AN ELISA STUDY OF AMBIENT AIR DIOXINS IN DOWNTOWN TORONTO

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Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) are a group of persistent, bioaccumulative chemicals that are toxic to both humans and wildlife. Atmosphere is the primary transportation medium, which is ultimately responsible for the wide environmental deposition of dioxins.Dioxins are largely man-made (Srogi, 2008; Mandal, 2005) with many different industries contributing to their release into the environment (CCME, 2004). Toxic effects of exposure to dioxins and furans (referred to herein as dioxins) include wasting syndrome, changes to the immune and reproductive systems, endocrine disruption and chloracne (Schecter et al., 2006; Mandal, 2005; Birnbaum and Tuomisto, 2000).

Human exposures to dioxin could be through dietary intake and air inhalation (Schecter*et al*, 2006). In the human population, nearly 90% of dioxin exposure was a result of consuming dioxin-contaminated meat, water and dairy products (Bilau*et al*, 2007). Besides dietary intake, the second human exposure pathway could be through direct air inhalation, which could account for about 7% of the total intake (Bilau*et al*, 2007). The remainders could be by skin absorption and accidental soil ingestion.

Due to the toxicity of dioxins, their creation and emission into the environment are controlled and monitored with international and national initiatives. Internationally, the Stockholm Convention on persistent organic pollutants has targeted them for reduction or elimination (Stockholm Convention, 2008). In Canada, the major dioxin reduction initiative is the *Canada Wide Standards (CWS) for Dioxins and Furans* (CCME, 2001). Although this initiative has achieved some interim successes, the CWS will have difficulty in reaching its goal of virtually eliminating all Canadian dioxin emissions. In order to reach this goal, increased testing of known and suspected dioxin emitting sources as well as validation of new pollution prevention technologies is recommended (CCME, 2004). An increase in source testing and technology validation will likely rely on gas chromatography-high resolution mass spectroscopy (GC-HRMS) as it has the necessary sensitivity and accuracy. The problem with an increased use of GC-HRMS for dioxin analysis is that it is expensive and time-consuming. As such, there is interest in finding new technologies that can reduce the use of GC-HRMS in instances where its high precision and accuracy are not always required. One such instance is the monitoring of sites for potential air dioxin contamination. If enzyme-linked immunosorbent assay(ELISA) can relieve some of the burden placed on GC-HRMS, GC-HRMS can become more available to help improve the successes of Canadian dioxin initiatives and thus improve the protection of human health and the environment.

Urban ambient air dioxins have undergone an encouraging ~200-fold drop from ~9 pg/m^3 in 1990s to ~40 fg /m^3 in 2000s (Smith *et al*, 1990). However, most of these measurements are intermittent, sporadic and usually not at the same location. Nearly all the monitoring practices were conducted inside U.S. supported by different levels of environmental authorities. In Canada, air dioxin concentrations had only been revealed once in a brief executive summary released by Canadian National Air Pollution Surveillance (NAPS) network in 1998.

In the past 2 decades, only few of the air dioxin samples had been collected from urban centers throughout North America (Hunt *et al*., 1997; Riggs *et al*., 1996). The US EPA tended to determine background level of dioxins in many of the remote and rural areas rather than dedicating itself to provide a clear image of air dioxins level in urban centers, where population are concentrated. Besides, barely any information related to dioxins can be found in the NAPS group's annual report. Is urban air safe to breath with respect to dioxin contamination? This question can only be answered by actually collecting and analyzing some air samples in urban centers. A number of publications on measuring ambient air dioxins level for both urban and rural indicate that populated urban regions are the primary sources of dioxins (Venier et al., 2009). The latest dioxins review article, which appeared 14 years ago (Lohmann& Jones, 1998)surmised that the general trend of dioxin concentrations in ambient air in most urban/industrial areas was estimated to fall within the range of 10-100 pg/m^3 (∑TEQ ~100-400 fg/m^3). On the other hand, many of the monitoring programs were discontinued after several successful monitoring years due to financial deficits caused by high tangible and intangible cost from implementing HRGC/MS in sample analysis (Harless*et al;* 1992). There is a strong need to find a cost-effective alternative that is able to provide up-to-date air dioxin concentration level with a reasonable laboratory cost.

Study objectives

In order to fill in the knowledge gap of ambient air dioxins in the past 2 decades and address the concern discussed, the objectives of this study aim to (1) measure the ambient air dioxin concentration at a selected metropolitan site; (2) project human exposure levels of air dioxins in the next 20 years at the site;and (3) validate ELISA as a cost-effective analytical method to analyze dioxin air samples. Achievement of these objectives will establish the technology for future study of mobile emission source of dioxins in urban area and identify potential emission sources and locate hot-spots. This extended abstract describes the results of the first objective.

Materials and methods

The first step was to identify the importance of air dioxins by estimating the potential amount of dioxins inhaled by human population. In 1990, a study indicated that the concentration of dioxins and furans in the outdoor atmosphere in metropolitan New York was reported to be in the range of 8.8pg/m^3 (Smith *et al*, 1990). Based on the reported dioxin concentration, a calculation was conducted to estimate inhalation exposure and level of dioxin accumulation. Maximum daily dioxin exposure through breathing was calculated by multipling aforementioned air dioxin concentration with average breath rate for different age groups provided by Lauralee (2006). Based on the mean body masses of different age groups in North America (Ogden *et al,* 2004), daily dioxin intake through breathing in pg/kg body weight is shown in Table 1.

