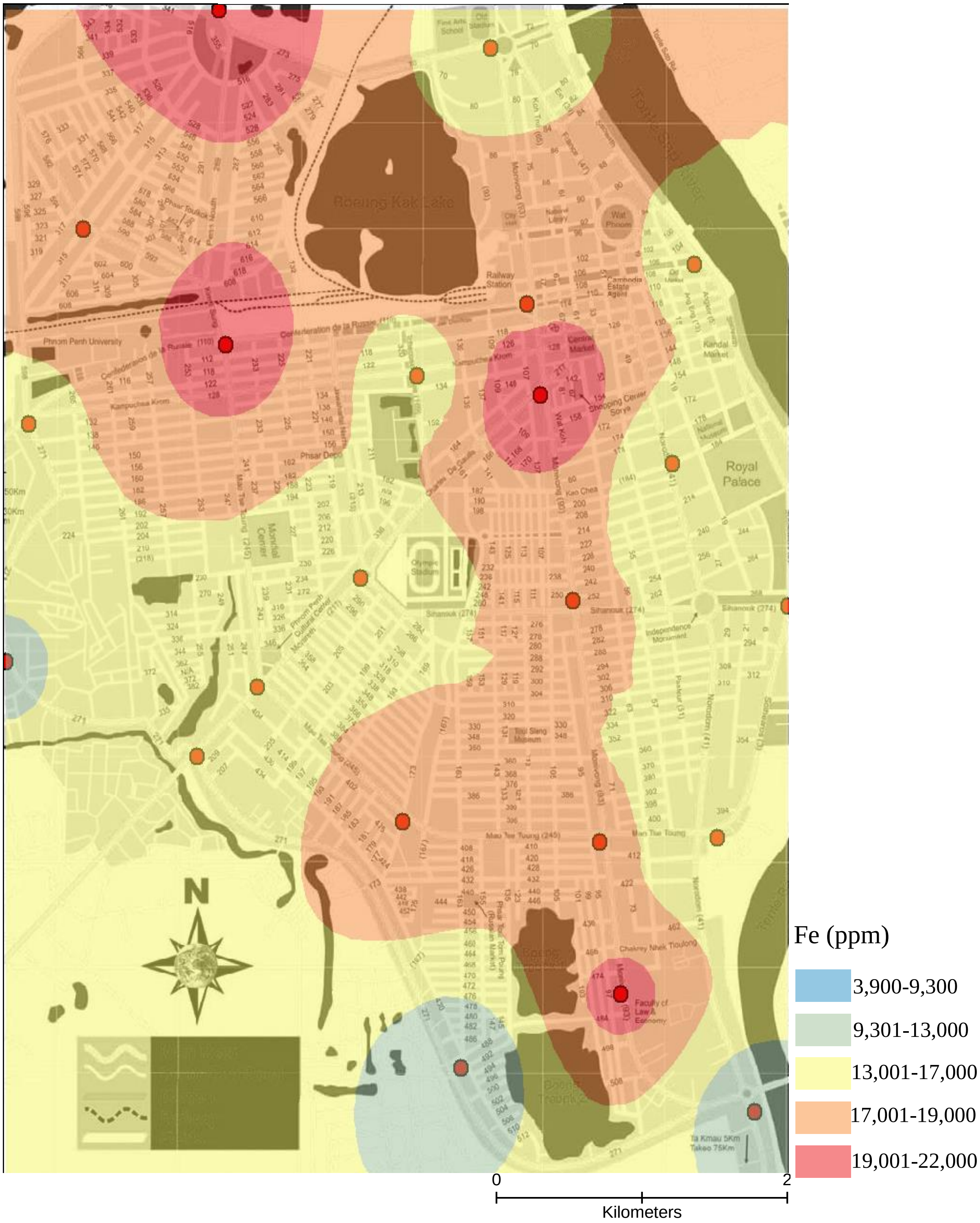

**Figure 31.** Spatial distribution of Fe in street dust.

# Manganese in Street Dust

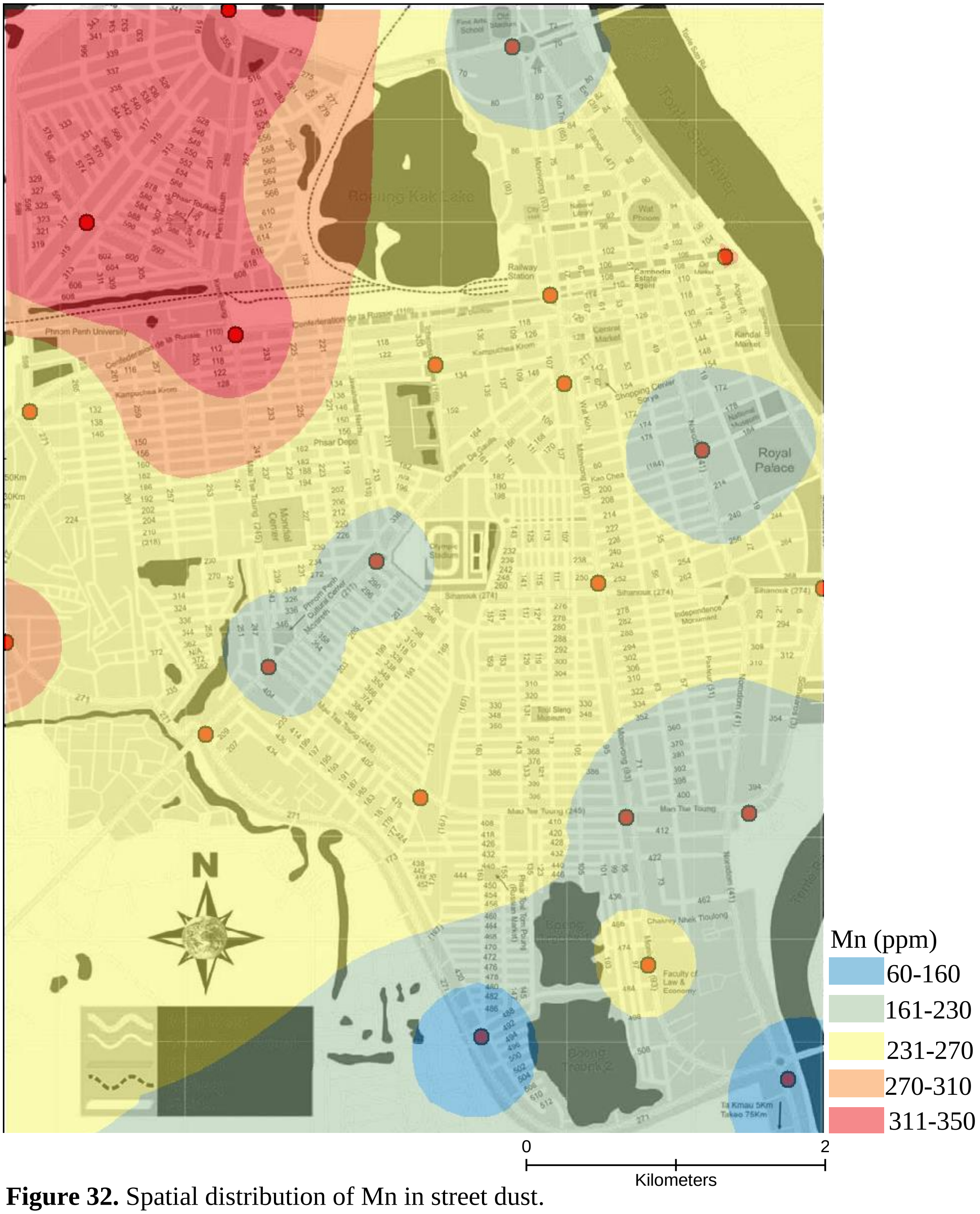

**Figure 32.** Spatial distribution of Mn in street dust.

# 5. DISCUSSION

## 5.1 Sources of Metals in Sewer, Wetland, and Street Dust

Levels of Pb in the sewer may be attributed to heavy traffic, vehicular emission of leaded gasoline and industrial discharge (Momani, 2006; Miguel et al. 1997, Zhu et al. 2007). Vehicular emission of leaded gasoline is to some extent still available in Cambodia within the EU guidelines, which is very modest relative to decades ago (German Technical Cooperation 2010, Chapter 1). Diesel fuel in Asia is known to contain Pb and other metals as well (Wang et al. 2003), but there is much less analysis of diesel fuel than gasoline. So, diesel fuel remains a suspect source of metals in Phnom Penh. Other sources of Pb may include atmospheric emissions from landfills, improper disposal of batteries, rubber coating, paints and PVC pipes (Levin et al. 2008; Weidenhamer and Clement 2007). Costner (2005) reported that open burning of domestic waste such as textiles/leather, wood, paper products, glass, aluminum cans, wire, plastics pipes and batteries can be a release source of dioxin and air pollution in Cambodia. Recycling PVC pipes is problematic because of the low market price of PVC recycled compared to virgin PVC; loss of material quality after recycling and high separation and collection costs (Greenpeace 2003). The variability of sampling at the new dumpsite suggested that more sampling would be required to provide a better estimate of the risks.

