BIOMOITORING DIOXINS AND HEAVY METALS IN BLOOD FOR THE RESIDENTS LIVING IN THE VICINITY OF THE MUNICIPAL WASTE INCINERATORS IN SEOUL, KOREA

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Abstract
The aims of this study are to determine the concentrations of dioxins and heavy metals in blood from individuals living in the vicinity area of the MSWI, to compare these levels for residents living near the MSWI and general population living in the urban area not including the MSWI, and to correlate the pollutants levels in blood for subjects. The blood samples were obtained between 2002 and 2006 from volunteer residents (n=131) and the general group (n=27). The average levels of pollutants in blood for the vicinity residents of the MSWI were 11.66 pg-$TEQ_{(WHO98)}$/g lipid, 43.40 ug/L, 2.23 ug/L, and 2.08 ug/L, respectively, PCDDs/Fs, Pb, Cd, and Hg. For general subjects, the average levels of pollutants in blood were 12.43 pg-$TEQ_{(WHO98)}$/g lipid, 47.02 ug/L, 1.75 ug/L, and 2.04 ug/L, respectively, PCDDs/Fs, Pb, Cd, and Hg for subjects. The levels of target pollutants in blood were only significantly correlated the age of subjects. When controlling for smoke habit, the PCDDs levels was significantly related Pb and Hg levels in blood for non-smokers. We conclude that there is the lack of relationship between pollutants emission from MSWI and body burden of PCDDs/Fs and heavy metals in their vicinity exposure from the MSWI. While the individual factors such as age and food consumption patterns are associated with the levels of PCDDs/Fs and heavy metals in blood.

Introduction
Toxic pollutants such as dioxins, polycyclic aromatic hydrocarbons (PAH) and heavy metals have been detected in stack emissions form municipal solid-waste incinerator (MSWI)[1-5]. Much of the concern about toxic contaminants from MSWI has focused on 2,3,7,8 tetrachlorodibenzo-p-dioxin and mercury (Hg) [4, 6-8]. While dioxins and heavy metals are produced by many other sources[9], MSW combustors are thought to be a major source to the environment [10-11]. Dioxins and heavy metals associated with MSWI stacks emissions that bioaccumulate in te food chain and have been shown to produce a wide range of adverse impacts on human health [12-14].
In Korea, the number of municipal and hazardous waste incinerators have increased since 1980. In addition, municipal waste incinerators are almost always located in residential areas. Therefore, the human health risks caused by dioxin and heavy metals are become an increasing public concern in Korea.
The aims of this study are to determine the concentrations of dioxins and heavy metals in blood from individuals living in the vicinity area of the MSWI, to compare these levels for residents living near the MSWI and general population living in the urban area not including the MSWI, and to correlate the pollutants levels in blood for subjects.

Materials and Methods
The blood samples were obtained between 2002 and 2006 from volunteer residents living near to the MSWI in urban area of Korea. The residents group was 131 vicinity residents living at distance < 300m from the MSWI for at least 5 years. For background exposure, the general group was 27 adults living in the urban area not including the MSWI. The participants answered a detailed questionnaire regarding the sociodemographic variables, lifestyle, possible exposure through occupational and non-occupational contact the locations of their former and present residences, and their food intake patterns.
For dioxin analysis, about 150ml of blood was collected without anticoagulant, centrifuged to remove cells, and frozen. The serum samples were extracted with a mixture of acetone and hexane (2:1, v/v) after the addition of 13C12-labeled internal standards (Andover, MA). The organic layer was washed with sodium oxalate saturated water, dried using an evaporator and then re-suspended in dichloromethane/hexane (1:1, v/v). The re-suspended layer was purified by gel permeation, silica gel, alumina and carbon fiber chromatography. Details on the sample

