

HEAVY METALS IN INDOOR SETTLED DUSTS IN TORONTO, CANADA

by

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ABSTRACT

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Total concentrations of nine potentially toxic heavy metals (Ba, Cd, Cr, Cu, Hg, Mn, Ni, Pb, and Zn) in indoor settled dusts from houses, offices, classrooms, and laboratories in Greater Toronto Area, Canada were determined. Mercury concentrations were determined using cold vapor atomic fluorescence spectroscopy (CVAFS), whereas the concentrations of eight other metals were determined using inductively coupled plasma atomic emission spectroscopy (ICP-AES). The results showed that the highest level of heavy metals was in the laboratory dusts. Metal concentrations (except those for Mn and Zn) in household, office, and classroom dusts were comparable. Cd, Cr, Cu, Ni, and Zn concentrations in the laboratory dusts and Cu and Zn concentrations in household, office, and classroom dusts exceeded the Canadian Soil Guideline. Metal concentrations in the indoor dusts found in this study were, in general, consistent with those reported in literature. Among the metals studied, Cd, Cu, Hg, Pb, and Zn showed the greatest enrichment in the indoor environments relative to their crustal abundances.

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DEDICATION

I would like to dedicate my thesis to my wife, Halla, my daughter, Sura, and my son, Hussain.

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LIST OF ABBREVIATIONS

AM	Arithmetic Mean
ANOVA	Analysis of Variance
Ar	Argon
Ba	Barium
CCME	Canadian Council of Ministers of the Environment
Cd	Cadmium
CF	Calibration Factor
Cr	Chromium
Cu	Copper
CVAFS	Cold Vapor Atomic Fluorescence Spectroscopy
EF	Enrichment Factor
GIS	Geographic Information System
GM	Geometric Mean
GTA	Greater Toronto Area
Hg	Mercury
Hg ⁰	Elemental mercury
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectroscopy
IPR	Initial Precision and Recovery
Max	Maximum
MDL	Method Detection Limit

Min	Minimum
Mn	Manganese
N ₂	Nitrogen
Ni	Nickel
NIST	National Institute of Standards and Technology
Pb	Lead
PVC	Polyvinyl Chloride
QC	Quality Control
RSD	Relative Standard Deviation
SAS	Statistical Analysis Software
SD	Standard Deviation
SRM	Standard Reference Material
SPSS	Statistical Package for Social Science
THg	Total mercury
USEPA	United State Environmental Protection Agency
Zn	Zinc

1. INTRODUCTION:

Indoor air quality is an environmental health concern because people spend up to 90% of their time indoors in places, such as homes, offices and schools (Klepeis et al. 2001; Sharpe 2004; Health Canada 2009; Tran et al. 2012). Indoor settled dusts contain various hazardous materials including heavy metals, which can affect human health (Dundar and Atundag 2002). Heavy metals in indoor dusts are an important indicator of pollution in urban environments (Lu et al. 2009).

1.1. Composition of indoor settled dusts:

Indoor settled dusts can be defined as fine ($\leq 100 \mu\text{m}$) settled airborne particles in the indoor local environment (Turner 2011). Indoor dusts have external and internal sources. External sources include materials, such as outdoor air particles, garden soil and road dusts, brought indoors from the outdoor environment. Internal sources include smoking, combustion processes (e.g., heating, cooking), building materials (e.g., paints), abrasion from indoor items (e.g., paper, carpet and clothing), and parts from indoor living organisms including occupants, pets, bacteria, fungi, and dust mites (Butte and Heinzow 2002). Indoor settled dusts are, therefore, a heterogeneous matrix of organic matter and inorganic materials. The composition of indoor dusts alters markedly with the season (e.g., temperature, indoor air circulation), age of the building, quantity of furniture and carpets as well as their preservation, and the occupants' living habits, including activities and use of personal products (Morawska and Salthammer 2003).

Consequently, the composition of indoor settled dusts can vary greatly between rooms of a given house and among geographic locations (Lioy et al. 2002).

1.2. Sources of heavy metals in indoor settled dusts:

Heavy metals can be defined as trace elements with atomic weights higher than 40.04 g mol⁻¹ (Banfalvi, 2011). Heavy metals, like barium (Ba), cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), manganese (Mn), nickel (Ni), lead (Pb), and zinc (Zn), exist in indoor settled dusts originating from internal and external sources and therefore show considerable enrichment in the indoor environments relative to their crustal abundances (Fergusson and Kim 1991, Rasmussen 2004). External sources could be heavy metals associated with particles that are airborne or that are tracked-in on clothing and footwear including soil, road dust, industrial and vehicular particulates (Turner 2011). Automobile emissions are considered as important sources of various heavy metals, including Ba (oil and diesel fuel additives), Cr (chromium plating, alloys), Cu (metal plating, brake lining), Mn (gasoline additives), Ni (metal parts, oil additives), Pb (tire and gasoline additives), and Cd and Zn (tire and oil additives) (Madany et al. 1994; Lisiewicz et al. 2000; Chattopadhyay et al. 2003; Khoder et al. 2010; Charlesworth et al. 2011).

Important internal sources of heavy metals include decorative paints, consumer and cosmetic products, appliances, rubber carpet backing and carpet pigments, worn construction materials, and combustion products of cooking, heating and smoking (Turner 2011). Paints have been recognized as serious sources of heavy metals. For example, yellow paint is associated with higher concentrations of Cd, Cu, Pb, and Zn in indoor dusts (Tong and Lam 2000; Chattopadhyay et al. 2003). High Cd levels in indoor dusts have also been attributed to carpet

wear (Kim and Fergusson 1993). Electrical and electronic appliances, such as televisions, washing machines, refrigerators, air conditioners, and personal computers contain significant amounts of heavy metals, including Ba, Cd, Cr, Cu, Hg, Ni, Pb, and Zn. For example, Cr is used in data tapes and floppy disks; Cd is used in rechargeable Ni-Cd batteries and as stabilizers in polyvinyl chloride (PVC), which is used as insulation coating on wires and cables (Lau et al. 2014). Products containing Hg include manometers, thermometers, electrical and electronic switches, and fluorescent lamps (Rutagi and Singh 2010; Huang et al. 2012).

1.3. Heavy metal exposure pathways:

Indoor settled dusts containing heavy metals are an important source of exposure for people, especially children and other vulnerable individuals. Inhalation, dust ingestion, and dermal contact are common pathways by which toxic heavy metals can enter the body (Morawska and Salthammer 2003). Through breathing, airborne dust particles pose considerable health risks, such as diverse respiratory illnesses, decreased lung function, and cardiovascular diseases (Turner and Hefzi 2010). Heavy metals such as Cd, Ni, and Pb are common examples of metals that cause negative health impacts from breathing and have been noticed from both occupational and ambient air exposure (Vincent 2005). Dust ingestion occurs, unwittingly, with food and drink, and with respect to young children via the mouthing of non-food items and repetitive hand-to-mouth activity (Butte and Heinzow 2002). Dermal contact is the other way for exposure of heavy metals. For example, Ni is classified as a skin sensitizer and it can cause allergic contact dermatitis (Mazinanian et al. 2013).

1.4. Health effects of heavy metals:

Heavy metals are usually non-degradable and their high levels can threaten biological life. Many of them such as Cu and Zn have some biological functions at low concentrations and cause toxic effects at higher than physiological concentrations (Banfalvi 2011). Some heavy metals, like Cd, Hg, and Pb, have no known physiological role in the human body and even at extremely low concentrations, they are toxic and cause various diseases (Willers et al. 2005). Heavy metals can cause anemia, kidney failure, brain dysfunction, liver cirrhosis, cancer, and cardiovascular diseases (Nriagu 1988). High exposure of Cd, Hg, and Pb may lead to the damage of bone, kidneys and the brain (Alfven et al. 2002; Chattopadhyay 2003; Barregard 2006). A number of heavy metals including Cd, Cr, Ni, Pb, and Zn are recognized as suspected carcinogens (Cook et al. 2005). Mn may cause liver dysfunction, neurologic and neuropsychiatric illnesses (Kramtz and Dorevitch 2004). The presence of Cu irritates the mucous membranes and disturbs the digestive system (Jabeen et al. 2001). Ba is associated with muscle cramps and interferes with the heartbeat (Khaparde et al. 2012). Some heavy metals (e.g., Ba, Cr, Ni and Zn) may cause asthma (Karntz and Dorevitch 2004; Khaparde et al. 2012).

1.5. Literature survey of concentrations of heavy metals in indoor settled dusts:

In recent years, several studies have been conducted to analyze heavy metals in indoor dusts, such as household, office and classroom dusts. The mean concentration values were in the range of 85-492 mg kg⁻¹ for Ba, 0.80-6.5 mg kg⁻¹ for Cd, 37-254 mg kg⁻¹ for Cr, 91-2740 mg kg⁻¹ for Cu, 0.20-3.63 mg kg⁻¹ for Hg, 76-772 mg kg⁻¹ for Mn, 26-471 mg kg⁻¹ for Ni, 28-406 mg kg⁻¹ for Pb, 396-3104 mg kg⁻¹ for Zn (Rasmussen et al. 2001; Chattopadhyay et al. 2003; Al-Momani 2007; Turner and Hafzi 2010; Kurt-Karakus 2012; Kefeni and Okankwo 2013).

Hassan (2012) has investigated heavy metals in dusts collected from households, stairs and entryways of some Egyptian homes. The results showed that the highest mean concentrations of Cd, Co, Cr, Cu, Ni, and Pb were observed in the entryway, followed by household and stair dusts. The study inferred that in addition to internal sources, heavy metals in household dust could originate from external sources because there was a correlation between the metal concentrations in household and entryway dusts.

Another study (Al-Momani 2007) was conducted to analyze heavy metals in house dust, street dust, and garden soil samples collected from Amman, Jordan. The results showed that the house dusts contained higher concentrations of Cd, Cr, Cu, Ni, Pb, and Zn than either street dusts or garden soils. Using diesel fuel for heating by metal furnaces was the main source leading to increase the concentrations of Ni, Pb, and Zn in the house dusts.

Chattopadhyay et al. (2003) found that although the concentrations of Pb in fine airborne particles in Sydney, Australia have decreased since the phasing out of leaded gasoline, the Pb levels in household dusts have remained constant. This is not due only to building up of Pb in the house from the old leaded paints, but also the historical accumulation of more than 80 years of leaded gasoline deposition in the urban area.

Rasmussen et al. (2001) have determined multi-element profiles of indoor dusts, exterior dusts and soils collected from 50 residences located in 10 different zones of Ottawa, the capital city of Canada. The study indicated that a significant amount of heavy metals, such as Cd, Hg, and Pb in household dusts was generated from sources within the indoor environment. The concentrations of these metals in household dusts were higher than their concentrations in either street dusts or garden soils. Moreover, total metal concentrations in indoor dusts may be

influenced by the ability of biogenic particles, such as fungi and molds that have built up heavy metals to high levels.

Another study, performed by Tong and Lam (2000), measured heavy metal concentrations in indoor dusts collected from houses across Hong Kong. The study suggested that the significant factors, which may affect heavy metal concentrations in household dusts, were traffic, age of the building, neighborhood, and wall paint.

Household and office dusts from Istanbul, Turkey have been analyzed to quantify Cd, Cr, Cu, Mn, Ni, Pb and Zn (Kurt-Karakus 2012). The results showed that there was no difference between the metal concentrations in household and office dusts. In addition, the authors examined several factors (e.g., age of building, number of occupants, last paint and pets) that might have influenced the concentrations of the heavy metals in the indoor dusts. They found that the number of occupants was the most significant factor affecting concentrations of heavy metals. Kefeni and Okonkwo (2013) have analyzed settled dusts collected from homes and offices in Pretoria, South Africa for evaluating heavy metal concentrations. Their results showed that the office dusts were more contaminated than home dusts.

Popoola et al. (2012) showed that Cd, Cr and Pb were detected in the classroom dust samples collected from primary schools in Lagos State, Nigeria. Although the amounts of the metals were lower than some reported values for dusts in a number of locations worldwide, the metal pollutants in classroom dusts could be an important source of exposure for children because they spend a lot of time in the classroom. Yap et al. (2011), also, examined heavy metals in classroom dusts collected from the ceiling fans in many schools located across Selangor,

Malaysia. The results showed that some elevated levels of Cd, Cu, Ni and Pb were related to anthropogenic sources.