Compared with the adult population, children with less than 6 years old are more vulnerable groups when facing dioxins exposure. This may be caused by: (1) children populations have more rapid breathing rate than adults; (2) children exposure is higher than adults on a body mass basis; (3) the small size of adipose tissue in children render them more vulnerable to PCDD/Fs; and (4) several literatures indicate that dioxins absorption rate in children are higher than adults. After identification of the vulnerable age groups, the next analysis was conducted to determine dioxin accumulation from birth to 6 years in both male and female populations and compare the theoretical calculated dioxin exposure through ambient air to the published exposure value of lifetime accumulation (Svati*et al*, 1999; Bilau*et al*; 2007).

Table 1Maximum Daily Dioxins Exposure in pg/kg Body Weight

Age Group	Daily dioxin intake by breathing (pg/kg)	
	Male	Female
Infant (<1 year)	4.45	4.57
Toddler (1-3 years)	4.05	4.19
Child (3-6 years)	2.12	2.21
Child (6-12 years)	1.66	1.64
Teenager (12-19 years)	1.09	1.17
Adult (20+ years)	1.15	1.36

The second step was to establish a field sampling program at the roof of Ryerson’s Engineering Building at downtown Toronto.Air samples were collected continuously on a weekly basis (i.e. 5-7 day continuous sampling to meet ELISA’s detection limit between MDL 4 pg TEQ to LOD 10 pg TEQ)from June 2012 to February 2013using two sets of high volume air samplers with an average flow rate of 0.5m^3/minutes, resulting in a total sample volume of 3600m^3 over 5 days. A pre-treated sampling head was attached to the inlet pipe of the sampler to collect particles carried out by airflow. Each sampling head was equipped with a 76mm glass fiber filter and a PUF foam plug, spiked before installation guided by an ELISA modified version of standard operating procedure (SOP-INCATPA) developed by DrYushan Su from Science and Technology Branch of the Environmental Canada. Collected air samples were stored in a 50mL borosilicate glass centrifuge tube, extracted by addition of DMF solution and cleared up by oxidizing with fuming sulphuric acid based on a valid ELISA protocol, which is validated to extract dioxins in soil samples described in the master thesis of Adrienne Lee (2011)and Eric Buan (2009).

Results and discussions

The cumulative amount of dioxin intake from birth to 6 years old was calculated to be 8.37 ng for male and 11.13 ng for female. Comparing these estimates to the literature values, the mean cumulative amount of dioxin intake for boys and girls from birth to 6 years are 51.79 ng and 53.55 ng, respectively. Dioxin inhalation is found to account for 16% (male) and 21% (female) of the mean dioxin accumulation among this age group. As a result, it is important to monitor the air dioxin concentration in populated areas.

It is noted from Figure 1 that the dioxin concentration varies from a minimum of 3.95pg/m^3 to a maximum of 10.25 pg/m^3. The observed dioxin concentrations are lower than those found at other North American locations. It may be attributed to the absence of anthropogenic activities nearby.Strong seasonal variation in dioxin concentration is also observed, with the peak concentration appears on winter time.

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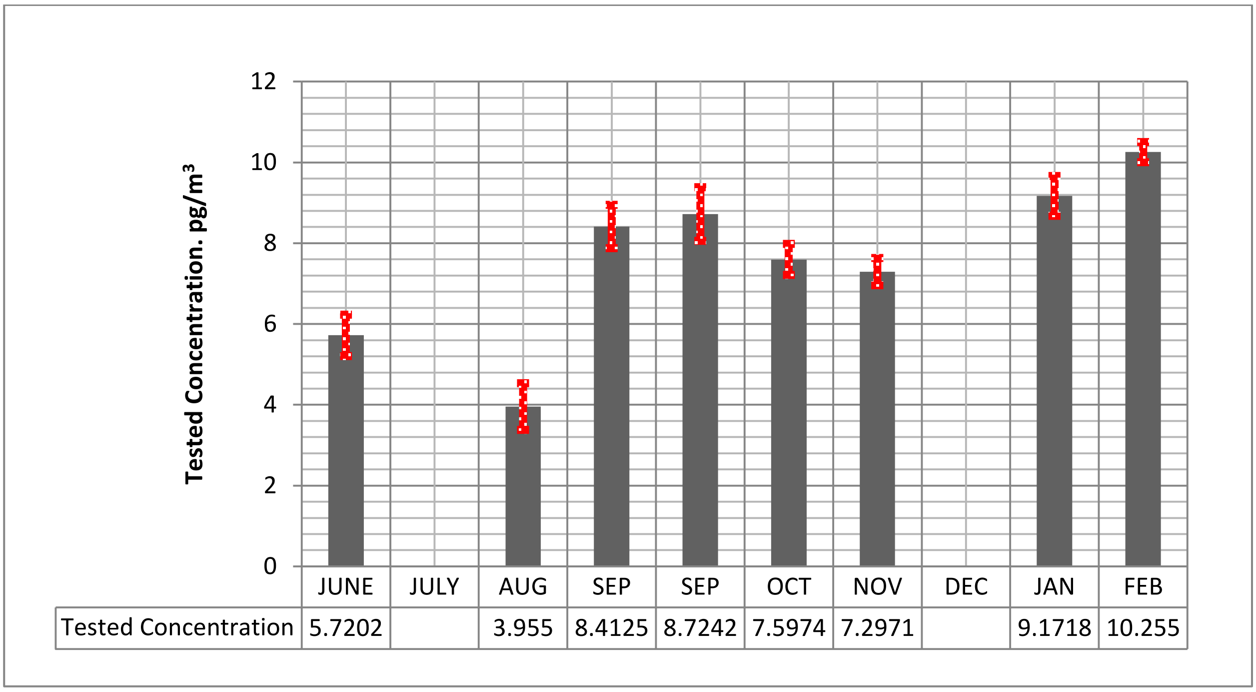

Figure 1 Weekly air dioxin concentration at the roof of Engineering Building in downtown Toronto