clean-up and fractionation methodologies have been described previously (Rantalainen and Ikonomou, 1998). The quantitative assessment of the dioxin levels in blood was analyzed by high-resolution gas chromatography and high-resolution mass spectrometry (HRGC-HRMS) according to the US EPA 1613 method. The School of Environmental Engineering, Pohang University, conducted the instrumental analysis and the Fisheries & Oceans Laboratory of Canada collaborated with our teams in the quality assurance/quality control (QA/QC) program.
PCDDs/Fs concentrations were reported as picograms TEQ/g lipid (pg TEQ/g lipid). Toxic equivalents (TEQ) were calculated using the toxic equivalent factors (TEFs) established by WHO in 1998. The EXCEL package was used for data management and SAS package was used for statistical analysis. PCDDs/Fs concentrations were reported as picograms Toxic-Equivalent per grams lipid (pg TEQ/g lipid). Toxic equivalents (TEQ) were calculated using the toxic equivalent factors (TEFs) established by WHO in 1998 [17-18].
For heavy metals analysis, approximately 5ml of blood were collected using a 6-ml vacutainer tube with an anticoagulant and kept frozen at -20 ℃ until the analysis. The lead (Pb) and cadmium (Cd) concentration in blood were determined by atomic absorption spectrophotometry with a graphite furnace (GF-AAS, Varian GTA-96, Australia). Sample preparation for total mercury (Hg) analyses of in blood included pre-treatment and digestion of the samples through the addition of nitric-perchloric and sulfuric acid solution. The digested samples were then analyzed by atomic absorption spectrophotometry attached with hydride generator (Shimadzue HVG-1, Japan). The calibration curve used a standard addition method and hydrogen phosphate was used as matrix modifiers. The method detection limit were 10 $\mu g/\ell$, 0.5 $\mu g/\ell$, and 0.0005 $\mu g/\ell$, respectively, Pb, Cd, and Hg. An internal quality control was performed using the certified Standard Reference Materials of blood-heavy metals (SRM: 955a-1 and 955a-2, NIST in USA). Recoveries of SRM were 93±7.5% for all metals.
The correlation matrix tests were performed on calculated statistical software (SAS 8.0 for Windows) at a 95% confidence levels.

Results and Discussion

The average ages of the subjects were 49 years old and 39 years old, respectively, the vicinity residents of the MSWI and general population. The percentages of smoker were 13% and 18%, respectively, the vicinity residents and general population. There was no significant difference in weekly food consumption patterns.
The detection ranges in blood were 1.00–35.93 pg-$TEQ_{(WHO98)}$/g lipid, 7.02-134 ug/L, 0.05-13.90 ug/L, and 0.34-5.10ug/L, respectively, PCDDs/Fs, Pb, Cd, and Hg for subjects (Table 1). The levels of PCDDs/Fs in blood for subjects in this study were similar to those of general population in USA [15]. The average concentrations of heavy metals were not exceeded the guidelines (100 ug/L of Pb, 5 ug/L of Cd, and 5.8 ug/L of Hg) in blood for general population by WHO (World Health Organization). The excess rates of WHO guideline were 2%, 5%, and 2%, respectively, Pb, Cd, and Hg in this study.
The average levels of pollutants in blood for the vicinity residents of the MSWI were 11.66 pg-$TEQ_{(WHO98)}$/g lipid, 43.40 ug/L, 2.23 ug/L, and 2.08 ug/L, respectively, PCDDs/Fs, Pb, Cd, and Hg. For general subjects, the average levels of pollutants in blood were 12.43 pg-$TEQ_{(WHO98)}$/g lipid, 47.02 ug/L, 1.75 ug/L, and 2.04 ug/L, respectively, PCDDs/Fs, Pb, Cd, and Hg for subjects (Table 1). For non-smokers, the average levels of target pollutants by gender were not showed significantly different. The levels of target pollutants for non-smokers in vicinity residents (NS-VR) were similar to that for no-smokers in general population (NS-GP); 11.90 (NS-VR) vs. 12.83 (NS-GP) pg-$TEQ_{(WHO98)}$/g lipid of PCDDs/Fs, 43.45 (NS-VR) vs. 49.24 (NS-GP) ug/L of Pb, 2.18 (NS-VR) vs. 1.56 (NS-GP) ug/L of Cd, and 2.03 (NS-VR) vs. 2.07 (NS-GP) ug/L of Hg. For non-smokers, the average levels of PCDDs/Fs, Pb and Hg were significantly increased by age (Figure 1). The levels of PCDDs/Fs, Pb, Cd, and Hg in blood were not significantly different between the groups and gender, whereas a significant correlation between the age of the subjects and the levels of all pollutants in blood could be observed.
When controlling for smoke habit, the PCDDs levels was significantly related Pb ($r=0.24$, $p=0.008$) and Hg ($r=0.28$, $p=0.02$) levels in blood for non-smokers. The correlations of PCDDs/Fs, Pb, Cd, and Hg levels in blood for smokers were not significant (Table 2). In Korea, the ingestion of foods accounted for 91% of the total dioxin intake, and more than 70% of dioxins intake by foods were come from consumption of fish and selfish [16]. These results indicate that the PCDDs/Fs, Pb, and Hg levels in blood were possibly affected similar sources as food stuff such as fish and shellfish.
We conclude that there is the lack of relationship between pollutants emission from MSWI and body burden of

PCDDs/Fs and heavy metals in their vicinity exposure from the MSWI. While the individual factors such as age and food consumption patterns are associated with the levels of PCDDs/Fs and heavy metals in blood.