From the previous studies, two points can be highlighted. Firstly, concentrations of heavy metals are most likely higher in indoor than outdoor settled dusts. Secondly, the important factors, which may affect the concentrations of heavy metals in indoor dusts, include traffic, building age, building materials, type of heating, neighborhood, number of occupants, ventilation behavior, and certain personal hobbies.

1.6. Study objectives:

To our knowledge, no data have been published on heavy metal concentrations in indoor dusts in Toronto, the largest city in Canada. Therefore, this study is the first to report heavy metal concentrations in indoor settled dusts collected from homes, offices, classrooms and laboratories in Greater Toronto Area (GTA).

The main objectives of the present study were:

- To quantify Ba, Cd, Cr, Cu, Hg, Mn, Ni, Pb, and Zn in the settled dusts collected from households, offices, classrooms and laboratories.
- To compare the concentrations of the heavy metals in household dusts with office, classroom, and laboratory dusts.
- To use the results to identify “hot spots” of heavy metals in indoor environments in the GTA.
- To compare the results of heavy metal concentrations with the values reported in literature worldwide.

2. MATERIALS AND METHODS:

2.1. Sample collection and preparation:

Household settled dust samples were collected from a total of 67 residences from different suburbs within the Greater Toronto Area (Fig. 1A) during January-April, 2012 and January-April, 2013. The dust samples were collected from different rooms including basement, kitchen, dining, living, and bedrooms. Samples of indoor settled dusts from offices, classrooms, and laboratories were collected during January-March, 2014 from the Kerr Hall building at Ryerson University (Fig. 1B) located in the downtown core of Toronto and surrounded by high traffic density roads.

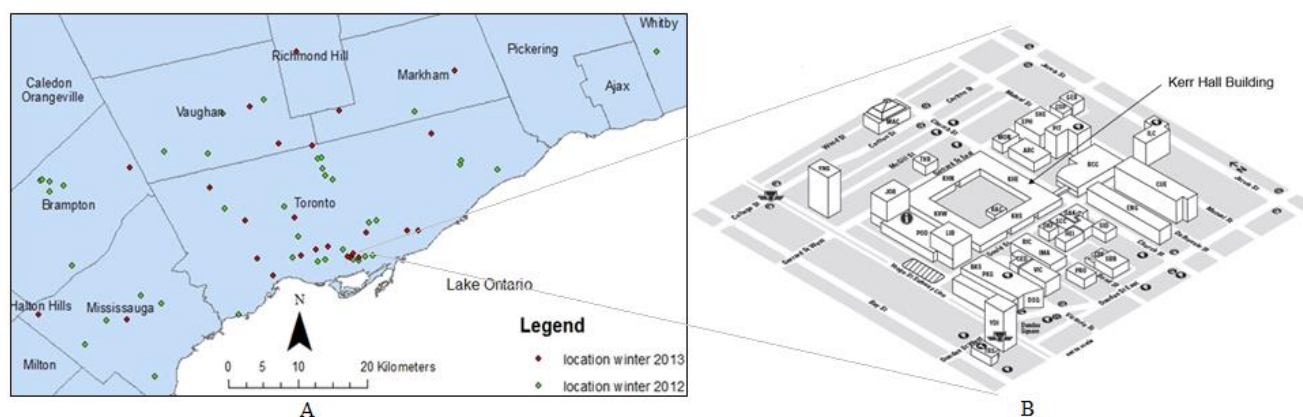


Fig. 1. Sampling locations: (A) residential within the Greater Toronto Area (GTA), Canada. Green and red dots represent sampling locations in the winter of 2012 and 2013, respectively; (B) non-residential in the downtown Toronto.

All dust samples were collected into resealable plastic bags (dimensions: 16.5 cm × 8.25cm) by gently sweeping from different surfaces, such as fans, bookshelves, window sills,

cabinets, refrigerators, projector screens, and fume hoods (Fig. 2). The samples were then double bagged and clearly labelled. Powder free gloves were worn during sample collections.



Fig. 2. Sample collection surfaces in the indoor environments.

The dust samples were screened to remove any visible hair, soil, and grit. The samples were then oven-dried at 45°C for 48 hours and homogenized using a mortar and pestle. All the results were reported based on dry weight.

2.2. Cleaning glassware:

All laboratory glassware and plastic containers were initially cleaned with soap, rinsed thoroughly with tap water, then with distilled water followed by Milli-Q water (18.2 MΩ-cm; Barnstead). The containers were filled with 10% HNO₃ (prepared from 67-70% HNO₃; PlasmaPure, SCP Science) for 48 hours to remove any heavy metals contamination. The glassware and plastic containers were then rinsed thoroughly several times and filled with Milli-Q water until use.

Digestion vessels were first filled with soap overnight and then brushed several times with soap, washed thoroughly with tap water, rinsed with distilled water and finally with Milli-Q water. The vessels were filled with 1:1 HCl (prepared from 34-37% HCl, PlasmaPure, SCP Science) for 48 hours, then rinsed with Milli-Q water several times and filled with 1:1 HNO₃ (prepared from 67-70% HNO₃, PlasmaPure, SCP Science) for 48 hours. Finally, the vessels were rinsed several times and filled with Milli-Q water until use.

2.3. Sample analysis:

2.3.1. Sample digestion:

Dust samples were digested in a QLAB Pro microwave digestion system (Questron Technologies Corp., Mississauga, Canada). Approximately 0.15 g of dust sample, 5 mL of 67-70% HNO₃ (PlasmaPure Plus, SCP Science), and 0.5 mL of 47-51% HF (TraceSELECT® for trace analysis, Fluka) were added into each lined digested vessel and digested at room temperature overnight. An additional 5 mL of 67-70% HNO₃ was then added and the vessels were sealed and digested in the microwave according to the USEPA Method 3051A (USEPA 2007). The temperature of each vessel was preheated to 130°C in three minutes. The temperature was then ramped from 130°C to 175°C in two minutes and 30 seconds. Finally the temperature was ramped from 175°C to 180°C in four minutes and 30 seconds. Eight dust samples and one blank were digested in each sample batch. After digestion, half of the solution volume (approximately 5 mL) was evaporated by heating on a hot plate (Fig. 3). Then 2.5 mL of 4% H₃BO₃ (99.999% trace metals basis, Aldrich) was added to complex the remaining HF. The

digestate was made up to 50 mL with Milli-Q water and stored in plastic bottles for analysis using inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and cold vapor atomic fluorescent spectroscopy (CVAFS).



Fig. 3. Setup for acid evaporation using a hot plate

2.3.2. Metal analysis using ICP-AES:

Ba, Cd, Cr, Cu, Mn, Ni, Pb, and Zn were analyzed by ICP-AES (Spectro Analytical Instruments, Model Spectroflame, Type FCPEA83F). Operation conditions of the ICP-AES are shown in Table A-1, the Appendix. Before analysis of dust samples, ICP-AES was calibrated using five multi-element standard solutions. These standard solutions were prepared from individual standard solutions having concentrations of $10000 \mu\text{g mL}^{-1}$ (Ultra Scientific, item numbers: IAA-056, IAA-048, IAA-024, ICP-129, IAA-026, IAA-082, and IAA-030 for Ba, Cd, Cr, Cu, Mn, Ni, Pb, and Zn, respectively). The five multi-element standard solutions were prepared to build up the calibration curves. The first multi-element standard solution contained

0.005 mg L⁻¹ Cd, 0.1 mg L⁻¹ Cr, Cu, Mn, and Ni and 0.3 mg L⁻¹ Ba, Pb, and Zn. The second multi-element standard solution contained 0.01 mg L⁻¹ Cd, 0.2 mg L⁻¹ Cr, Cu, Mn, and Ni, and 0.6 mg L⁻¹ Ba, Pb, and Zn. The third multi-element standard solution contained 0.05 mg L⁻¹ Cd, 1 mg L⁻¹ Cr, Cu, Mn, and Ni, and 3 mg L⁻¹ Ba, Pb, and Zn. The fourth multi-element standard solution contained 0.1 mg L⁻¹ Cd, 2 mg L⁻¹ Cr, Cu, Mn, and Ni, and 6 mg L⁻¹ Ba, Pb, and Zn. The last multi-element standard solution contained 0.15 mg L⁻¹ Cd, 3 mg L⁻¹ Cr, Cu, Mn, Ni, and 9 mg L⁻¹ Ba, Pb, and Zn. Three batches of these multi-element standard solutions were prepared and digested in the same manner as mentioned for the dust samples. The average of the three batches was used to build up the calibration curves and the coefficient of determination (R²) values were ≥ 0.9986 (Fig. 4). The concentrations (mg kg⁻¹) of heavy metals in the dust samples were calculated from the following equation:

$$\text{Sample concentration (dry weight, mg/kg)} = C \times V \times D / W \dots\dots\dots 1$$

where C is the digest concentration (mg L⁻¹), V is the final volume of the digestate (L), D is the dilution factor, and W is the weight of dried sample (kg).

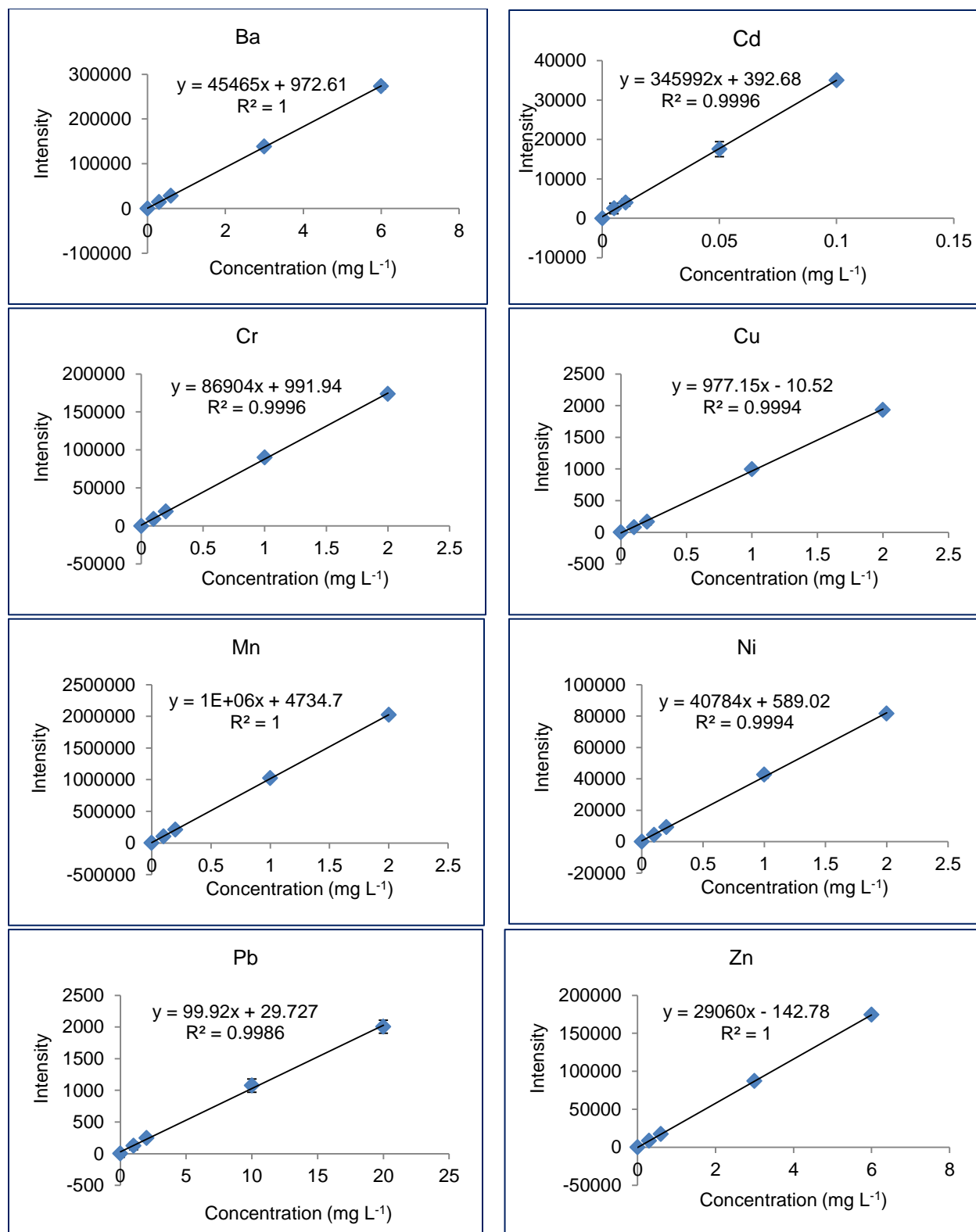


Fig. 4. Calibration curves for heavy metal analysis using ICP-AES.

