Extractable Organic Halogens (EOX: Cl, Br and I), Polychlorinated Naphthalenes and Polychlorinated Dibenzo-*p*-Dioxins and Dibenzofurans in Ashes from Incinerators Located in Japan

Masahide Kawano*, Morio Ueda*, Mitsuaki Matsui, Yuji Kashima**, Muneaki Matsuda* and Tadaaki Wakimoto***

* Department of Environment Conservation, Ehime University, 3-5-7 Tarumi, Matsuyama 790-8566, Japan
** Department of Hygiene, School of Medicine, Yokohama City University, 3-9 Fukuura, Kanazawa-Ku, Yokohama 236, Japan

Introduction

Many organohalogen compounds are now known to be formed by the thermal processes of municipal solid waste combution[1,2]. PCDD/DFs and chlorinated naphthalenes (PCNs), which are a family of persistent organochlorine compounds, are detected in emissions of municipal waste incinerators (MWI)[3]. From the available information, it would appear that PCNs have high chronic toxicity potential in animals[4] and exhibit the same binding affinity with the aryl hydrocarbon receptor (AhR) as non-ortho PCBs[5].

Recently, it has been reported that some toxic components except for PCDD/DFs, PCBs and PAHs could be present in incinerator fly ash[6]. The toxicological properties of organohalogen compounds are well known. Accordingly, it is thought that hitherto unknown organohalogen compounds could be present in emissions of MWI. Analysis of extractable organic halogens (EOX) will be of help to understand the levels of unknown organic halogens when EOX and known organic halogen concentrations are compared[7]. It will also provide important information regarding investigation for dioxinlike toxicities in organohalogen compounds residued in ash. The aim of this study is to measure the levels of EOX and to compare them with the levels of PCNs and PCDD/DFs in ash from incinerators.

Materials and Methods

Ash samples - bottom ash and fly ash - were collected from small-scale incinerators (SSI) and MWI located in Japan. There are many SSI in Japan. It is suggested that they are one of the sources of PCDD/DFs.

EOX, PCNs and PCDD/DFs in each sample (20g) were extracted with a Soxhlet apparatus using dichloromethane and toluene. The extract was treated with concentrated sulfuric

acid and cleaned up using silica gel, alumina and activated carbon column chromatographies. Internal standards (^{13}C-PCDDs and ^{13}C-PCDFs) were spiked to the samples. GC-MS analysis was carried out by HRGC-HRMS (JEOL SX102A-HP5890II) equipped with a CHROMPACK CP-Cil 88 and DB-5 for dioxins and DB-5 for PCNs.

The concentrations of organic halogens (Cl, Br and I) were measured by instrumental neutron activation analysis. The crude extract of the ash sample was sealed in polyethylene vials and covered with polyethylene bags on the surface. Activation technique was performed by using neutron flux at a rate of 3.7 x 10^{13} n/cm^2 · sec for two minutes using a research reactor, JRR-3, Japan Atomic Energy Research Institute (JAERI), Tokai, Japan. The gamma-rays from ^{38}Cl, ^{80}Br and ^{128}I were measured by gamma-ray spectrometry technique using a pure germanium detector (EG & G ORTEC MODEL GEN-15180) connected to a multi-channel analyser (CANBERA SERIES 35 PLUS).

Results and Discussion

As shown in Table 1, EOX concentrations ranged from 4.9 μg/g (dry weight basis) to 73 μg/g. On the other hand, PCDD/DF and PCN concentrations ranged from 11 ng/g to 2,100 ng/g and from 0.74 ng/g to 610 ng/g, respectively. The order of these concentrations obtained from the bottom ashes from SSI was EOX>PCNs>PCDD/DFs. However, the order was EOX> PCDD/DFs>PCNs in the fly ash samples from MWI. So far we have found no data for EOX in ash samples. Thus, it may be that the data obtained by the present study are the first figures regarding EOX concentrations in ash from incinerators.

It is possible to get figures for the concentration of unknown compounds by subtracting those of the known compounds from those of extractable organic chlorine (EOCl) in the same sample. The results of calculation show a very small amount of known organochlorines like PCDD/DFs and PCNs to have been present as a fraction of EOCl (Figure 1). This is implies that a large part of EOCl is composed of unknown compounds.

The relationships between unknown EOCl concentrations versus PCDD/DF and PCN concentrations in ash samples we investigated. As a result, no statistical correlations were observed among samples, suggesting that most constituents of unknown fractions as well as PCDD/DFs and PCNs in EOCl have been formed under the combustion processes. However, ash samples from different sites differed widely in EOX levels as well as in PCDD/DF and PCN levels. Namely, it is estimated that the qualities and quantities of solid wastes and the conditions of combustion would affect the formation of EOX in the combustion processes.

Some toxic constituents have been found in the emissions of MWI[1]. It is well known that 2,3,7,8-tetrachlorodibenzo-*p*-dioxin is the most toxic component among the PCDD and PCDF

congeners[8]. At the same time, it is suspected that hitherto unknown toxic compounds may be residued in ashes from MWI[6] and SSI. Consequently, it is important to measure their levels and to make clear their toxic potentials for organisms, including humans.

Table 1. Concentrations (μg/g) of EOX (Cl, Br and I) in ash samples.

Sample No.	EOCl	EOBr	EOI
SP.1*	19	0.12	0.021
SP.2*	29	<0.005	0.080
SP.3*	31	0.18	0.098
SP.4*	71	<0.005	0.20
SP.5**	60	0.38	9.3
SP.6*	45	<0.005	0.32
SP.7**	71	1.5	0.71
SP.8*	37	<0.005	0.011
SP.9*	11	<0.005	0.010
SP.10*	13	0.064	<0.005
SP.11*	9.1	<0.005	<0.005
SP.12*	4.9	<0.005	<0.005

*Bottom ash samples from SSI.
** Fly ash samples from MWI.

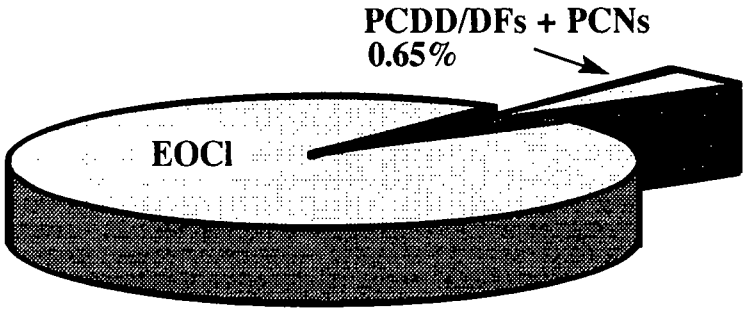

Figure 1. Composition of PCDD/DFs and PCNs in EOCl determined in sample No. SP.7 from MWI.

We have constructed a hypothesis that the amounts of unknown organohalogen compounds formed by waste incineration are higher by orders of magnitude than PCDD/DFs and PCNs. Further, a large part of EOX was occupied by unknown compounds in environmental samples such as soils, sediments[9,10] and organisms[7]. It is necessary to investigate the contribution of the emissions from combustion processes to their residues.

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