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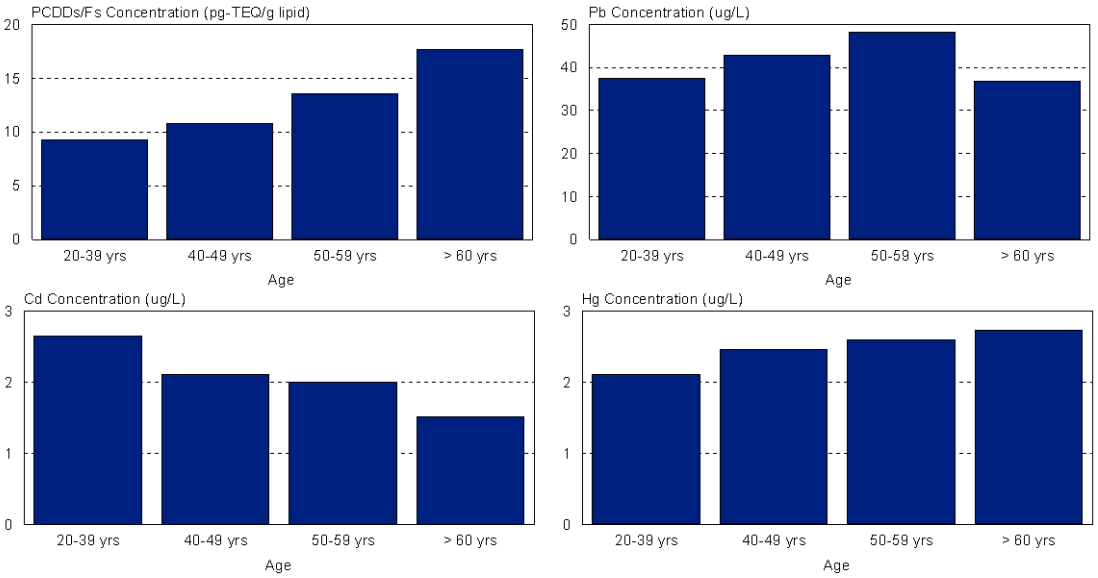
Table 1. The concentration of PCDDs/Fs and heavy metals in blood of the subjects

Target pollutants	MSWI[1)] Vicinity residents (n=131)			General population (n=27)		
	Mean	SD	Range (Min.-Max.)	Mean	SD	Range (Min.-Max.)
PCDDs/Fs (pg-$TEQ_{(WHO98)}$/g lipid)	11.66	6.58	1.00 – 32.02	12.44	7.73	1.68 – 35.93
Pb (ug/L)	43.41	20.05	7.02 – 102.80	47.02	22.78	15.69 – 96.81
Cd (ug/L)	2.23	2.32	0.05 – 13.90	1.75	0.93	0.11 – 3.42
Hg (ug/L)	2.08	1.19	0.34 – 5.10	2.04	1.10	0.50 – 3.77

1) MSWI : Municipal Solid Waste Incinerator 2) SD : Standard deviation



* Toxic equivalents (TEQ) of PCDDs/Fs were calculated using the toxic equivalent factors (TEFs) established by WHO in 1998.

Figure 1. Comparison of PCDDs/Fs and heavy metals levels in blood by age groups

Table 2. Correlation of target pollutants levels in blood for non-smokers

		Target pollutants			
		PCDDs/Fs	Pb	Cd	Hg
Non-smokers (n=139)					
PCDDs/Fs	r coefficient	1.0000			
	(p-value)				
Pb	r coefficient	0.2375**	1.0000		
	(p-value)	(0.0087)			
Cd	r coefficient	-0.1225	0.2008	1.0000	
	(p-value)	(0.2393)	(0.0510)	(0.4723)	
Hg	r coefficient	0.2781*	0.1505	-0.1029	1.0000
	(p-value)	(0.0164)	(0.1857)	(0.4723)	
Smokers (n=19)					
PCDDs/Fs	r coefficient	1.0000			
	(p-value)				
Pb	r coefficient	-0.2004	1.0000		
	(p-value)	(0.4740)			
Cd	r coefficient	-0.4661	0.3816	1.0000	
	(p-value)	(0.1085)	(0.1983)	(0.2689)	
Hg	r coefficient	0.4493	0.2154	-0.6157	1.0000
	(p-value)	(0.3119)	(0.6084)	(0.2689)	

* $p<0.05$, ** $p<0.01$