2.3.3. Hg analysis using CVAFS:

2.3.3.1. Preparation of reagents:

Stannous chloride (SnCl₂): In a 50 mL volumetric flask, 10 g of SnCl₂·2H₂O (ACS reagent, EMD) was dissolved in 5 mL 32-35% HCl (PlasmaPure Plus, SCP Science) and then the volume was brought to the mark using Milli-Q water. The SnCl₂ solution was purged for 1 hour with Hg-free nitrogen (N₂) gas at 500 mL min⁻¹. The solution was prepared fresh monthly and stored in the refrigerator when not in use.

Hydroxylamine hydrochloride (HN₂OH.HCl): 15 g of NH₂OH.HCl (ACS reagent, J.T. Baker) was dissolved in Milli-Q water and brought to 50 mL. This solution was purified by the addition of 50 µL of SnCl₂ and purged for 1 hour with Hg-free N₂ gas at 500 mL min⁻¹. The solution was prepared fresh monthly and stored in the refrigerator when not in use.

Bromine monochloride (BrCl): Inside a fume hood, 1.1 g of KBr (ACS reagent, EM Science) was dissolved in 100 mL of 32-35% HCl. The solution was kept well mixed using a magnetic stir bar for approximately 1 hour. Then 1.5 g of KBrO₃ (ACS reagent, J.T. Baker) was added slowly to the solution while stirring. After all KBrO₃ was added, the container was loosely capped and the solution was stirred for another hour before tightening the lid.

2.3.3.2. Determination of total Hg:

The analysis of total Hg (THg) was based on the USEPA Method 1631B (USEPA 1999) and Appendix to Method 1631 (USEPA 2001). Briefly, 2 mL of the digestate of the dust sample (Section 2.3.1) was added to a bubbler containing 100 mL of Milli-Q water and 0.5 mL of BrCl

solution. After 1 hour, the excess of BrCl was removed by addition of 0.25 mL of $\text{NH}_2\text{OH}\cdot\text{HCl}$. After 5 minutes, 0.5 mL of SnCl_2 solution was added to reduce Hg^{2+} into elemental Hg (Hg^0). The reduced Hg was then purged with Hg-free N_2 gas at 350 mL min^{-1} for 20 minutes and collected onto a gold trap (Fig. 5).

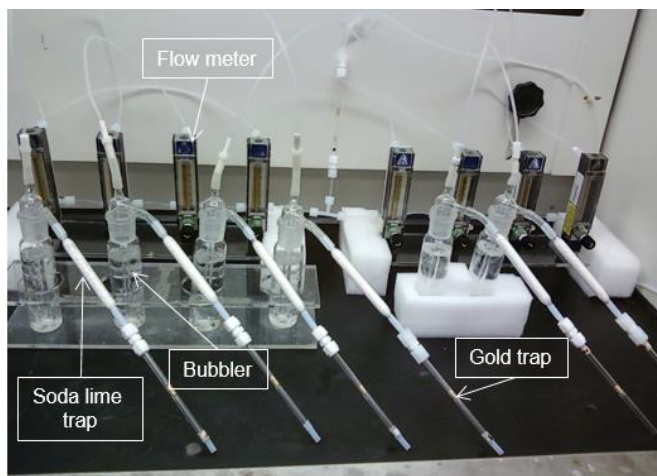


Fig. 5. Bubbler setup for purging and trapping of the Hg^0 .

The gold trap (i.e., the sample trap) then was heated up to 450°C for three minutes in a stream of argon (Ar) gas to desorb the Hg from the sample trap onto another gold trap (i.e., the analytical trap). Finally, the analytical trap (Fig. 6) was heated up to 450°C for three minutes and the released Hg was fed into CVAFS (Brooks Rand LTD., Seattle Washington, USA) for detection and quantification. The Mercury Guru 2.2 software was used to integrate the peak area of the detected signals.

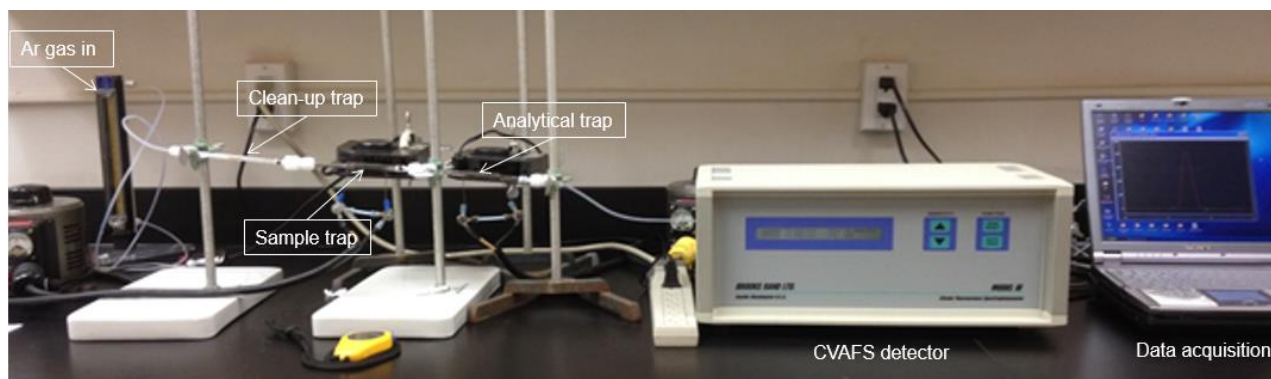


Fig. 6. Apparatus setup for CVAFS analysis of the THg.

Five non-zero points and the results of analysis of three bubbler blanks were used for the calibration. The standard solutions were prepared from the stock Hg standard $10000 \mu\text{g mL}^{-1}$ (ICP-180, Ultra Scientific). The concentrations of the first, second, third, fourth, and fifth standard solutions were 0.5 ng L^{-1} , 5.0 ng L^{-1} , 25 ng L^{-1} , 50 ng L^{-1} , and 100 ng L^{-1} , respectively. The standard solutions were digested and analyzed. The calibration factor (CF_x) for Hg in each of the five standards was calculated using the following equation:

$$\text{CF}_x = (A_x - A_B) / C_x \dots\dots\dots 2$$

where A_x is the peak area for Hg in the standard, A_B is the mean peak area for Hg in the bubbler blanks, and C_x is the concentration of the standard analyzed (ng L^{-1}). Then the mean calibration factor (CF_m), the standard deviation of the calibration factor (SD), and the relative standard deviation (RSD) of the calibration factor ($\text{RSD} = 100 \times \text{SD} / \text{CF}_m$) were calculated. The RSD of the calibration factor was 12% and the average of the percent recoveries of the lowest standard was 77%, which were in the EPA recommended range (i.e., RSD is $\leq 15\%$ and the recovery of the lowest standard is 75-125%) stated in the USEPA Method 1631 and Appendix to Method

1631 (Table A-2, the Appendix). To calculate the concentration of Hg in dust samples, equation 3 below was used.

$$C_{\text{Hg}} = (A_s - A_B) \times V \times 0.1 / (CF_m \times v \times w) \dots\dots\dots 3$$

where C_{Hg} is the concentration of Hg in the dust sample (ng g^{-1} , dry weight), A_s is the peak area for Hg in the digestate, A_B is the peak area for the average of the bubbler blanks, V is the volume of the digestate (mL), which was 50 mL, 0.1 is the volume in the bubbler (L), CF_m is the mean value of the calibration factors from the calibration, v is the digestate volume analyzed (mL), and w is the dry sample weight (g).

2.4. Quality control (QC):

2.4.1. Blanks:

Method blanks were used to evaluate external metal concentration introduced by analytical procedures. Before sample analysis, 30 blanks were digested and analyzed and the results are shown in Fig. A-1, the Appendix. During the sample analysis by ICP-AES and CVAFS, one method blank was included in each sample batch (up to eight samples). All blanks were digested and analyzed using the same analytical procedures but without dust samples. The concentrations of metals in the samples were calculated after blank correction.

2.4.2. Method detection limit:

Thirty blanks were digested and analyzed by ICP-AES to calculate the method detection limit (MDL) at the respective wavelengths selected for each metal. The standard deviation (SD) of the blanks was used to calculate the MDL using equation 4 according to the USEPA method “40 CFR Part 136, Appendix B”.

$$\text{MDL} = t \times \text{SD} \dots\dots\dots 4$$

where t is the Student’s t value at a 99% confidence level and SD is the standard deviation of the replicates. The Student’s t value was 2.46 at a 99% confidence level for 29 degrees of freedom ($n-1$). The method detection limits were calculated to be 5.75 mg kg⁻¹ for Ba, 0.42 mg kg⁻¹ for Cd, 0.74 mg kg⁻¹ for Cr, 28.3 mg kg⁻¹ for Cu, 0.13 mg kg⁻¹ for Mn, 1.44 mg kg⁻¹ for Ni, 13.0 mg kg⁻¹ for Pb, and 2.59 mg kg⁻¹ for Zn.

To calculate the method detection limit of Hg, seven replicates having concentration of 2.5 ng L⁻¹ were digested and analyzed using CVAFS. The standard deviation of the seven replicates was used to calculate the MDL using the equation 4. The Student’s t value was 3.14 at a 99% confidence level for 6 degrees of freedom ($n-1$). The MDL of Hg was calculated to be 0.49 ng g⁻¹ (0.00049 mg kg⁻¹; Table A-3, the Appendix).

2.4.3. Method validation:

The accuracy of the methods was evaluated by analysis of a Standard Reference Material (SRM 2584, Trace Element in Indoor Dust) obtained from the National Institute of Standards

and Technology (NIST). The SRM 2584 sample was digested and analyzed (in triplicate) in the same manner as the dust samples. The agreement between the certified values and measured values for each metal was satisfactory (using *t*-test) with the recoveries being between 90% and 103%. The results for the SRM analysis are given in Table 1.

Table 1. Recovery and precision for the determination of metals in SRM 2584 (NIST, Trace Element in Indoor Dust) using ICP-AES.

Element	Measured value (mg kg ⁻¹) ^a	RSD % ^b	Certified value (mg kg ⁻¹)	Recovery % ^c
Cd	10.4 ± 0.5	5	10.0 ± 1.1	104
Cr	121.6 ± 12.8	10	135.0 ± 9.1	90
Hg ^d	4.98 ± 0.24	5	5.20 ± 0.24	96
Pb	10024 ± 263	3	9761 ± 67	103
Zn	2460 ± 77	3	2580 ± 150	95
Ba	1228 ± 31	3	1300	94
Cu	299 ± 14	5	320	93
Mn	360 ± 9	2	370	97
Ni	87 ± 2	2	90	97

^a Measured value is the mean concentration for three replicates ± standard deviation (SD)

^b RSD is the relative standard deviation for three replicate = (SD/ mean) × 100

^c Recovery = (measured value/ certified value) × 100

^d Hg was analyzed by CVAFS

In order to determine the analytical precision, a triplicate of the SRM 2584 was analyzed and the RSD was 2-10% (Table 1). Also, nine selected dust samples were analyzed in triplicate and the RSD values were 1-9% for Ba, 2-18% for Cd, 1-5% for Cr, 6-18% for Cu, 2-8% for Hg, 1-9% for Mn, 1-9% for Ni, 2-20% for Pb, and 2-16% for Zn.