The release and availability of As in the sediments can be attributed to both anthropogenic and natural activities. While As is used in textiles, tanning and anti-fouling paints, it is also released as a result of natural weathering of minerals (Sampson et al. 2008; USEPA 2007). Zinc may be sourced from vehicle oils, tires, and galvanized steel, and body rust (Councell et al. 2004; Zhu et al. 2007). However, upon the analysis of the tires, it can be implicated that tires are also a source of Zn in Phnom Penh. The levels of Pb and As in the tires were too low to be considered the major source of the metals in street dust. Zinc is not potent as Pb, Hg, or As, but it can induce allergic responses such as asthma to sensitized individuals such as children. The most common effect of direct exposure to tire rubber is allergy or dermatitis. Inhalation of components of tire rubber, photoxidized by light, or dust may exacerbate asthmas, and can lead to respiratory problems (Sullivan 2006). The levels of Zn in street dust can be minimized via street wash and sweeping.

The levels of Fe are lower in the sewer than in the wetland. The wetland is categorized as a lacustrine floodplain consisting of fine-textured sediments and depending on the lithology and occurring watershed pattern of the Mekong and Tonle Sap River (White et al. 1997). It is highly likely that the presence of high Fe content is the result of the natural abundance of Fe oxide in typical soil (Lahav et al. 2004), and not the effluent discharge from the surrounding industries. Even though the discharged effluents might be voluntarily minimized, an external regulatory body from the government such as the Ministry of Environment is required for monitoring. The levels of Fe in the sewer seem to be evenly distributed in the samples collected, and this could be the cause of the metal accumulation and deposition at the sewer exit points into the wetland like T2P and M4P

Initially it was anticipated that Cr would be found at a tannery factory, so-called “Tannery gate”. However, nothing of major concern was found in street dust at or around the site. Surprisingly, Cr was detected at the old dump, which necessitates more analysis including the new dumpsite. Furthermore, sewer sediment samples from the above and ground and some more street dust samples could provide some insight about the level of Cr at the old dumpsite and near the tanneries. The tanning process uses vats and if the vats were dumped, Cr would mostly enter the sewers. Sludges from the vats would likely be disposed of in the dumps. The adverse effects of Cr include decreased pulmonary function, ulcerations of the septum and bronchitis and dermatitis. Nevertheless, Cr in street dust in Phnom Penh is not a major problem as reported in some industrial Chinese city street dust samples, which are at least 2 to 3 times higher (Tanner et al. 2008; Ho et al. 2003).

The results of the sediments from the Boeung Cheung Ek wetland show there is a potential risk of metal contamination in the sewer systems in Phnom Penh; however, these metals are still among the lowest levels reported in other studies (Table 14). Wastes from textiles companies may receive treatment according to international guidelines prior to discharge, but such a monitoring is not publically available and likely inconsistent, hence posing problems. Therefore, it is important that effluent treatment complies with international guidelines and be more transparent to the public as much as to the world.

**Table 17.** Metal concentrations of street dust in Phnom Penh compared with other cities.

| Location | Pb | Cu | Zn | Reference |
|---|---|---|---|---|
| Phnom Penh (Cambodia | 38* | 60.3* | 170.3* | This study |
| Kavala (Greece) | 301* | 124* | 272* | Christoforidis and Stamatis(2009) |
| Baoji (China) | 408* | 123* | 715* | Lu et al. (2009) |
| Hangzhou (China) | 202* | 116* | 321* | Zhang and Wang (2009) |
| Coventry (U.K.) | 47* | 226* | 385* | Charlesworth et al. (2003) |
| Kuala Lumpar (Malaysia) | 2,466* | 35* | 344* | Ramlan and Badri (2008) |
| London (U.K) | 370* | 79* | 372* | Schwar et al. (1988) |
| Ulsan (Korea) | 153* | 181* | 324* | Duong and Lee (2011) |
| Various sites (Hong Kong) | 160* | 126* | 1,170* | Li et al. (2001) |
| Hamilton (Canada) | 84-276 | 73-171 | 390-413 | Irvine et al. (2009) |
| Atlanta (U.S.A) | 93* | 22-1,445 | 68-1,115 | Deocampo et al. (2012) |
| Zagazig (Egypt) | 49-179 | 56-63 | 164-283 | El-Sayed et al. (2010) |
| Mutah (Jordan) | 143* | 69* | 132* | Manasreh (2010) |

*Note:* *Mean concentration (ppm)

## 5.2 Significance Analysis of Sewer, Wetland and Street Dust Samples

Student t-tests showed that while the mean of Pb concentration of the sewer samples was significantly higher than those of the wetland ($\alpha$=0.05), the mean concentrations of As in both the sewer and wetland ($\alpha$=0.05) were not significantly different. In addition, the student t-tests confirmed there were significant differences between the mean of Zn in the sewer and the wetland with the sewer being higher ($\alpha$=0.05). The mean of Cu in the sewer samples were statistically higher than those of the wetland at 0.08. The fact that the samples from the wetland showed lower metal concentrations than those of the sewer samples suggested that there is minimal sedimentation from the sewer and less retention in the wetland. Irvine et al. (2008) found that macrophyte growth in the wetland may promote filtration and settling of particle-bound contaminants and bacteria such as E. *coli*.

There was a significant difference in Pb in the sewer and the street dust with the mean of the Pb in the sewer being higher than that of the street dust. Moreover, there also was a statistical difference between Pb in the street dust and the wetland with the Pb level in the street dust being higher ($\alpha=0.05$). The order of decreasing of Pb is: Pb sewer > Pb street dust > Pb in wetland. The decreasing order of Pb suggested that Pb in the sewer is mainly derived from anthropogenic sources such as industrial and household discharge.

While the mean of Zn levels in the street dust samples is statistically the same as the Zn levels in the wetland, the mean of Zn in street dust is statistically different from that of the sewer with the mean of Zn in the sewer being higher ($\alpha=0.08$). The mean Cu in the sewer is statistically higher than that of the wetland and street dust samples. The means of As, Fe and Mn in street dust samples are statistically lower than those of the sewer and the wetland.

### 5.3 Grain Size Analysis

The grain size distributions of both the sewer and the street dust sediments show some variation. The $D_{50}$ of the sewer particle size ranges from 0.31 to 0.39 mm, whereas the individual $D_{50}$ of the street dusts varies from 0.10 to 0.55 mm. The mean $D_{50}$ of the sewer sediments is 0.35 mm while the mean $D_{50}$ of the street dusts is 0.17 mm. The sewer sediments possessing a larger grain size could be the result of sedimentary aggregation with adhesive materials and other organics, which were avoid being collected during the street dust sampling. Irvine et al. (2002) found that the event in which organic substances from the streets and mineral particles aggregated to form large masses of sediments in the sewer was the result of street runoffs during storm events.

Smaller street dust grain size particles may be more common for metal contaminants to bind to, offering low density and high mobility in runoff. The increase in metal concentrations corresponds to the decrease in size of sediment particles. Finer particles offer more relatively higher specific surface area to contaminants, enabling a better adsorption of trace elements; especially for particle size <0.63 mm (Irvine et al. 2009; Karmacharya and Shakya 2012; Xiang et al. 2010; Zafra et al. 2011). Table 15 provides a perspective of grain size distribution in Phnom Penh compared with other cities.