The initial precision and recovery (IPR) solution with a concentration of 5 ng L⁻¹ was analyzed to demonstrate the ability of the CVAFS to provide acceptable precision and recovery. The average percent recovery and the RSD for the four replicates of the IPR solution were calculated to be 104% and 4%, respectively (Table A-4, the Appendix). The results met the QC acceptance criteria (i.e., IPR recovery is 75-125% and IPR precision is < 20% RSD) of the USEPA Method 1631B and Appendix to Method 1631.

2.4.4. Calibration Verification:

For ICP-AES analysis, a multi-element standard solution with a concentration of 1.0 mg L⁻¹ for each metal was used prior to and after the analysis of every 20 samples to verify calibration of the instrument. The percent recoveries for each metal were 100-108% for Ba, 107-112% for Cd, 89-99% for Cr, 102-113% for Cu, 92-100% for Mn, 90-100% for Ni, 98-110% for Pb, and 90-96% for Zn. For CVAFS analysis, a standard solution of Hg with a concentration of 40 ng L⁻¹ was used prior to and after the analysis of every eight samples. The percent recovery of this standard solution was calculated to be 98-122%, which was in the EPA range (i.e., 77-123%) according to the USEPA Method 1631B and Appendix to Method 1631.

2.5. Statistical analysis:

The data of metal concentrations in the indoor dusts showed log-normal distributions (Fig. A-2, the Appendix). Therefore, the data were log-transformed prior to performing the statistical tests, including *t*-test, analysis of variance (ANOVA), and Pearson's correlation analysis. The comparison between the mean concentrations of metals in household dusts collected in the winter of 2012 and 2013 was performed using *t*-test (the statistical functions in Microsoft Excel, 2013). Also, the *t*-test was used to compare between the certified values of metal concentrations in the SRM and the observed values. One-way ANOVA (using the Statistical Analysis Software; SAS 10.2) was conducted for multi-comparison among the mean concentrations of the metals in different indoor dusts (i.e., household, office, classroom, and laboratory dusts). The correlations between metal concentrations in each indoor environment were performed by the Pearson's correlation analysis (using the Statistical Package for Social Science; IBM SPSS Statistics 21).

3. RESULTS AND DISCUSSION:

3.1. Heavy metal concentrations in household dusts:

Household settled dusts collected from 67 residences during the winter of 2012 and 2013 within the Greater Toronto Area (GTA) were analyzed for the total content of heavy metals. The concentrations of the metals studied are presented in Table 2. All values were based on dry weight. For household dusts collected in the winter of 2012, Zn showed the highest arithmetic mean concentration (419 mg kg^{-1}) followed by Cu (156 mg kg^{-1}), Ba (102 mg kg^{-1}), Pb (87.6 mg kg^{-1}), Mn (63.9 mg kg^{-1}), Cr (52.7 mg kg^{-1}), Ni (27.6 mg kg^{-1}), Cd (4.01 mg kg^{-1}), and Hg (0.66 mg kg^{-1} ; Table 2). Zn concentration (1345 mg kg^{-1}) was also the highest in household dusts collected in the winter of 2013 followed by Cu (248 mg kg^{-1}), Mn (136 mg kg^{-1}), Ba (111 mg kg^{-1}), Cr (109 mg kg^{-1}), Pb (83.8 mg kg^{-1}), Ni (38.4 mg kg^{-1}), Cd (2.88 mg kg^{-1}), and Hg (1.01 mg kg^{-1} ; Table 2). For all results (winter of 2012 and 2013), the same trend was observed in which Zn was the highest concentration (778 mg kg^{-1}) followed by Cu (191 mg kg^{-1}), Ba (106 mg kg^{-1}), Mn (92.1 mg kg^{-1}), Pb (86.3 mg kg^{-1}), Cr (74.7 mg kg^{-1}), Ni (31.8 mg kg^{-1}), Cd (3.73 mg kg^{-1}), and Hg (0.80 mg kg^{-1} ; Table 2). The *t* test was performed to compare the metal concentrations in household dusts collected in the winter of 2012 and 2013. The results showed that there were statistically no significant differences ($p < 0.05$) between metal concentrations in household dusts collected in the winter of 2012 and 2013 except that Mn and Zn concentrations were significantly higher ($p < 0.05$) in the winter of 2013 than those in the winter of 2012 (Fig. 7).

Table 2. Total metal concentrations (mg kg⁻¹, dry weight) in the household dust samples collected in GTA, Canada.

Sampling Period		Ba	Cd	Cr	Cu	Hg	Mn	Ni	Pb	Zn
Winter 2012 (<i>n</i> = 41)	AM	102	4.01	52.7	156	0.66	63.9	27.6	87.6	419
	SD	111	9.49	50.4	119	1.29	43.8	17.5	186	308
	GM	65.0	2.03	42.8	122	0.33	49.0	22.8	38.3	327
	Median	68.8	1.69	40.6	125	0.37	58.4	22.6	36.9	359
	Min	1.52	0.23	8.90	21.8	0.01	5.57	5.04	3.09	67.9
	Max	525	60.3	336	642	8.02	168	78.2	1141	1345
Winter 2013 (<i>n</i> = 26)	AM	111	2.88	109	248	1.01	136	38.4	83.8	1345
	SD	118	3.18	284	263	1.93	207	52.9	138	2989
	GM	61.9	1.47	51.8	175	0.51	77.8	21.7	36.8	569
	Median	72.1	1.61	43.6	159	0.46	78.6	24.3	35.3	480
	Min	1.81	0.10	9.46	23.8	0.07	7.81	2.59	5.18	115
	Max	462	10.9	1490	1249	10.1	1076	261	622	14684
All results (<i>n</i> = 67)	AM	106	3.73	74.7	191	0.80	92.1	31.8	86.3	778
	SD	113	8.37	181	190	1.57	137	35.7	169	1910
	GM	63.7	1.87	46.1	140	0.39	58.6	22.4	37.8	405
	Median	71.4	1.67	42.5	136	0.39	58.5	23.0	36.1	386
	Min	1.52	0.10	8.90	21.8	0.01	5.57	2.59	3.09	67.9
	Max	525	60.3	1490	1249	10.1	1076	261	1141	14684
Canadian Soil Guideline ^a		500	10	64	63	6.6	N/A	50	140	200

AM = arithmetic mean; SD = standard deviation; GM = geometric mean; Min = minimum value; Max = maximum value; N/A = not available.

^a Canadian Soil Quality Guideline (residential/ parkland) obtained from Canadian Council of Ministers of the Environment (CCME 2014).

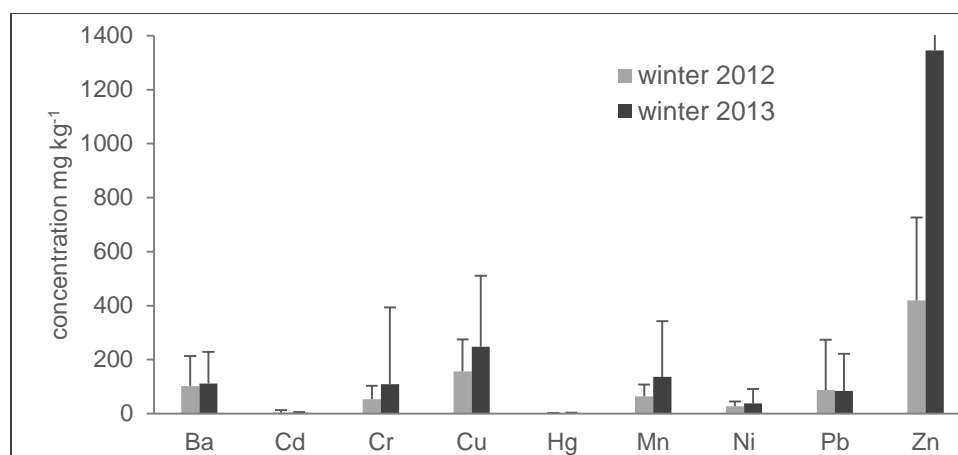


Fig. 7. Comparison of the arithmetic mean concentrations of metals in the household dusts collected in the winter of 2012 and 2013.

To the best of our knowledge, there are no guidelines for heavy metals in dusts. Therefore, in several studies heavy metal concentrations in dusts have been compared with soil guidelines for metals (Hassan 2012; Kurt-Karakus 2012; Kefeni and Okonkov 2013; Lu et al. 2014). The Canadian Soil Guideline (residential/ parkland) provided by Canadian Council of Ministers of the Environment (CCME) was used for comparison purposes. The CCME guideline values (CCME 2014) for metals in soil were listed in Table 2; CCME 2014). Looking at Table 2, it can be seen that Ba (106 mg kg⁻¹), Cd (3.73 mg kg⁻¹), Hg (0.80 mg kg⁻¹), Ni (31.8 mg kg⁻¹), Pb (86.3 mg kg⁻¹) concentrations in household dusts collected in the winter of 2012 and 2013 were lower than the CCME guideline values, whereas Cr (74.7 mg kg⁻¹), Cu (191 mg kg⁻¹), and Zn (778 mg kg⁻¹) concentrations were higher than the acceptable levels in the CCME guideline.

The concentrations of heavy metals were plotted on the GTA map using Geographic Information System (GIS) software (Esri ArcMap 10.2) and the results are depicted in Fig. 8 to Fig. 16. Elevated levels of metal concentrations were observed and most of them located in downtown Toronto, which is characterized by higher density of traffic and population. The

arithmetic mean concentrations of metals in downtown Toronto ($n = 12$) and the other regions of the GTA ($n = 55$) were 161 mg kg^{-1} and 93.2 mg kg^{-1} for Ba, 2.80 mg kg^{-1} and 4.00 mg kg^{-1} for Cd, 78.3 mg kg^{-1} and 73.9 mg kg^{-1} for Cr, 251 mg kg^{-1} and 177 mg kg^{-1} for Cu, 1.47 mg kg^{-1} and 0.65 mg kg^{-1} for Hg, 93.8 mg kg^{-1} and 91.7 mg kg^{-1} for Mn, 29.4 mg kg^{-1} and 32.3 mg kg^{-1} for Ni, 190 mg kg^{-1} and 64.7 mg kg^{-1} for Pb, and 630 mg kg^{-1} and 817 mg kg^{-1} for Zn, respectively.

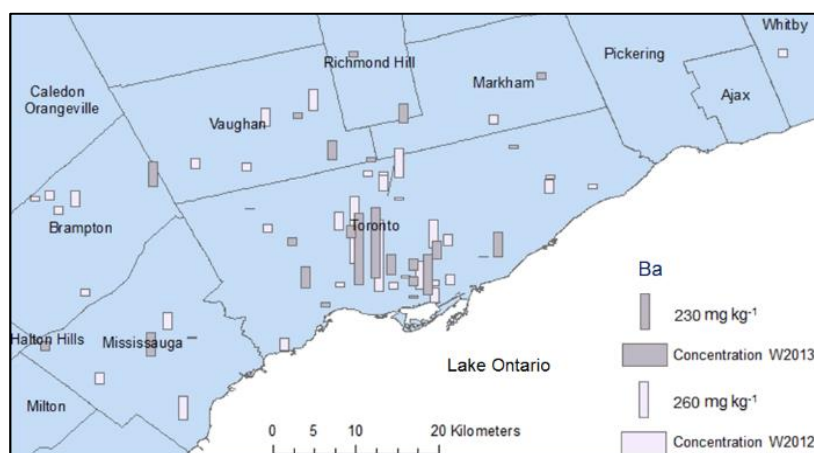


Fig. 8. Geographical distribution of Ba concentrations in the household dusts collected in the winter of 2012 and winter 2013 in GTA, Canada.

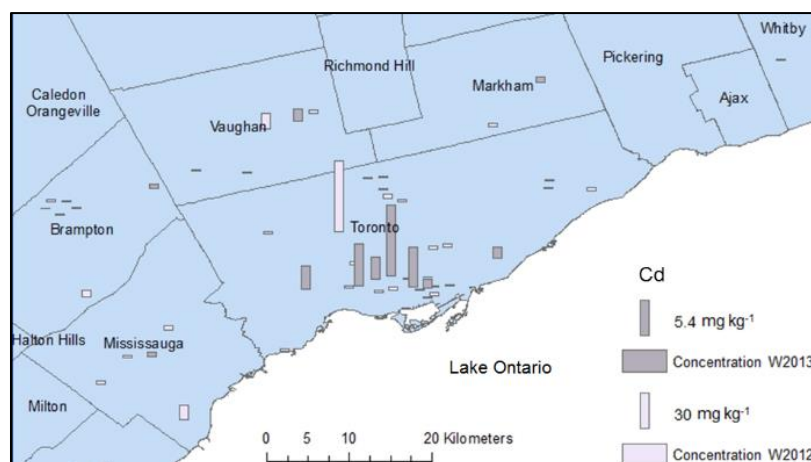


Fig. 9. Geographical distribution of Cd concentrations in the household dusts collected in the winter of 2012 and winter 2013 in GTA, Canada.

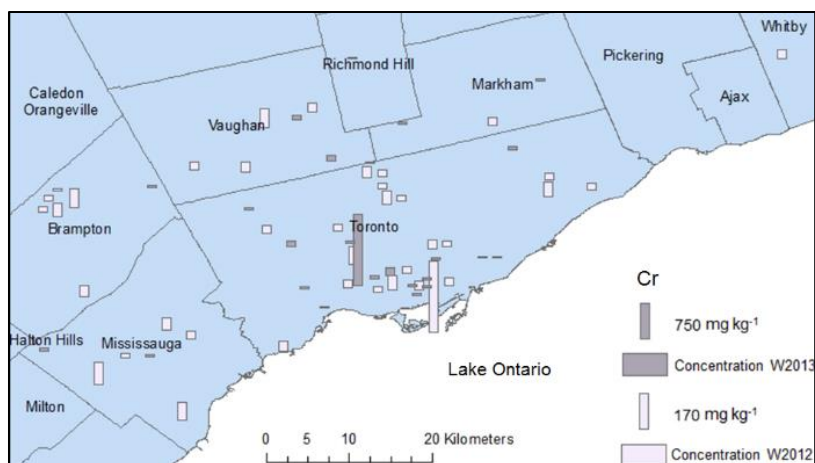


Fig. 10. Geographical distribution of Cr concentrations in the household dusts collected in the winter of 2012 and winter 2013 in GTA, Canada.

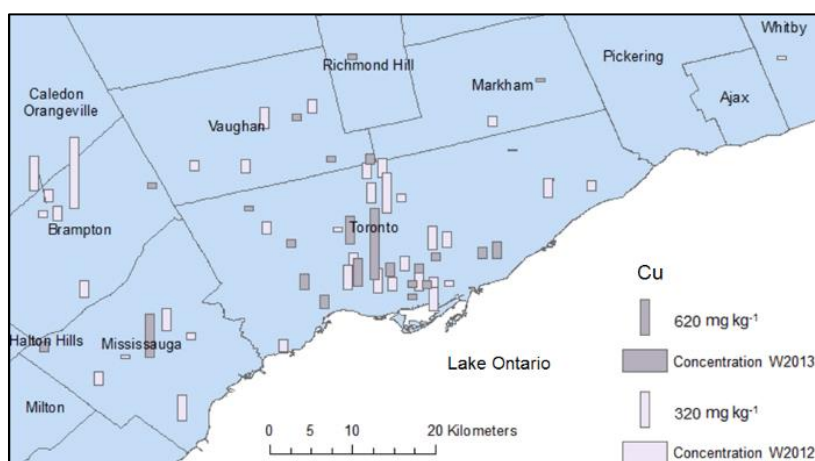


Fig. 11. Geographical distribution of Cu concentrations in the household dusts collected in the winter of 2012 and winter 2013 in GTA, Canada.

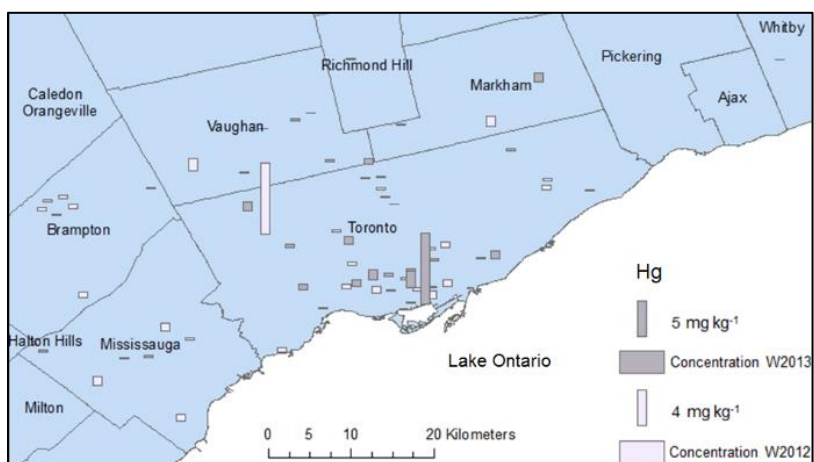


Fig. 12. Geographical distribution of Hg concentrations in the household dusts collected in the winter of 2012 and winter 2013 in GTA, Canada.

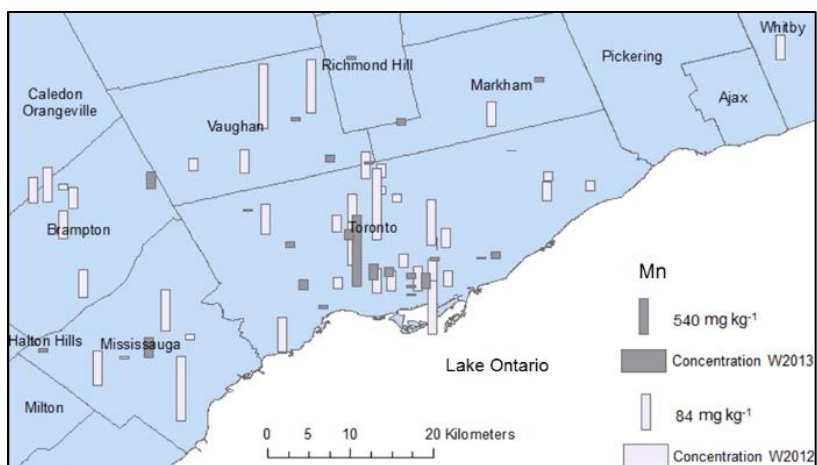


Fig. 13. Geographical distribution of Mn concentrations in the household dusts collected in the winter of 2012 and winter 2013 in GTA, Canada.

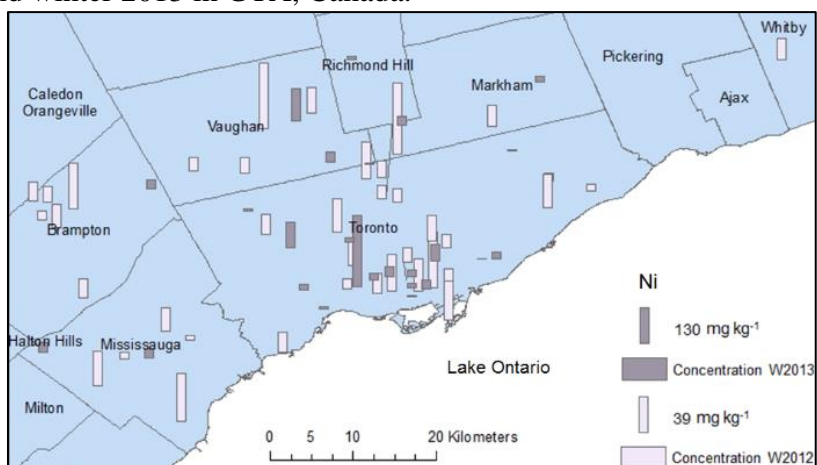


Fig. 14. Geographical distribution of Ni concentrations in the household dusts collected in the winter of 2012 and winter 2013 in GTA, Canada.

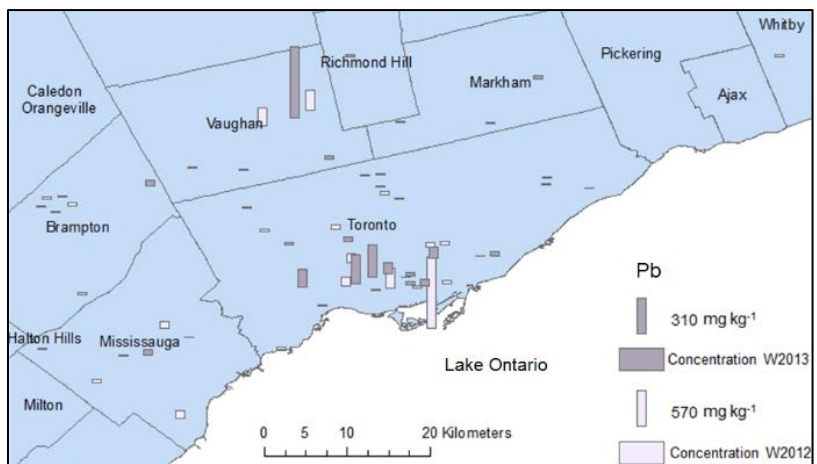


Fig. 15. Geographical distribution of Pb concentrations in the household dusts collected in the winter of 2012 and winter 2013 in GTA, Canada.

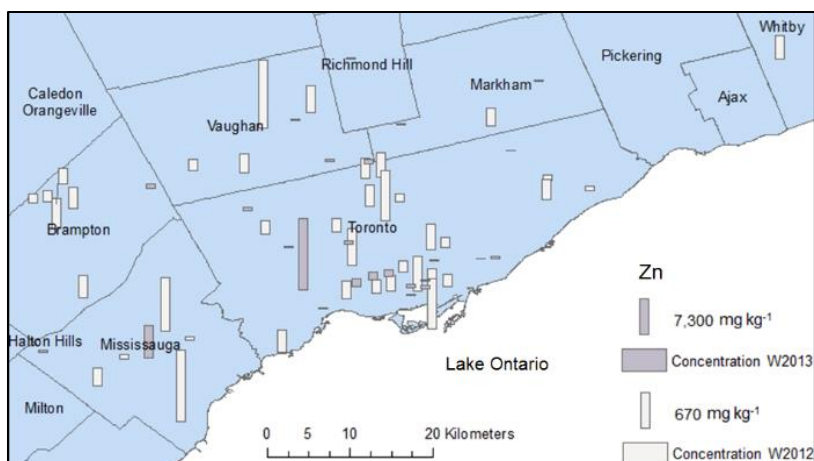


Fig. 16. Geographical distribution of Zn concentrations in the household dusts collected in the winter of 2012 and winter 2013 in GTA, Canada.

Figure 17 shows the comparison between the metal concentrations in downtown Toronto and the other regions of the GTA. Except Pb, there were statistically no differences between metal concentrations in downtown Toronto and the other regions of the GTA. The Pb concentration in household dusts in downtown Toronto was significantly higher ($p < 0.05$) than the concentration in the other regions of the GTA. This could be attributed to the accumulation of Pb from the use of leaded gasoline and leaded paints in the past (Chattopadhyay et al. 2003; Charlesworth et al. 2011).

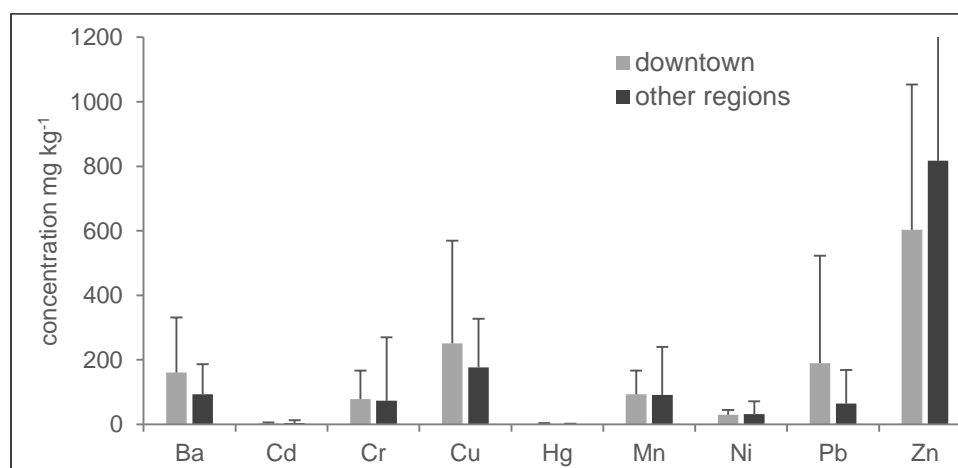


Fig. 17. Comparison of the arithmetic mean concentrations of metals in the household dusts from downtown Toronto and the other regions of GTA, Canada.