**Table 18.** Average $D_{50}$ of the street dust samples in Phnom Penh compared with other countries

| Location | $D_{50}$ (um) | Reference |
|---|---|---|
| Phnom Penh (Cambodia) | 170* | This study |
| Cantabria (Spain) | 247* | Zafra et al. (2011) |
| Lanzhou (China) | 118* | Guan et al. (2008) |
| Hawaii (U.S.A) | <63* | Sutherland (2003) |
| Kobe (Japan) | 190-210 | Adachi and Tainosho (2005) |

* Average $D_{50}$ (um)

### 5.4 Kriging Analysis of Street Dust Samples

The highest concentration of Pb was observed in areas of high volume traffic at intersections of main streets and boulevards and some gas stations in the city. For instance, any street dust samples obtained from areas around the Central Market contained from 47 to 62 ppm of Pb. Similarly, the highest Pb levels were found at the intersection of Street 271 and Monyreth Boulevard (St.217), and Russian Boulevard and Mao Tse Tong Boulevard. These Pb concentrations are not extreme and among the lowest levels reported in other studies (Table 14). These intersections are some of the busiest intersections in the city, and there usually is traffic congestion during rush hours of the day. High volume traffic in the city can generate fine and coarse particulate matter; especially by vehicular exhaust and re-entrained dust. Vermette el al. (2011) showed an increased level of air pollution in the Phnom Penh can be attributed to increased vehicle traffic and re-entrained dust, and suggested that selective paving of those hot spots will result in a reduction in the level of airborne coarse particulates. The least contaminated areas were those that are associated with recreational activities. Lead concentrations were high in the city center and low at the edges of the city (Figure 17).

The correlation matrix of the heavy metal in Table 10 showed that Pb has a high positive correlation with Zn (0.70). This correlation reflects vehicular emission of both Pb and Zn. Zhang and Wang (2009) found the same correlation with Pb and Zn in commercial and industrial areas in Hangzhou, China. Sources of Pb in the Chinese study included a Pb recycling plant, land fill, smelter, coal combustion, brake linings and leaded gasoline. In addition, Pb also has a high correlation with Cu (r=0.51), which is associated with brake linings (Guney et al. 2010)

Concentrations of As in street dust were highest in areas in which car and motorcycle wash service is provided. It seems to be a pattern that areas in which there involves groundbreaking and excavating of underground soils, the As concentrations were highest. For instance, street dust samples collected in the proximity to a big plot of land that currently is being used to construct an International Finance Complex (Figure 18) near the river front contained up to 54 ppm of As, which would exceed the guidelines of the USEPA, NYSDEC and PSQ of 9.8 ppm, 33 ppm and 33 ppm, respectively. Arsenic is naturally occurring in soil and ground water in Asia and Cambodia, entering solution after reductive release from solid phases under anaerobic conditions (Polizzotto et al. 2008). It is a newly emerging issue for Cambodia, and there have been reported cases of health implication associated with the contaminant in the provinces of Cambodia, India, Bangladesh and the US (Murphy et al. 2010; Sampson et al. 2008; Mitra et al. 2002).

Like Pb distribution, Cu appears to exist in places where there was high traffic volume. In addition, similar higher concentrations of Cu were associated with areas in which there are industrial operations and gas stations along the Mao Tse Tong Blvd and almost all of the major streets in Toul Kork District. The levels of Zn were most eminent in areas where there were automobile repair shops, and may be attributed to its extensive use in lubricating oils and tires (De Miguel et al. 1997; Adachi and Tainosho 2005; Golding 2008). It is evident that the Zn was lowest in areas where there was very low volume traffic and in distance from automobile workshop and gas stations.

# 6. CONCLUSION

Although the levels of metals in the sewer, wetland and street dust samples exceeded the guidelines specified by the USEPA, NYSDEC and PSQG, the mean values of all metals detected in this study are still lower than those reported in other studies in Hong Kong, Greece, China, Korea and Malaysia.

Levels of Pb, Zn and Cu decreased with distance from the first sampling site (M1) of the Meanchey sewer channel, preferentially accumulating in the sewer before being particle bound and settled in the wetland to lower concentrations and discharged into the Mekong and Bassc Rivers. M1 and T1 are geographically different in that the former is surrounded by more industrial firms, which discharge wastes into the Meanchey sewer, whereas the latter collects household wastes and storm water runoff. Since gasoline in Cambodia complies with the EU guideline on the use of Pb content, and based on the data from the two sewer systems, it can be concluded that Pb-based gasoline is not the major cause of Pb in the sewer and street dust. Other plausible explanations of Pb in the samples collected could be attributed to diesel fuel and open burning of PVC pipes, but such an assumption should be verified by a future study. It is also likely that there was minimal sedimentation from the sewer and retention, as well as filtration in the wetland.

The level of contaminants in street dust decreased with distance from their sources of high volume traffic areas, industries, gas stations, and motor workshops. The least contaminated areas included places where there are recreational activities and centers, as well as quiet areas. Sediment should be regularly dredged from the sewers to maximize channel flow capacity and minimize pollutant loadings reaching the wetlands. Source track down, particularly for Pb, should be conducted to support development of management strategies. For the best management practice of street dusts, continuous street sweeping may reduce the amount of pollutant loadings bound to the street dust particles, and have been proven to be one of the most effective strategies.

Finally, it would be essential for any future work to specifically determine the locations of large garment factories on GIS maps and collect street dust samples near the factories for metals analysis. The work should also include samples collected near the landfills. Upstream and downstream sediments of the garment factories should be assessed with records of rainfall and different seasons.

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# Chapter 3: Metal Contamination in Low-Cost Jewelry, Toys and Paints in Cambodia

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# 1. INTRODUCTION

## 1.1 Background

Cambodia imports most of its consumer products from nearby and regional countries such as Singapore, China, Hong Kong, Thailand and Vietnam. The consumer products and materials imported range from refined petroleum oils, mineral or chemical fertilizers, polyvinylchloride (PVC), and electronic appliances to gold, hair products, medical supply and articles of plastic (The Observatory of Economic Complexity 2012; Trading Economics 2012). The industrial development and the economic growth of Cambodia have increased for consumer products and goods (Index Mundi 2013). The influx of consumer products requires a more rapid, effective monitoring and quality control. Consumer products that are imported and sold in Cambodia can contain chemical contaminants that pose serious adverse health effects on consumers. A study by Murphy et al. (2012) reported that in Cambodia up to a third of the skin creams analyzed contained mercury (Hg) higher than the Association of Southeast Asian Nations (ASEAN) recommended guideline of 1 μg/g (1ppm). Mercury can impair kidney function and neurodevelopment. Similarly, studies in the U.S., India, and China have found elevated lead (Pb) levels in consumer products such as children’s toys, low-cost jewelry items, and paints (Weidenhamer and Clement 2007; Omolaoye et al. 2012; Aliyev et al. 2011; Clark et al. 2006)

Lead is hazardous to both adults and children, and even exposure to low levels of Pb (<10 μg/dl) can impair neurodevelopment in children and interfere the heme biosynthesis pathway (Lanphear et al. 2000; Lidsky and Schneider 2003). Lead is added to paints and plastic toys as a coloring agent and to prevent free radicals from reacting to form HCL (Greenway and Gerstenberger 2010; Kumar and Pastore 2007). In low-cost jewelry, Pb is mixed with low quality materials that may be sourced from electronic waste, to lower the cost of manufacturing and to imitate glossy, shiny better quality jewelry (Yost and Weidenhamer 2007)

The purpose of this chapter is to evaluate the level of metal content in inexpensive jewelry, children's toys and paints that are sold in markets in Phnom Penh, Cambodia. The findings of this study may shed light on Pb levels found in the above mentioned items, and alert children, parents and other consumers of the risks. The results could also lead to future clinical studies on blood lead level (BLL) in children and subsequent treatment of toxicity. Ideally improved insights will lead to better government management of these toxic products.

## 1.2 Chapter Objectives

The aims of this chapter are to: 1). use a handheld X-ray fluorescence (XRF) analyzer to assess whether inexpensive jewelry, children's toys and paints purchased from markets in Phnom Penh are contaminated with metals and 2). compare the findings with various international guidelines such as the United States Consumer Safety Product Commissioner (USCSPC), the European Standard EN71-3 Safety of Toys (EU), and the Australian Competition and Consumer Commission guidelines (ACCC).

## 1.3 Chapter Structure

The body of this chapter is presented in seven parts. Part One is the Introduction, and Part Two is the Literature Review discussing the pertinent research on metal contamination in inexpensive jewelry, plastic toys and paints. Part Three is the description of the methods used to conduct this study including the analytical aspects. Details of the study areas are also included in Part Three. Part Four provides the analytical results while Part Five is the discussion. The conclusions are discussed in Part Six, and Part Seven is the list of the references cited in this chapter.

# 2. LITERATURE REVIEW

## 2.1 Lead and Its Use

Lead is an element that has been a well-known poison for 3,000 years (Lidsky and Schneider 2003). Lead was one of the first discovered metals, and used historically in beads and pigments (Lessler 1987). Lead has been smelted and used in cosmetics, medicinal preparations, gasoline and paint pigments and glasses for many decades. In the early 1990s, scientists discovered that Pb exposure can cause irreversible damage to children's neurological development (Sciarillo et al. 1992). The most common effects of Pb are associated with lower intellectual functioning and anemia in children, and renal function abnormality, as well as immune compromise (Fels et al. 1998; Canfield et al. 2003; Meyer et al. 2008).

## 2.2 Effects of Lead on Human Health

Many studies have suggested that at a certain level, Pb has the potential to impair neurodevelopment; especially for children who are much more vulnerable than adults. For example, BLL as low as 3 μg/dl could result in neurobehavioral deficits such as visual motor impairment, attention, reaction time and off-task behaviors (Chiodo et al. 2004). Bellinger (2008) found that adverse outcomes such as reduced IQ performance and academic deficits occurred at BLL <10 μg/dl, and at prolonged exposure there was an association with attention deficit hyperactivity disorder (ADHD). Similarly, Sciarillo et al. (1992) reported that children aged 2 through 5 years had an 18-point increase in the Total Behavior Problem Score (TBPS) when their BLLs were as high as15 μg/dL.

The effects of excessive Pb exposure have been reported in both men and women. While the effects of exposure to Pb among men included chromosomal damage, abnormal prostatic function and changes in serum testosterone, the effects in women were premature delivery, pregnancy hypertension and miscarriage (Winder 1993). Other physiological effects such as alterations of menstrual cycle, hyperestrogenism, and increased spontaneous abortion rate in wives of workers exposed to Pb were also observed (Baranski 1993).

Fels et al. (1998) used both children exposed to Pb with BBLs (BLL>100 μg/L) and a control group to test the hypothesis that children were vulnerable to Pb-induced kidney damage. It was concluded that the pattern of effects on proximal and distal tubular, interstitial and glomerular markers was similar to the one reported on adults, including increased excretion of prostaglandins, $\beta_2$-microblobulin and Clara cell protein in exposed children. Cardenas et al. (1993) reported on the changes in urinary excretion of eicosanoids including a decrease in 6-keto-PGF excretion and increased excretion of thromboxane, which might be involved in the loss of renal function or in the development of high blood pressure in selected subjects with history of prolonged exposure to Pb at work.

At the immunological level, Basaran and Undeger (2000) investigated the immune competence by comparing 25 male storage battery workers with the same number of workers who have no previous record of Pb exposure. The results indicated that industrial exposure to Pb was associated with a depression of T helper lymphocytes, Ig G, Ig M, C3 and C4 complement levels, as well as a decline in chemotaxis, a cell-to-cell communication chemical signal. The compromised immune competence renders individuals exposed to Pb as more prone to other infectious diseases.

## 2.3 Lead in Inexpensive Jewelry

In the U.S., there are at least 4 million children exposed to Pb and approximately half a million U.S. children ages 1 to 5 years old with BLLs above 5 μg/dl (CDC 2013). Recognizing Pb exposure can affect every system in the body, the CDC initiated the Childhood Lead Poisoning Prevention Program which is committed to eliminating BLLs > 10 μg/dL by 2020 (CDC 2013). However, despite the efforts trying to eliminate Pb exposure to children, there have been numerous cases reported in which Pb-associated workers and children have been the victims of exposure. One such exposure pathway is via low-cost jewelry items, which are imported to the U.S. annually from developing countries such as China (Weidenhamer and Clement 2007).

A study conducted by Weidenhamer and Clement (2007) found that 77 out of 130 inexpensive jewelry samples imported from China exceeded the former U.S. Consumer Product Safety Commission (USCPSC) guideline of 0.06% (600 ppm) with the average Pb concentration of the samples being 40%, compared to a similar study by Maas et al. (2005) at 30%. Moreover, of 311 inexpensive jewelry samples purchased, Maas et al. (2005) found more than 50% of the samples contained more than 3.0% Pb in at least one portion of the jewelry piece while 39.5% of the samples contained more than 50% Pb and 29.2% contained more than 75% Pb.

The above findings supported the recalls of Pb-contaminated jewelry that cost the life of a four-year old child in Minnesota after ingesting a 99.0% Pb-contaminated charm, and these results highlighted the consequences of inexpensive jewelry and the need to strictly monitor, as well as to regulate the distribution of imported Pb-containing products to the U.S. (Weidenhamer and Clement 2007). In 2011, the CDC made a recall of 150 million pieces of metallic toy jewelries that were being sold in the U.S to reassess the Pb content or ban from the shelves if the total Pb content was considered to be unacceptable. This recall prompted the CDC to establish a tighter monitoring mechanism on products such as inexpensive jewelry items imported into the country.

A similar life threatening incident was reported in 2009 when an American born child of Cambodian parents was found to have been wearing an amulet infused with admonition from a monk in Cambodia that contained more than 45% Pb. This finding led to sampling of the child's blood to assess the level of Pb, which was 20 μg/dL at the time (CDC 2011). After the finding, the CDC (2011) advised immigrant parents who recently had traveled to foreign countries and had their children wearing amulets or jewelry items coated with potentially high level of Pb to register for a blood Pb level test. Levels of Pb in the low cost jewelry can reflect the scrap metal used in the manufacturing, as low-cost source materials include toxic electronic wastes that are shipped to poor countries (Worldwatch Institute 2006; Weidenhamer and Clement, 2007).

### 2.4 Lead in Children's Toys

Toys are an integral of part of a child's developmental processes and they play with toys to adapt to the world (Kumar and Pastore 2007). As mentioned above, Pb is widely used in consumer products, although its level varies. In children's toys, Pb is used as a pigment and is very hazardous, particularly to children, as their hand-to-mouth habits can chip off parts of the surface of the contaminated toy, or their physical interaction can cause the toxic element to leach out. Because toys are an intimate part of a child's development, such toys contaminated with Pb can obstruct the child's neurological development processes (Omolaoye et al. 2012).

Similar to inexpensive or plastic jewelry, over the past few years there have been multiple recalls of toys because of chemical safety hazards (Guney and Zagury 2012). In November 2008, the USCPSC issued a press release to alert parents about the previously recalled toy products with elevated Pb concentration that could still be available for sale at second-hand shops (Kerr and Metzler 2008). Table 1 provides some of the selected recalls on children's toys containing excessive Pb concentrations between 2007 and 2011.

**Table 19.** A list of toys recalled with elevated Pb in recent years (2007-2011) by the USCPSC (USCPSC 2011).

| Manufacturer | N | Description | Substrate | Origin |
|---|---|---|---|---|
| LM Import & Export | 1,900 | Toy Cars | Paint | China |
| American Girl Crafts | 7,500 | Beads & Bracelets | Paint | China |
| Super Rigs Play Sets | 700 | Toy Trucks | Paint | China |
| Greenbrier International | 300,000 | Beads & Cars | Paint | China |
| Toy World Group Ltd. | 16,000 | Military Figures | Paint | China |
| Mattel Inc. | 253,000 | Toy Cars | Paint | China |

Despite several federal recalls on toys contaminated with high levels of Pb, the ensuing studies continued to find excessive Pb content in children's toys. For instance, Greenway and Gerstenberger (2010) analyzed 535 toys with the XRF XLt 797 2W collected from 10 different daycare centers in Las Vegas, Nevada and found 29 toy samples (5.4%) contained a Pb concentration higher than the USCPSC guideline in 2008 of 600 ppm. However, there have been several reviews on the acceptable level of Pb content on toy surface coatings and paints, and now the current permissible Pb content has been reduced to 90 ppm (USCPSC 2011). Two possible reasons of Pb found in toys were the use of Pb stabilizers and Pb chromate as a yellow color enhancer (Greenway and Gerstenberger 2010). Inorganic Pb stabilizers are compounds that have been used in various products such as polyvinyl chloride (PVC) pipes to provide rigidity and high heat stability.