3.2. Heavy metal concentrations in office, classroom, and laboratory dusts:

The concentrations of Ba, Cd, Cr, Cu, Hg, Mn, Ni, Pb, and Zn in settled dusts collected from offices ($n = 11$), classrooms ($n = 11$), and laboratories ($n = 15$) from the Kerr Hall building at Ryerson University located in the core of downtown Toronto (Fig. 1) are listed in Table 3. The results showed that the metal concentrations in the laboratory dusts were relatively higher than those in the office and classroom dusts. Amongst the heavy metals studied, Zn showed the highest concentrations and Hg showed the lowest concentrations in all indoor dusts (i.e., the office, classroom, and laboratory dusts). The arithmetic mean concentration of Zn in laboratory dusts was 3198 mg kg^{-1} , followed by Cu (631 mg kg^{-1}), Mn (224 mg kg^{-1}), Ni (170 mg kg^{-1}), Ba (154 mg kg^{-1}), Cr (145 mg kg^{-1}), Pb (137 mg kg^{-1}), Cd (25.3 mg kg^{-1}), and Hg (3.55 mg kg^{-1} ; Table 3). In office dusts, the Zn concentration was 1912 mg kg^{-1} , followed by Cu (258 mg kg^{-1}), Ba (99.4 mg kg^{-1}), Mn (98.9 mg kg^{-1}), Pb (76.9 mg kg^{-1}), Cr (63.6 mg kg^{-1}), Ni (42.3 mg kg^{-1}), Cd (6.94 mg kg^{-1}), and Hg (0.94 mg kg^{-1} ; Table 3). The concentration of heavy metals in the classroom dusts followed the sequence of Zn (1353 mg kg^{-1}), Cu (246 mg kg^{-1}), Mn (225 mg kg^{-1}), Ba (121 mg kg^{-1}), Cr (52.3 mg kg^{-1}), Pb (49.0 mg kg^{-1}), Ni (47.3 mg kg^{-1}), Cd (2.47 mg kg^{-1}), and Hg (0.62 mg kg^{-1} ; Table 3). The concentrations of Cd, Cr, Cu, Ni, and Zn in the laboratory dusts were higher than the CCME guideline values, whereas Ba, Hg and Pb concentrations were lower than the guideline values specified by CCME (Table 3). The Cu and Zn concentrations in the office and classroom dusts were higher than the CCME guideline levels and the rest of the metals (i.e., Ba, Cd, Cr, Hg, Ni, and Pb) were below the CCME guideline values (Table 3).

Table 3. Total metal concentrations (mg kg⁻¹, dry weight) in the dust samples collected from offices, classrooms, and laboratories in GTA, Canada.

Sampling Location		Ba	Cd	Cr	Cu	Hg	Mn	Ni	Pb	Zn
Office (<i>n</i> = 11)	AM	99.4	6.94	63.6	258	0.94	98.9	42.3	76.9	1912
	SD	44.9	6.82	12.0	113	0.46	39.5	12.5	63.8	1781
	GM	89.9	3.63	62.5	237	0.85	91.2	40.4	57.8	1467
	Median	94.2	5.14	67.0	213	0.87	109	39.5	59.1	1126
	Min	41.1	0.13	44.5	123	0.42	43.1	20.8	16.6	698
	Max	184	19.1	80.3	460	1.94	159	58.1	229	6634
Classroom (<i>n</i> = 11)	AM	121	2.47	52.3	246	0.62	225	47.3	49.0	1353
	SD	91.2	1.69	29.4	160	0.32	44.4	10.4	32.9	885
	GM	86.7	1.88	45.3	203	0.47	221	46.3	38.5	1116
	Median	101	2.47	38.7	188	0.69	224	47.3	40.8	890
	Min	10.5	0.50	18.2	61.9	0.04	174	30.9	11.1	412
	Max	312	5.31	97.5	518	1.01	335	67.6	116	3058
Laboratory (<i>n</i> = 15)	AM	154	25.3	145	631	3.55	224	170	137	3198
	SD	43.2	45.6	136	386	3.01	86.0	103	109	1766
	GM	148	11.0	110	539	2.35	209	143	103	2768
	Median	152	11.9	86.9	411	2.62	216	146	86.0	3571
	Min	84.3	0.65	44.1	223	0.31	117	40.7	22.8	1084
	Max	266	185	513	1392	9.68	390	443	350	7887
Canadian Soil Guideline ^a		500	10	64	63	6.6	N/A	50	140	200

AM = arithmetic mean; SD = standard deviation; GM = geometric mean; Min = minimum value; Max = maximum value; N/A = not available.

^a Canadian Soil Quality Guideline (residential/ parkland) obtained from Canadian Council of Ministers of the Environment (CCME 2014).

3.3. Comparison of the results from different indoor environments:

Figure 18 shows the comparison of metal concentrations in household, office, classroom, and laboratory dusts. In general, the highest levels of metal concentrations were observed in laboratory dusts. This could be attributed to the presence of metallic particles originated from various laboratory equipment and practices, such as chemical reagents, worn metallic constructions, plated, and galvanized surfaces. Cd, Cr, Cu, Hg, and Ni concentrations in laboratory dusts were significantly higher ($p < 0.05$) than the corresponding concentrations in household, office, and classroom dusts. Ba and Pb concentrations in household, office, classroom, and laboratory dusts were statistically comparable. Mn concentrations in laboratory and classroom dusts were comparable and they were significantly higher ($p < 0.05$) than the Mn concentration in household and office dusts. Zn concentrations in the laboratory, office, and classroom dusts were comparable and they were higher ($p < 0.05$) than the concentrations in household dusts. On the other hand, the Pb level in household dusts collected in downtown Toronto was relatively higher than the Pb levels in indoor dusts collected from the offices, classrooms, and laboratories (Fig. 18).

In general, metal concentrations in household dusts were lower than those in the laboratory dusts, but they, except Mn and Zn, were comparable with those in the office and classroom dusts. The Mn concentrations in the classroom dusts were significantly higher ($p < 0.05$) than the concentrations in household dusts, and Zn concentrations in the office and classroom dusts were higher ($p < 0.05$) than the corresponding values in household dusts (Fig. 18).

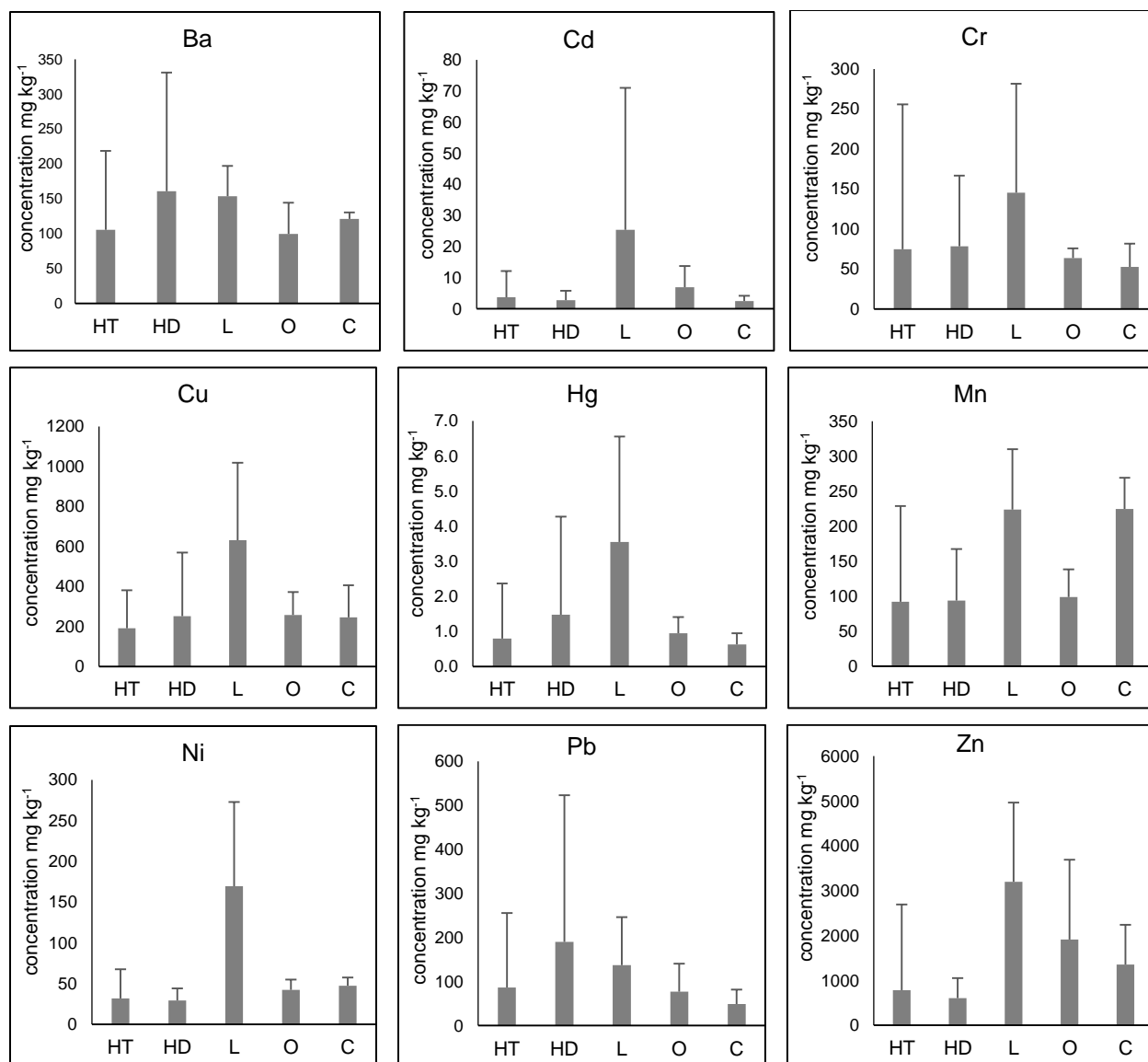


Fig. 18. Comparison of the arithmetic mean concentrations of metals in indoor settled dusts collected from different indoor environments: HT = House Total; HD = House Downtown; L = Laboratory; O = Office; C = Classroom.

3.4. Comparison of the results observed in this study with literature values:

The concentrations of heavy metals found in the present study with those reported in different cities around the world are compared in Table 4. The Ba concentrations in household dusts in Toronto were lower than the values reported for Ottawa, Canada (Rasmussen et al. 2001) and Dharan, S. Arabia (Turner and Hefzi 2010), but they were higher than those in Amman, Jordan (Al-Momani 2007). The Cr and Pb levels in household dusts in Toronto were lower compared with the levels reported for Sydney, Australia (Chattopadyay et al. 2003), Pretoria, South Africa (Kefeni and Okonkwo 2013), Amman, and Ottawa. Whereas, the Cr and Pb levels in Toronto were higher than those for Istanbul, Turkey (Kurt-Karakus 2012) and Dharan. Lower Cd concentrations were observed in household dusts in Toronto compared with those found in Amman, Sydney, and Ottawa whereas the Cd level in Toronto was higher than Istanbul, Pretoria, and Dharan. Elevation of Cu in household dusts was found in the present study when compared with Amman, Sydney, Istanbul, Pretoria, and Dharan and lower when compared to Ottawa.