Kumar and Pastore (2007) tested 111 non-branded toy samples from three major cities in India, namely Delhi, Mumbai and Chennai, and found the level of Pb ranging from 0.65 – 2,104 ppm, with the Mumbai average being the highest (278.3 ppm). Twenty percent of the samples analyzed exceeded the USCPSC guideline of 600 ppm in painted toys. Similarly, a study on 26 brands of toys from different districts of Uttar Pradesh, India showed that all toys contained Pb in varying concentrations with the highest being 1.12ppm, but most samples contained Pb within the permissible guideline of the USCPSC (Ahmad et al. 2012). Ahmad et al. (2012) also found that there were associations between the Pb content and the color of the toys.

In Turkey, Aliyev et al. (2011) collected 50 toys, 19 of which were manufactured in Turkey and 31 samples were imported from China. The results from the AAS analysis indicated that the mean Pb on the surface of the toys imported from China was 85.3ppm compared with 41.4 ppm of the toys made in Turkey. The difference in Pb content between these two groups of toys was significant ($P<0.05$).

### 2.5 Lead in Paints

Mounting evidence has suggested that Pb-based paint can pose a serious hazard to human health, particularly for children (Lanphear et al. 1998; Jacobs et al. 2002; Fewtrell et al., 2004; Lin et al. 2009). In a study of three houses in an urban Sydney neighborhood which had previously been decontaminated, Gulson et al. (1995) showed that the houses could be re-contaminated within months with new leaded paints, which could be a concern for the families with young children and pregnant mothers. Due to their pica, children could accidently swallow parts of paint coated with excessive Pb content and could raise the BLLs, which may lead to adverse health implications later on.

Like Pb in contaminated jewelry and plastic toys, to the knowledge of the authors, data regarding Pb-based paints in Cambodia are non-existent but, because Cambodia imports household paints from neighboring countries, understanding the literature published on the region's household paints may reflect the same scenario for Cambodia. Lead poisoning is a major public health issue in the US, but little attention has been given to Pb-based paints (Clark et al. 2009). A report by the New York State Department of Health (NYSDH) showed that painting, repair and renovation activities were the sources of Pb exposure in children's BLLs >20 μg/dL (CDC 1997). Subsequent evidence exists to justify that BLLs < 10 μg/dL could be associated with Pb-contaminated paints and goods, even though regulations in paints and Pb hazard on older houses were enforced by the federal government (USEPA 2001; Lanphear et al. 2000 & 2002).

In China, Lin et al. (2009) ascertained that although there are regulatory limits on Pb in paints, the regulations were not well enforced. Their study revealed that Pb-based paints were still present in both new housing and existing residential paints. Approximately 50% of the 58 new paints tested had Pb content equal to or higher than 600 ppm, China's current Pb guideline for paint, and 14% exceeded 5,000 ppm. Despite the implementation of a Pb-based paint guideline since 1986, 55% of the samples analyzed had Pb content equal to or higher than 90 ppm, the current US Pb standard in paint (Lin et al. 2009). The authors also observed a relationship between the Pb levels and the paint colors, with the highest Pb concentrations found in yellow, green and red.

Clark et al. (2006) compared the Pb content in paints bought from four Asian countries, namely China, India, Malaysia and Singapore, and found that 56% of 9 samples from China contained Pb content higher than 600 ppm, the US Pb guideline for paint at the time of the study and also China's current Pb paint guideline; and 44% were equal to or higher than 5,000 ppm. In a follow-up paper published by the same authors, Clark et al. (2009) reported that Pb-based paints collected in China were among the lowest concentrations of all paints from the twelve countries. Over 43.8% of paint samples from China had Pb content equal to or higher than 90 ppm, and 32.8% were equal to or higher than 600 ppm. The inconsistency of the results from this study compared with other studies warrants further investigation.

In India, Kumar and Gottesfield (2008) tested 69 samples of latex and enamel paints from six brands, and found that all of the latex (water-based) paints had Pb content within the USCPSC guideline of 600 ppm and all of the enamel paints (oil-based), except for one, had Pb levels higher than 600 ppm. In Taiwan, Ewers et al. (2011) analyzed five brands of new enamel household paints and found Pb content up to 15.8%. The mean of the Pb content in paints in Taiwan was higher than those in China as observed by Clark et al (2009). Additionally, the Pb content by color was found to be higher in paints from Taiwan than in China. Lead content was correlated with color of the paint, but not the price per liter, with yellow containing the highest Pb concentrations. Clark et al (2009) observed the Pb concentration in various paint colors and found that the highest average Pb content was present in yellow paint at 37,665 ppm, and the lowest was in white at 37 ppm, which is lower than the current US guideline of 90 ppm.

# 3. METHODOLOGY

## 3.1 XRF Calibration

The XRF analyzer (Niton Thermo Fisher, Billerica, MA; model XL3t) used in this study was calibrated in the Thermo Fisher Scientific laboratories Billerica, Massachusetts, USA, verified several times in Phnom Penh with certified reference materials supplied by Thermo Fisher Scientific, and validated by comparison with another independent portable analytical tool, the LPA-1 XRF, from the Environmental Health and Safety of Buffalo State, The State University of New York. The results of validation are showed in Table 2.

**Table 20.** Calibration of XRF XL3t and LPA-1XRF with a standard reference.

| Color* | Standard value | LPA-1 XRF | XRF XL3t |
|---|---|---|---|
| Yellow paint | 10,000 | 8,765 | 8,389 |
| Green paint | 19,000 | 16,450 | 15,555 |

*Note:* Values are in parts per million (ppm)
*NIST Traceable Reference Material, RMD Inc.

## 3.2 Lead in Inexpensive Jewelry

Inexpensive jewelry pieces were purchased randomly from three markets in Phnom Penh while other jewelry pieces were provided by female students attending a vocational training institute at the time (Don Bosco Vocational Training Institute). In total, there were 74 jewelry pieces collected, most of which cost less than around 5 USD a piece.

Although the origin of these jewelry pieces could not be geographically determined, it is likely that they were imported from the neighboring counties and China. Inexpensive jewelry pieces produced in China are exported to the U.S. markets. Weidenhamer and Clement (2007) found in their study that 130 jewelry pieces out of 230 were manufactured in China. Another report published by Weidenhamer and Clement (2007) suggested that recycled electronic circuit board solders and other electronic product waste materials may be used to manufacture heavily leaded jewelry pieces, which are exported into the U.S.

Prior to and after the analysis, jewelry pieces were kept in plastic bags to prevent cross contamination in an acceptable laboratory working setting. Because each jewelry piece was different from one another in terms of length, composition and style, the jewelry piece part analyzed varied from one sample to another. The types of jewelry pieces analyzed are given in Table 3.

### 3.3 Lead Concentration in Children's Toys

Thirty-two children's toys were purchased from local markets, some from Thailand and Don Bosco Institute, a Christian vocational training center. After the toys were tested on Plastic Mode for the duration of 30 seconds, they were kept in plastic bags in the laboratory under the optimal condition. The types of children's toys analyzed are given in Table 4.

### 3.4 Lead Concentration in Paints

In this study, 21 paints including 8 replicates were randomly purchased from three shops in Phnom Penh. The objective was to determine if paints sold in markets would contain Pb. The selection goal was to purchase different paint colors and analyze for different Pb content, in addition to other metals**.**

Prior to analysis, the paint cans were manually shaken for 30 seconds to homogenize the content. Then, an Eppendorf pipette was used to transfer 1ml of the sample on to a Mylar film. The sample was then analyzed with the XRF on Plastic Mode for 30 seconds.

# 4. RESULTS

## 4.1 Lead Concentration in Inexpensive Jewelry

Seventy-four jewelry pieces collected from various markets in Phnom Penh were analyzed. Of the 74 jewelry pieces tested, 31 (41.8%) were found with Pb levels exceeding 90 ppm. Levels of Pb of these 31 jewelry pieces ranged from 110 – 439,370 ppm. The overall average of Pb of the 74 jewelry pieces was 28,860± 76,655 ppm. Eighteen samples (24%) had Pb concentration between 0.009%-2.9% while 6 samples (8.1%) had Pb concentrations between 3-9.9%. Eight samples (10.8%) contained between 10-49.9% Pb. For the calculation of the means, non-detectable values were substituted with a zero (0) (Singh and Nocerino 2001). The distribution of Pb concentration in jewelry items is shown in Figure 1. Table 3 provides a list of the jewelry items tested in this study.

**Table 21.** Mean metal concentrations of inexpensive jewelry pieces.

| No. | Samples | # of Samples | Pb | Hg | As | Cd | Cr |
|---|---|---|---|---|---|---|---|
| 1. | Bracelet | 18 | 54,579 | 30 | 129 | ND | 4,455 |
| 2. | Ring | 12 | 587.3 | ND | ND | 283 | 432 |
| 3. | Earring | 8 | 7,468 | ND | ND | ND | 1,018 |
| 4. | Necklace | 21 | 35,849 | 464 | 63 | ND | 278 |
| 5. | Watch | 5 | ND | 306 | 41 | ND | 71,200 |
| 6. | Spoon | 1 | ND | ND | ND | ND | 15,800 |
| 7. | Hairclip | 7 | 50,414 | ND | ND | ND | 65 |
| 8. | Bow | 1 | ND | 676 | 352 | ND | ND |
| 9. | Anklet | 1 | 1,637 | 2,198 | ND | ND | ND |
| Total | | 74 | | | | | |
| Mean | | | 28,860 | 198 | 56 | 45 | 6,322 |
| Median | | | ND | ND | ND | ND | ND |
| Std. Dev. | | | 76,655 | 849 | 237 | 394 | 26,645 |
| USCPSC Surface Coatings guidelines | | | 90 | 75 | 60 | 25 | 60 |
| EU Toy Safety guidelines | | | 90 | 75 | 60 | 25 | 60 |
| Australian Toy Safety guidelines | | | 90 | 75 | 60 | 25 | 60 |
| # of samples exceeded all guidelines | | | 31 | 1 | 6 | 6 | 13 |

*Note:* All values are in parts per million (ppm). Non detect abbreviated ND and substituted with a zero (0).

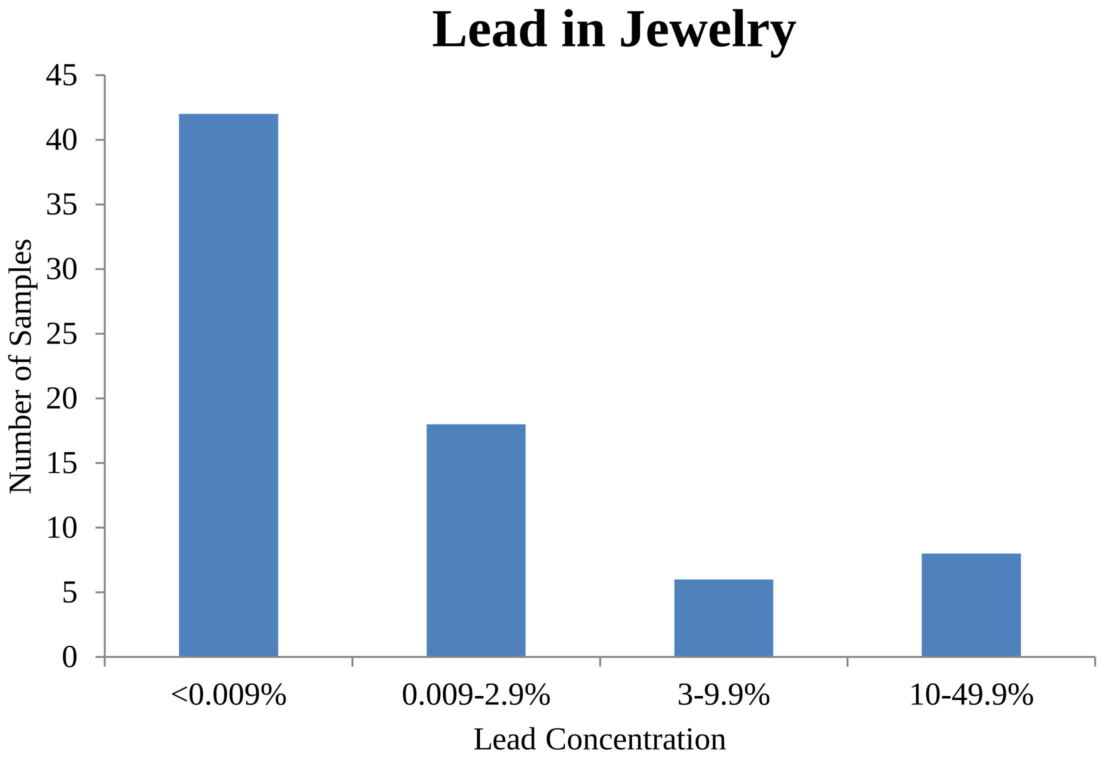

**Figure 33.** The number of jewelry samples with four corresponding categories of Pb concentrations.

The highest Pb concentration detected was 43.9%. Eighteen bracelets were bought from two markets and some were provided by the students at Don Bosco Institute, and eight exceeded the USCPSC guideline of Pb of 90 ppm (Figure 2). Two out of a total of 12 rings were Pb contaminated with 4,219 and 2,828 ppm. Five earring samples (62%) transcended the guideline of 90 ppm, whereas none of the students' watches had detectable Pb. Eleven out of 21 necklaces (52%) and four out of seven hairclips exceeded, by at least 20 and 17 folds of 90 ppm respectively.

## Lead in Necklace

**Figure 34.** The "lobster-claw" clasp of this necklace contains 27.8% Pb.

### 4.2 Other Metals

Of the 74 samples analyzed, one sample was detected with elevated Cd at 3,396 ppm. Six samples contained Hg and As higher than all of the three guidelines (USCPSC, EU and Australian) of 60 and 25 ppm respectively, and thirteen samples were detected with Cr higher than the guideline of 60 ppm.

### 4.3 Analysis of Significance

Due to the fact that the sample data were not normally distributed (tested on SPSS v. 16), the analysis of variance (ANOVA) could not be used. Such a test would violate a number of assumptions required to carry out a proper test. Instead, an alternative non-parametric test, Kruskal-Wallis, was used and the required assumptions for conducting such a test must also be met. All of the calculations were done on SPSS. Of all the jewelry items tested, no significant difference was observed between the groups (P=0.19).

### 4.4 Lead Concentration in Children's Toys

Out of 32 toy samples tested, 11 samples (36.6%) were found to contain Pb concentrations greater than 90 ppm, the USCPSC, EU and Australian guideline. The mean value was 4,953 ± 16,714 ppm while the median was 27 ppm. Non-detectable values were substituted with a zero value for that particular element. The highest Pb concentration measured was 100,850 ppm, and the lowest value detected was 35 ppm. None of the toys was detected in the range of 3-9.9%, but one was found in the range of 10-49.9% Pb. The list of the toy samples analyzed is given in Table 4. Figure 3 shows Pb distribution in children's toys.

**Table 22.** Mean metal concentrations in children's toys

| No. | Samples | # of Samples | Pb | Hg | As | Cd | Cr |
|---|---|---|---|---|---|---|---|
| 1. | Sword | 2 | 75.5 | 8,239 | 2,047 | 61 | 139 |
| 2. | Truck | 9 | 45.7 | ND | 202 | ND | 48 |
| 3. | Snake | 1 | ND | ND | ND | ND | ND |
| 4. | Car | 5 | ND | ND | ND | ND | ND |
| 5. | Handcuff | 2 | 5,285 | ND | ND | ND | ND |
| 6. | Hairclip | 2 | 8,638 | ND | ND | ND | ND |
| 7. | Mini stars | 4 | 36,550 | ND | ND | ND | ND |
| 8. | Doll | 1 | ND | ND | ND | ND | ND |
| 9. | Bead | 6 | 3,103 | ND | ND | ND | ND |
| Total | | 32 | | | | | |
| Mean | | | 4,953 | 422 | 131 | 3 | 19 |
| Median | | | ND | ND | ND | ND | ND |
| Std. Dev. | | | 16,714 | 2,652 | 577 | 17 | 78 |
| USCPSC Surface Coatings guideline | | | 90 | 75 | 60 | 25 | 60 |
| EU Toy Safety guideline | | | 90 | 75 | 60 | 25 | 60 |
| Australian Toy Safety guideline | | | 90 | 75 | 60 | 25 | 60 |

*Note:* All values are in parts per million (ppm). Not detects (ND) calculated by substituting with a zero (0).