Limited data were available in literature about Hg concentrations in household dusts. However, the concentrations found in Toronto were lower than those in Ottawa and higher than Dharan (Table 4). Mn levels in Toronto were lower than the levels reported for Amman, Ottawa, Istanbul, Pretoria, and Dharan, but higher than those found for Sydney. Ni concentrations were lower compared with the concentrations reported for Amman, Ottawa, Istanbul, and Pretoria and higher compared with Sydney and Dharan. The Zn concentrations found from this study were lower than Amman and Istanbul, but higher than Ottawa, Sydney, Pretoria, and Dharan. On the other hand, the concentrations of heavy metals in office dusts in Toronto were lower than those reported for Istanbul and Pretoria except Cd and Zn. Cd concentrations were higher than Istanbul

and Pretoria while Zn concentrations were higher than those found for Pretoria (Table 4). In general, the concentrations of heavy metals in indoor dusts in Toronto were in the range of the values reported in literature for a number of locations worldwide.

Table 4. Comparison of the arithmetic mean concentrations (mg kg^{-1}) of heavy metals in indoor dusts presented in this study with those reported in literature.

Location	<i>n</i>	Sampling method	Source	Ba	Cd	Cr	Cu	Hg	Mn	Ni	Pb	Zn	Reference
Toronto, Canada	67	Gentle sweeping	House	106	3.73	74.7	191	0.80	92.1	31.8	86.3	778	This study
Toronto, Canada	11	Gentle sweeping	Office	99.4	6.94	63.6	258	0.94	98.9	42.3	76.9	1912	This study
Toronto, Canada	11	Gentle sweeping	Class	121	2.47	52.3	246	0.62	225	47.3	49.0	1353	This study
Toronto, Canada	15	Gentle sweeping	Lab	154	25.3	145	631	3.55	224	170	137	3198	This study
Amman, Jordan	20	Vacuum cleaner	House	85	4.46	77	160	...	284	47	206	3104	Al-Momani 2007
Sydney, Australia	82	Vacuum cleaner	House	...	4.4	83.6	147	...	76.1	27.2	389	657	Chattopadhyay 2003
Ottawa, Canada	50	Vacuum cleaner	House	492	6.46	86.7	206	3.63	269	62.9	406	716	Rasmussen et al. 2001
Istanbul, Turkey ^a	8	Vacuum cleaner	Office	...	1.8	254	513	...	655	471	192	1970	Kurt-Karakus 2012
Istanbul, Turkey ^a	31	Vacuum cleaner	House	...	0.80	55	156	...	136	263	28	832	Kurt-Karakus 2012
Pretoria, South Africa	6	Vacuum cleaner	Office	...	2.53	160	2740	...	772	69.8	126	1300	Kefeni and Okonkwo 2013
Pretoria, South Africa	8	Vacuum cleaner	House	...	1.47	109	186	...	457	59.5	110	669	Kefeni and Okonkwo 2013
Dharan, S. Arabia	9	Vacuum cleaner	House	426	1.51	37	91.1	0.20	121	26.1	35.5	396	Turner and Hefzi 2010

^a Median values are reported.

3.5. Heavy metal correlations:

Correlations between heavy metals could be a useful tool to get some information on the sources of metals in indoor environments (Manta et al. 2002; Hassan 2012). The Pearson's correlation coefficients (r) between heavy metals in household dusts are given in Table 5. No significant correlations were observed between Hg and other metals, which may indicate different sources of Hg from other metals. Strong correlations were found between Ba and Mn ($r = 0.79, p < 0.01$), Mn and Ni ($r = 0.71, p < 0.01$), and Mn and Zn ($r = 0.72, p < 0.01$). The strong correlations may imply common sources of these metals. Moderate correlations ($r = 0.5 - 0.6$) were found between the following pairs of metals: Ba - Ni, Ba - Pb, Ba - Zn, Cd - Pb, Cr - Mn, Cr - Pb, Cu - Mn, Cu - Zn, Mn - Pb, Ni - Pb, and Pb - Zn (Table 5). These pairs of metals may partially share similar sources. Weak correlations ($r < 0.5$) between Ba and Cd, Ba and Cr, Ba and Cu, Cd and Cr, Cd and Cu, Cd and Mn, Cd and Ni, Cr and Cu, Cr and Zn, Cu and Ni, Cu and Pb, and Ni and Zn (Table 5) may suggest different sources of these metals (Yaghi and Abdu-Wahab 2004, Al-Momani 2007).

Correlations between metals for office dusts are shown in Table 6. Strong correlations were found between Mn and the following metals: Ba ($r = 0.84, p < 0.01$), Cd ($r = 0.72, p < 0.05$), and Cu ($r = 0.82, p < 0.01$). Also, a strong correlation was observed between Pb and Cd ($r = 0.79, p < 0.01$). Moderate correlations ($r \sim 0.6, p < 0.05$) were found among Ba, Cu, and Ni (Table 6).

Table 5. Inter-metal correlations for the household dusts.

	Ba	Cd	Cr	Cu	Hg	Mn	Ni	Pb	Zn
Ba	1								
Cd	0.38**	1							
Cr	0.47**	0.30*	1						
Cu	0.45**	0.13	0.28*	1					
Hg	0.15	0.08	0.12	0.29*	1				
Mn	0.79**	0.27*	0.58*	0.56**	0.17	1			
Ni	0.63**	0.38**	0.67**	0.35**	0.05	0.71**	1		
Pb	0.58**	0.59**	0.57**	0.37**	0.06	0.61**	0.66**	1	
Zn	0.56**	0.29*	0.44**	0.58**	0.18	0.72**	0.47**	0.57**	1

* Correlation is significant at $p < 0.05$

** Correlation is significant at $p < 0.01$

Table 6. Inter-metal correlations for the office dusts.

	Ba	Cd	Cr	Cu	Hg	Mn	Ni	Pb	Zn
Ba	1								
Cd	0.53	1							
Cr	-0.20	-0.26	1						
Cu	0.64*	0.57	-0.11	1					
Hg	0.06	0.43	-0.35	-0.27	1				
Mn	0.84**	0.72*	-0.14	0.82**	-0.08	1			
Ni	0.61*	0.33	-0.55	0.60*	0.09	0.52	1		
Pb	0.32	0.79**	-0.06	0.12	0.55	0.43	0.10	1	
Zn	0.15	0.62*	0.00	0.28	0.46	0.42	-0.12	0.40	1

* Correlation is significant at $p < 0.05$

** Correlation is significant at $p < 0.01$

Table 7 shows the correlations between heavy metals for the laboratory dusts. Strong correlation was found between Cd and Pb ($r = 0.88$, $p < 0.01$), which was approximately the same correlation observed for the office dusts. Moderate correlations were found between Ba and Mn ($r = 0.55$, $p < 0.05$), Cd and Hg ($r = 0.58$, $p < 0.05$), Cr and Ni ($r = 0.68$, $p < 0.01$), Hg and Pb ($r = 0.69$, $p < 0.01$), and Pb and Zn ($r = 0.55$, $p < 0.05$).

Table 7. Inter-metal correlations for the laboratory dusts.

	Ba	Cd	Cr	Cu	Hg	Mn	Ni	Pb	Zn
Ba	1								
Cd	0.39	1							
Cr	0.03	0.03	1						
Cu	0.24	-0.09	-0.15	1					
Hg	0.12	0.58*	-0.20	0.36	1				
Mn	0.55*	0.40	0.32	-0.27	-0.23	1			
Ni	-0.14	0.37	0.68**	-0.13	0.30	0.13	1		
Pb	0.41	0.88**	-0.12	0.10	0.69**	0.25	0.28	1	
Zn	0.03	0.23	-0.01	0.14	0.30	-0.06	0.20	0.55*	1

* Correlation is significant at $p < 0.05$

** Correlation is significant at $p < 0.01$

The correlations between metals for classroom dusts are given in Table 8. Most of the metals were strongly or moderately correlated with each other. In general, the pattern of the correlations between the metals for various indoor dusts (i.e., household, office, classroom, and laboratory dusts) seems to be different from one indoor environment to another. This might be attributed to a huge number and variety of sources of heavy metals available in indoor dusts.

Table 8. Inter-metal correlations for the classroom dusts.

	Ba	Cd	Cr	Cu	Hg	Mn	Ni	Pb	Zn
Ba	1								
Cd	0.75 ^{**}	1							
Cr	0.76 ^{**}	0.64 [*]	1						
Cu	0.84 ^{**}	0.76 ^{**}	0.82 ^{**}	1					
Hg	0.77 ^{**}	0.60	0.63 [*]	0.90 ^{**}	1				
Mn	0.72 [*]	0.69 [*]	0.59	0.56	0.37	1			
Ni	0.48	0.61 [*]	0.71 [*]	0.56	0.27	0.71 [*]	1		
Pb	0.84 ^{**}	0.87 ^{**}	0.64 [*]	0.80 ^{**}	0.69 [*]	0.78 ^{**}	0.52	1	
Zn	0.85 ^{**}	0.77 ^{**}	0.74 ^{**}	0.91 ^{**}	0.75 ^{**}	0.59	0.55	0.78 ^{**}	1

* Correlation is significant at $p < 0.05$

** Correlation is significant at $p < 0.01$

3.6. Enrichment of measured metals:

Enrichment factors (EF) of heavy metals can provide useful information about the degree of enrichment of the metals in dust samples compared to their abundance in earth's crust (Al-Momani 2007). Moreover, the EF can be used to distinguish between the metals originating from human activities (anthropogenic sources) and those from natural origin (Meza-Figueroa et al. 2007). The EF can be calculated from the following equation (Al-Momani 2007, Lu et al. 2014):

$$EF = (C_x / C_{ref})_{sample} / (C_x / C_{ref})_{crust} \dots\dots\dots 5$$

where C_x is the concentration of the metal of interest and C_{ref} is the concentration of the reference metal for normalization. The data on the average abundances of the metals in the earth's crust reported by Mason and Moore (1982) were used in the present study for the metal concentrations in the crust. Mn was used as a reference metal (Loska et al. 1997; Uduma and

Awagu 2013) assuming that its anthropogenic sources are insignificant. The enrichment factor value close to one indicates natural origin (natural level). Whereas, the EF value greater than 10 is used as an indicator of contamination from anthropogenic sources (Al-Momani 2007; Meza-Figueroa et al. 2007; Lu et al. 2014). The calculated enrichment factors for the metals in household, office, classroom, and laboratory dusts are shown in Table 9. Cd, Cu, Hg, Pb, and Zn in all indoor dusts studied had enrichment factors greater than 10 (Table 9), which indicated that anthropogenic sources were the predominant sources of these metals. Also, the higher EF values may refer to the significant internal sources of these metals (Turner and Simmonds 2006). On the other hand, the EF values of Cr and Ni were, in general, lower than 10, which suggested that these metals partially originated from anthropogenic sources and moderately contaminated by these metals. The natural origin was the main source of Ba in all indoor dusts as its EF value was close to one (Table 9).

Table 9. Enrichment factors for heavy metals in the indoor dust samples.

Location	Ba	Cd	Cr	Cu	Hg	Mn	Ni	Pb	Zn
House	3.1	345	10.2	52.8	170	1	6.1	82.9	128
Office	2.3	268	7.4	46.2	132	1	6.0	52.5	268
Classroom	1.1	36	2.2	16.5	33.1	1	2.7	15.0	79
Laboratory	1.7	554	6.4	59.7	248	1	10.7	49.6	224

Looking at Table 9, it can be seen that the EF values of Cd, Hg, and Zn in household, office, and laboratory dusts were higher than 100, which could be indicative of gross contamination. The EF values of the heavy metals studied in the classroom dusts were less than

the corresponding values in household, office, and laboratory dusts (Table 9). Therefore, the least contamination levels of the heavy metals were in the classroom dusts.