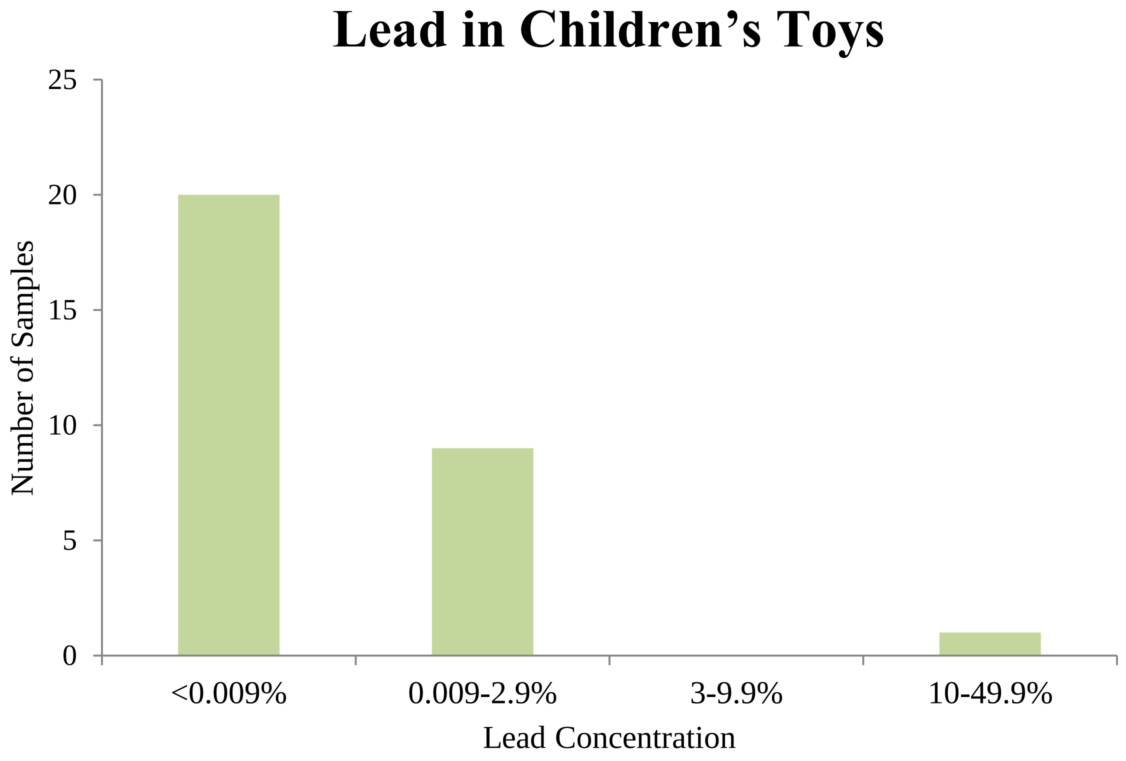

**Figure 35.** The number of toy samples with four corresponding categories of Pb concentrations.

### 4.5 Other Metals

One sample contained with 109 ppm of Cd, while four samples contained Cr ranging from 92-402 ppm. The top surfaces of two toy cars were found with 1% and 2% Hg (Figure 4). If adults or parents are not aware, children could swallow or ingest parts of the paint into their mouth, which could result in a serious health implication.

**Mercury in Children’s Toys**

**Figure 36.** The glossy paint of the car is 1% Hg.

## 4.6 Lead Concentration in Paints

The analysis showed that 90.5% of the paints had Pb levels greater than the recommended guideline of 90 ppm of the USCPSC, and the mean Pb level was 11,833±13,302 ppm while the median was 4,961 ppm. The lowest level was 82 ppm while the highest level was 43,970 ppm. The results of the analysis on paints are given in Tables 5 and 6.

Of 8 different paint colors, red had the highest mean concentration of Pb (24,606±13,238 ppm). Levels of Pb detected in the samples from this particular color ranged from 15,350-43,970 ppm. The concentrations in yellow paints ranged from 705-33,150 ppm. The overall mean value of Pb in yellow paints was 21,560±10,764 ppm. Green paints had a range of concentration from 1,753 to 4,961 ppm, with the mean value of 3,015±1,220 ppm. One black and one brown paint had concentrations of 516 and 334 ppm respectively. One blue paint was detected below the Pb guideline of 90 ppm at 82 ppm. The grey paint had no detectable Pb concentration whereas the mean value of white paints was 824±234 ppm.

**Table 23.** Statistics for Pb-based paint samples

| Samples | N | Min | Max | Mean | STD | S.E. |
|---|---|---|---|---|---|---|
| Yellow | 5 | 705 | 33,150 | 22,322 | 10,171 | 406 |
| Red | 5 | 15,350 | 43,970 | 24,949 | 10,586 | 459 |
| Green | 5 | 1,753 | 4,961 | 3,215 | 1,277 | 75 |
| Black | 1 | (-) | (-) | 516 | (-) | 22 |
| Grey | 1 | (-) | (-) | ND | (-) | ND |
| Brown | 1 | (-) | (-) | 334 | (-) | 22 |
| Blue | 1 | (-) | (-) | 82 | (-) | 13 |
| White | 2 | 560 | 1,088 | 824 | 373 | 35 |

*Note:* All values are in parts per million (ppm). Not Detectable abbreviated ND. (-) Value not available due to limited sample size.

**Table 24.** Concentrations of Pb in paints from the three local shops

| | Yellow | Red | Green | Black | Grey | Brown | Blue | White |
|---|---|---|---|---|---|---|---|---|
| Shop I | 26,724 | 43,970 | 4,961 | - | - | - | - | - |
| Rep. Shot 1 | 31,264 | 33,105 | 5,044 | - | - | - | - | - |
| Duplicate 1 | 28,732 | 15,350 | 2,667 | - | - | - | - | 1,088 |
| Shop II | 33,150 | 17,693 | 2,872 | - | - | - | - | - |
| Duplicate 2 | 7,055 | 17,994 | 1,753 | - | - | - | - | 560 |
| Shop III | 12,141 | 28,023 | 2,823 | 526 | ND | 334 | 82 | - |
| Rep. Shot III | 17,190 | 18,506 | 2,387 | 190 | ND | 74 | 68 | - |
| Mean | 21,560 | 24,606 | 3,015 | 358 | ND | 204 | 75 | 824 |
| Std. Dev. | 10,764 | 13,238 | 1,220 | 238 | ND | 184 | 10 | 373 |

*Note:* All values are in parts per million (ppm). Not Detectable abbreviated ND.

**Table 25.** Concentration of Pb in paints compared with those reported in other studies.

| Color | Country | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Cambodia | | Nigeria[1] | | Taipei[2] | | China[3] | | India[4] | | Malaysia[5] | |
| | Median<br>Median | | Mean<br>Mean | Median<br>Median | | Mean<br>Mean | Median | | Mean | Median | | Mean |
| | *N* | (SD) | *N* | (SD) | *N* | (SD) | *N* | (SD) | *N* | (SD) | *N* | (SD) |
| Yellow | 26,724 | 22,322 | 40,515 | 42,271 | 34,245 | 64,400 | 17,600 | - | 90,000 | 159,200 | | - |
| | 149,000 | | | | | | | | | | | |
| | 5 | 10,171 | 4 | 5,393 | 5 | - | 9 | - | 2 | - | - | - |
| Red | 18,506 | 24,949 | 24,457 | 23,744 | 5,369 | 17,830 | 752 | - | 6,538 | | | |
| | 5 | 10,586 | 4 | 15,877 | 5 | - | 16 | - | | | | |
| Green | 2,823 | 3,215 | 12,216 | 15,976 | 24,124 | 33,130 | 8,950 | - | 21,250 | 39,200 | - | 24,200 |
| | 5 | 1,277 | 3 | 9,410 | 5 | - | 5 | - | - | - | - | - |
| White | 824 | 824 | 4,110 | 3,035 | 4.5 | 1,115 | 21 | - | 991 | | | |
| | 2 | 373 | 5 | 1,864 | 5 | - | 8 | - | | | | |
| Blue | 82 | 82 | 3,615 | 3,457 | 725 | 3,427 | 139 | - | 5,600 | | | |
| | 1 | 10 | 5 | 1,729 | 5 | - | 5 | - | | | | |
| Grey | ND | ND | | | | | 100 | - | | | | |
| | 1 | 13 | | | | | 2 | - | | | | |
| Brown | 334 | 334 | | | | | | | - | 10,980 | | |
| | 1 | 184 | | | | | | | - | - | | |
| Black | 526 | 526 | | | | | 218 | - | 3,618 | | | |
| | 1 | 238 | | | | | 7 | - | | | | |

*Note:* [1] Adebamowo et al (2007), [2] Ewers et al. (2011), [3]Lin et al, (2009), [4] Kumar and Gottesfeld (2008), [5] Clark et al. (2006). All values are in parts per million (ppm).