4. CONCLUSIONS:

The present study is the first of its kind in Toronto. It has provided baseline data for metal concentrations in the Toronto household dusts and office, classroom, and laboratory dusts as well. The results showed that no significant differences were observed in the concentrations of metals (except Mn and Zn) in household, office, and classroom dusts. Among the studied indoor dusts, the laboratory dusts exhibited the highest concentrations of the metals under investigation. However, elevated levels of Pb were found in downtown Toronto household dusts compared with the other regions of the GTA household dusts as well as office, classroom, and laboratory dusts. According to the CCME guideline, Cr, Cu and Zn concentrations in household dusts, Cu and Zn in office, classroom dusts and Cd, Cr, Cu, Ni, and Zn in laboratory dusts exceeded the acceptable limits. On the other hand, metal concentrations in indoor dusts were, in general, in the range of the corresponding values reported in literature for a variety of locations worldwide. Different correlation patterns were observed between metal concentrations. This might be attributed to the large number of different anthropogenic sources of the metals in the indoor environments. Based on crustal backgrounds, Cd, Cu, Hg, Pb, and Zn in the indoor dusts were highly enriched (with EF values exceeded 100 for Cd, Hg, and Zn) indicating anthropogenic sources for these metals in the indoor environments. Further detailed investigations are needed to identify the potential sources that contribute to the enrichment of these metals. This study suggest that indoor settled dusts can be used as an indicator for heavy metal pollution in indoor environments.

5. FUTURE WORK:

Besides heavy metals in indoor dusts, metals in exterior dusts and soils should be analyzed and correlated to figure out the impact of external sources of the metals on the indoor dusts. The speciation of metals and their health risks need to be studied. The bioaccessibilities of metals in indoor dusts also should be conducted to obtain default values for risk assessments. Finally, organic pollutants, such as polycyclic aromatic hydrocarbons, which cause cancer, should be included for the future monitoring studies besides the heavy metals.

APPENDIX:

Table A-1. Operation conditions for the ICP-AES analysis of heavy metals in dust samples.

Parameter	Value
RF power	1200 W
Auxiliary gas flow rate	20 mL min ⁻¹
Coolant gas flow rate	40 mL min ⁻¹
Nebulizer gas flow rate	30 mL min ⁻¹
Integration time	10 s
Analyte lines	Ba 455.403 nm, Cd 226.502 nm, Cr 267.716 nm, Cu 654.792 nm, Mn 257.610 nm, Ni 231.604 nm, Pb 168.215 nm, Zn 213.856 nm

Table A-2. Calibration of CVAFS for the determination of total mercury (the average of bubbler blanks = 30602).

	Concentration (ng L ⁻¹)	Peak Area	Net Peak Area	Calibration Factor (CF _x)	Measured Concentration ^a	% Recovery
First Trial	0.5	47056	16454	32908	0.39	78
	5.0	242324	211722	42344	5.0	100
	25.0	1144836	1114234	44569	26.4	105
	50.0	2287323	2256721	45134	53.4	107
	100.0	4531930	4501328	45013	106.5	106
Second Trial	0.50	47558	16956	33912	0.40	80
	5.0	242018	211416	42283	5.0	100
	25.0	1145276	1114674	44587	26.4	105
	50.0	2303936	2273334	45467	53.8	108
	100.0	4499615	4469013	44690	105.7	106
Third Trial	0.50	46156	15554	31108	0.37	74
	5.0	245085	214483	42897	5.1	101
	25.0	1173213	1142611	45704	27.0	108
	50.0	2436701	2406099	48122	56.9	114
	100.0	4568982	4538380	45384	107.3	107
Mean (CF _m)				42275		
SD				5215		
% RSD				12		

^a Measured concentration (ng L⁻¹) = Net peak area/ CF_m.

Table A-3. Method detection limit (MDL) for the CVAFS analysis of THg using seven replicates of 2.5 ng L⁻¹ based on EPA Method 40 CFR 136, Appendix. (CF_m = 42275).

Replicate (2.5 ng L ⁻¹) Number	Net Peak Area	Measured Concentration (ng L ⁻¹)	Measured Concentration (ng g ⁻¹) ^a
1	127191	3.00	1.00
2	128615	3.04	1.01
3	101765	2.41	0.80
4	99580	2.36	0.79
5	114275	2.70	0.90
6	113293	2.68	0.89
7	156803	3.71	1.24
Mean			0.95
SD			0.16
MDL			0.49

^a Measured concentration (ng g⁻¹) = Measured concentration (ng L⁻¹) x volume (L)/ weight (g), where the volume of digestate is 50 mL (0.05 L) and the weight is taken as 0.15 g.

Table A-4. Initial precision and recovery (IPR) for the CVAFS analysis of THg using four replicate of 5 ng L⁻¹ according to the EPA Method 1631B and Appendix to Method 1631. (CF_m = 42275).

Replicate (5 ng L ⁻¹) Number	Net Peak Area	Measured Concentration (ng L ⁻¹)	% Recovery
1	209560	4.96	99
2	219101	5.18	104
3	222279	5.26	105
4	232568	5.50	110
Mean			104
SD			4
% RSD			4

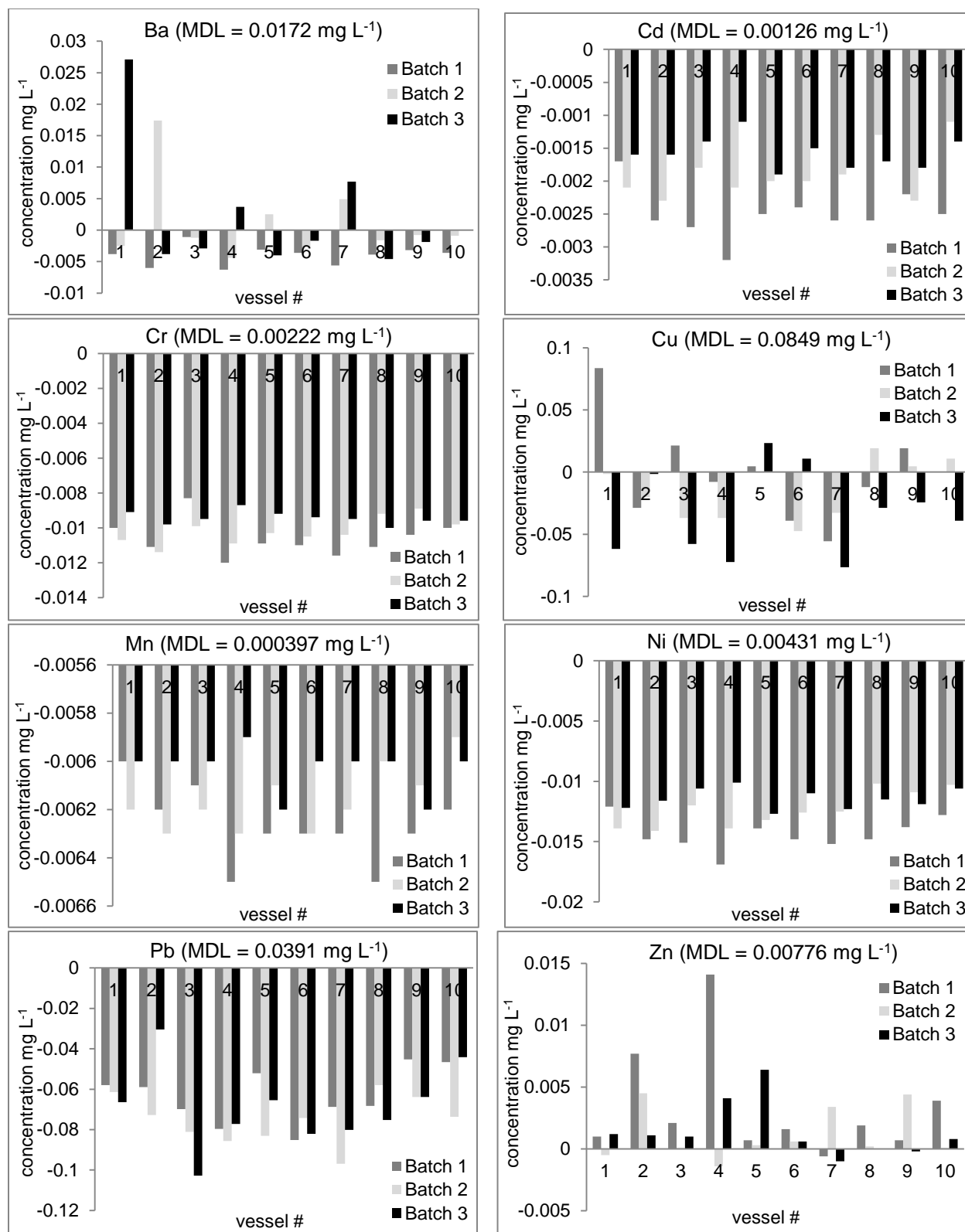


Fig. A-1. Results of the ICP-AES analysis for three batches of blanks (10 blanks for each batch).

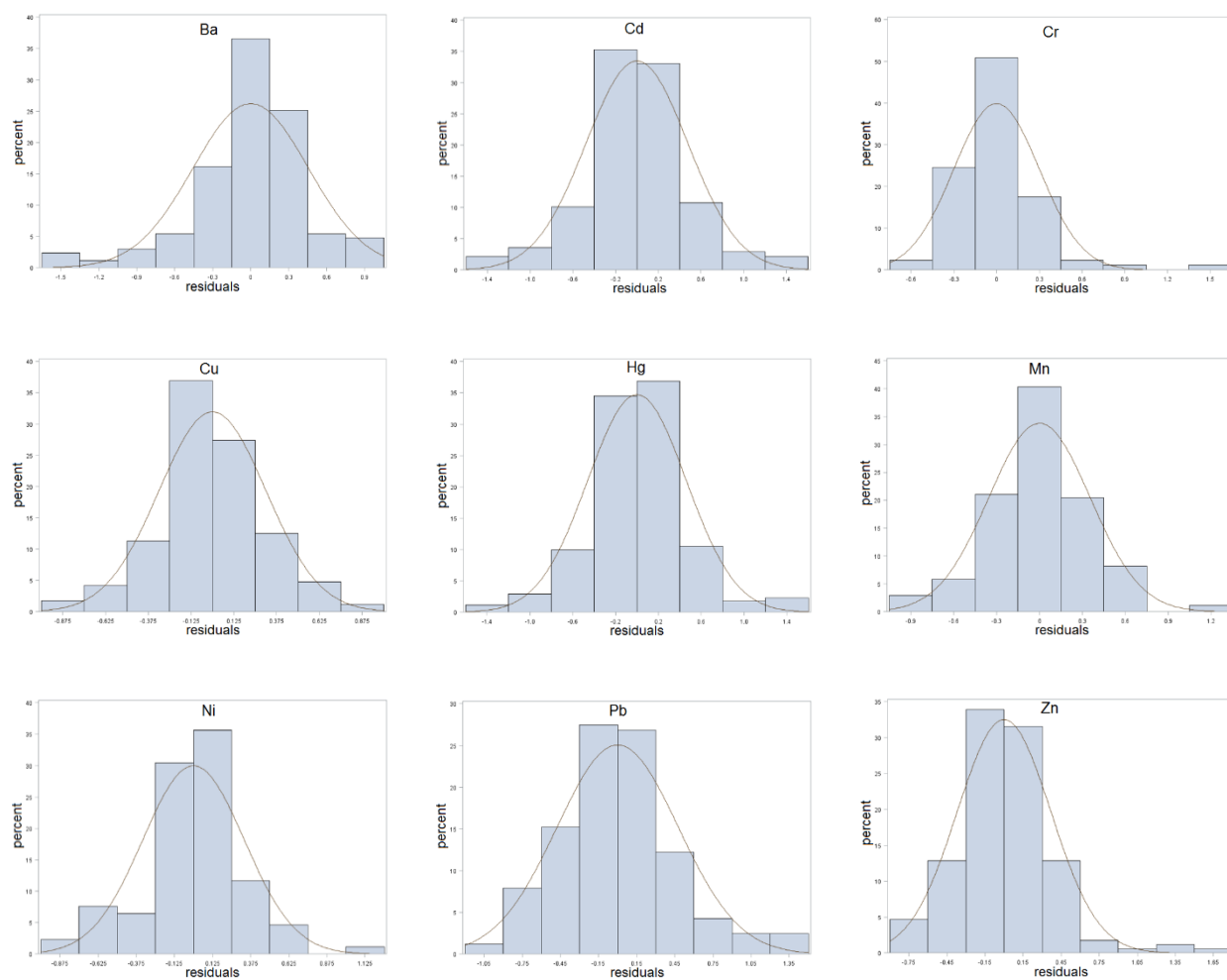


Fig. A-2. Histograms of metal concentrations with normal distribution curves after log transformation

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