### 4.7 Analysis of Significance

Three groups of paints (yellow, red and green) were tested for significant differences (Chi Square test), and other colors were not analyzed due to limited sample size. The null hypothesis ($H_0$) was that there was no significant differences in Pb content distribution in all three colors at $\alpha=0.05$. The Chi Square test showed that there was a significant difference between the colored paints ($P<0.05$).

# 5. DISCUSSION

## 5.1 Lead Concentration in Jewelry Items

Thirty one jewelry pieces (31%) exceeded the USCPSC, EU and Australian Toy Safety guideline of 90 ppm, up to 4,881 times (the highest concentration of 439,370 ppm). The overall average exceeded the guideline about 320 times (the overall average of 28,860 ppm). Twenty four percent of the contaminated jewelry pieces contained Pb in the range of 0.009-2.9%, and 8% fell in the range of 3-9.9%. Kruskal-Wallis, a non-parametric test, indicated that there were no significant differences within the groups of jewelry items ($P=0.19$, $\alpha=0.05$). If the violations to the assumptions of ANOVA were to be disregarded, the result would also show a no significance difference between groups ($P=0.34$). So, the results of the two types of tests were consistent.

Surveying 42 major retailers in California, Cox and Green (2010) found that 60 pieces (4%) of 1500 jewelry pieces did not comply with the state's Pb guideline. Additionally, they also noticed that the "lobster-claw" clasp tended to contain higher Pb content than other parts of the jewelry. Their findings are, therefore, in an agreement with this study. In this study, the clasp of a necklace contained the highest Pb content up to 43.9%. The jewelry pieces in the decreasing order of Pb (mean values) were hairclips, 88,224 ppm; earrings, 72,070 ppm; necklaces, 64,544 ppm; bracelets, 14,030 ppm; rings, 3,523 ppm; anklet, 1,632 ppm; bow, ND; spoon, ND; and watches, ND.

As mentioned above, the prices of these jewelry pieces are quite cheap which suggested the jewelry was marketed towards young children of developing countries. Children like to suck and chew toys and there are major risks that Pb could be dissolved in saliva, or a piece of Pb could be easily followed. Again, an example of such a case occurred to a Cambodian child wearing an amulet brought over from a rural Cambodian market, which had a total Pb content of

45%. The boy had been wearing the amulet since he was three months old, and the boy was observed mouthing it. After the amulet was removed from the child's body, the BLLs progressively decreased (Clark et al. 2009).

The concentrations of Pb appeared to vary with the nature of the jewelry items. It was impossible to determine the Pb content based on visual inspection. However, upon careful inspection, it was observed that jewelry sections appeared to have some type of coating or plating: shiny chrome-colored plastic coatings, shiny chrome-colored metallic platings, and dull grey metallic platings, which were similar to those described by Maas et al. (2005).

### 5.2 Lead Concentration in Children's Toys

Eleven toy samples (36.6%) exceeded the USCPSC, EU and Australian Toy Safety guideline of 90 ppm. The mean value of Pb was 4,953±16,714 ppm, which was 55 times higher than the acceptable level. The highest Pb level detected was 100,850 ppm, and none of the samples was found in the range of 3-9.9%.

No amount of Pb is considered safe for children, and their pica can result in chewing and ingesting the toy's surface coated with Pb, contributing to elevated BLLs. Previous research by Middleton (2000) indicated handling keys with Pb contents of 1.4-1.9% could result in the transfer of Pb to the skin. Maas et al (2005) cited a couple of other studies that showed handling of Pb-contaminated items with lower Pb weight-percent can result in significant transfer of Pb to the skin. Additionally, up to 4μg of Pb could be transferred from the skin to the surface of food items after a single handling of items contaminated with Pb, according to a study cited by Maas et al. (2005). Like the jewelry items, Pb content could not be determined by visual inspections.

Different parts of the toy may or may not possess any Pb concentration or may contain uneven concentrations. The toys appeared in different colors and designs to which children are attracted.

### 5.3 Lead Concentrations in Paints

The reduction of the threshold level from 600 to 90 ppm (Weidenhamer and Clement 2007) was a reinforcement aimed at reducing public health concern with respect to the use of Pb in paints and its adverse health effects on children. Comparison of the Pb-based paints in this study with those in other countries indicated that the Pb contents found in the selected paints in this study were generally lower than those reported in other research. For instance, the means of yellow paints analyzed in Nigeria and Taipei were 42,271 and 64,400 ppm respectively while the mean of the yellow paints found in this study was 21,560 ppm. Moreover, previous studies in India and Malaysia reported the mean concentration of 90,000 and 149,000 ppm (Table 7) in yellow paint respectively.

However, red paints tested in this study appeared to be slightly higher than those reported in other studies. The concentration of Pb in red paints averaged 24,606 ppm, while for the Nigeria and Taipei samples the average concentrations were 23,744 and 17,880 ppm. The black and white paints had higher Pb concentration than those reported in China by Lin et al. (2009).

That being said, green, brown and blue paints had lower Pb concentrations than those analyzed in Nigeria, Taipei, India and Malaysia (Table 7). It seemed that the red and yellow colors had higher Pb content than other colors. The Chi Square test indicated there was a significant difference with respect to Pb distribution in yellow, red, and green paint ($P<0.05$). From the literature, it seemed to be red and yellow paints that contained higher Pb levels, but it is premature to conclude that red or yellow paints would always contain a higher level of Pb than other paint colors.

# 6. CONCLUSION

In this study, up to 31% (total 74) of low-cost jewelry pieces contained Pb higher than the recommended level of 90 ppm, ranging from 110-278,280 ppm. The average of Pb was 28,860 ppm, which was 320 times higher than the guideline. Of the contaminated 42 samples, 18 had Pb content within 0.009-2.9%; 6 were between 3-9.9% and 8 contained Pb from 10-49.9%. The distribution of Pb-contained jewelry pieces varies widely, hence more sampling is needed to further assess and pinpoint the sources, as well as the origin of Pb use. The order of decreasing frequency of other metals detected in the low-cost jewelry pieces was Cr >Hg>Cd≥As. No significant differences in Pb were found between the groups of jewelry items.

Over 36% (total 32) of toys chosen for this study exceeded the USCPSC, EU and Australian Toy Safety guidelines of 90 ppm. The mean of the toys was 4,953±16,714 ppm, which is 55 times high than the acceptable level of 90 ppm. One sample fell within the range of 10-49.9% Pb while none was detected between the range of 3-9.9%. The order of decreasing frequency of other metals was Cr>Hg>Cd. About 91% of the paint samples exceeded the guideline of 90 ppm of the USCPSC, EU and Australian guidelines for paints. The highest concentration of Pb detected was 4.3% (red). There was a significant difference in Pb content between yellow, red and green paints (Chi-Square test)

We do not have any baseline information beside this study about the frequency of high Pb levels in consumer products. However, the data from this study are adequate by itself to show that the risks of Pb, especially in some toys, are very substantial, and the primary immediate objectives are to establish the ability to detect these products within a regulatory agency in Cambodia and to restrict the sales and use of these toxic products.

Because there is a lack of treatment facility and procedure with respect to Pb poisoning in Cambodia, a number mitigation and prevention measures can be implemented to make the public aware of the potential adverse health effects. For instance, description of the materials used in the product on labeling could help inform parents to consider whether or not the toy or jewelry pieces would be suitable for play. Another more realistic approach is to educate young school children and teachers about the subject matter at educational institutions, so that they could protect themselves from accidental exposure. A more restrictive regulatory mechanism related to border security such as disseminating information about the contaminated, illegal products and effects on the country's economy associated with the import, including equipping officers with a tool for screening the incoming goods, such as the XRF analyzer, could be enforced and implemented.

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