CHARACTERISTICS OF EXTRACTABLE ORGANIC HALOGENS IN ASH SAMPLES FROM MEDICAL SOLID WASTE INCINERATOR

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Introduction

Various organohalogen compounds are known to be formed during the incineration processes of municipal solid waste (MSW) [1]. As a consequence of their toxicity, polychlorinated aromatic hydrocarbons (PCAHs) including polychlorinated dibenzo-*p*-dioxins (PCDDs), dibenzofurans (PCDFs), co-planar PCBs, and polychlorinated naphthalenes (PCNs) in MSW have been seriously concerned. Recently, we have reported that the organic iodine in fly ash from MSW incinerator was detected by instrumental neutron activation analysis (INAA) [2]. However, it remains elusive which organic iodine compounds are formed during the incineration of solid waste.

The purpose of this study is to measure the levels of extractable organic halogens (EOX) in each fraction of the column chromatography for PCDDs and PCDFs (PCDD/DFs) analysis and to compare them with the those of PCDD/DFs, PCNs, and non-*ortho* PCBs in ash from the incinerator of medical solid waste (MedSW) that might contain iodine used as antiseptic.

Materials and Methods

Ash samples: Bottom ash and fly ash were collected from MedSW, MSW, and domestic solid waste (DSW) incinerators located in Japan.

Determination of PCDDs, PCDFs, PCNs, and non-ortho PCBs: Ash samples (100-200g) were extracted with toluene using a Soxhlet apparatus. The extracts were concentrated and approximately one-third volume stored for EOX determination. The remainders were separated

into two, one was provided for the clean-up procedure directly, another for monitoring the recoveries of PCDD/DFs and non-*ortho* PCBs by adding the internal standards (^{13}C-PCDD/DFs and ^{13}C-non-*ortho* PCBs). Then both extracts were treated with concentrated sulfuric acid and cleaned up using silica gel, alumina and activated carbon column chromatography. GC-MS analysis was performed by HRGC-HRMS (JEOL SX102A-HP589011) equipped with a CHROMPACK CP-Sil88 for tetra- to hexachlorinated PCDD/DFs, and J&W DB-5 for hepta- and octachlorinated PCDD/DFs, non-*ortho* PCBs, and PCNs.

Determination of EOX: EOX concentrations of the crude extract (CE), the extract treated with conc. sulfuric acids (SE), the second fraction of silica gel column eluted by 10 % dichloromethane in hexane (Sil-2 Fr.), the first fraction eluted by 100 % hexane (Al-1 Fr.) and the second fraction eluted by 50 % dichloromethane in hexane (Al-2 Fr.) through alumina column were determined by INAA as described elsewhere [3]. All fractions were rinsed three times with 5 volume of distilled water purified by MILLI-Q SP reagent water system (Millipore, Co. LTD) before INAA.

Results and Discussion

The concentrations of extractable organic chlorine (EOCl), bromine (EOBr), and iodine (EOI) in CE were 150 to 1200, 0.8 to 25, and 0.3 to 38 nmol/g ash, respectively. EOCl concentrations were independent of ash types, but there is a tendency that EOBr concentration is high in fly ash compared with those in bottom ash. In addition, EOI in MedSW was higher than that in other solid wastes (Fig. 1).

The levels of EOCl and EOBr in CE were not related to those in SE as well as in the fractions of column chromatography. However, there was a positive correlation between the concentrations of EOI in CE and in Sil-2 (data not shown, $p<0.0001$).

The amounts of EOX in Sil-2 Fr., Al-1, and Al-2 Fr. varied among samples, but the rate of Sil-2 Fr., Al-1, and Al-2 Fr. was similar in EOCl and EOI in each sample (Fig. 2).

The relationship among EOX concentrations in each fractions was correlated to EOCl and EOI in Sil-2 Fr. and in Al-1 Fr. but not to those in Al-2 Fr. (data not shown, Sil-2: $p<0.05$, Al-1: $p<0.0001$)

The chlorine content (%) in PCDDs, PCDFs, PCNs, and non-*ortho* PCBs which were extracted as

EOCl in Al-2 Fr. were 2.3 to 40, 7.6 to 48, 1.5 to 14, and 0.2 to 3.2 %, respectively (Fig. 3). Thus, the chlorine contents were PCDFs > PCDDs > PCNs > non-*ortho* PCBs. It has been reported [1)], however, the chlorinated aromatic hydrocarbons (PCAHs) level in emission gas from MSW incinerator was polychlorinated phenols > polychlorinated benzene > PCNs > PCBs, PCDFs > PCDDs. Moreover, the relative contents of PCNs versus PCAHs were obviously lower than those reported in the paper [1)]. Also, in our previous study [2)], the levels of EOX, PCDDs, PCDFs, and PCNs in ash samples were varied among the different sites where ash samples were collected. Therefore, it has to be considered how incineration conditions affect the formation of PCAHs, and affects the qualities and quantities of solid wastes.

In Al-2 Fr., EOCl concentrations were correlated to PCDFs, PCNs and non-*ortho* PCBs concentrations, respectively (PCDFs: $p<0.0001$, PCNs and non-*ortho* PCBs: $p<0.005$) and EOI had relationship with only PCDDs ($p<0.05$, Fig. 4).

These results suggest that several ash samples from MedSW and MSW are likely to contaminate by iodinated dibenzo-*p*-dioxins. However, this speculation has to be proven by further GC-MS analysis identification of the compounds in ash from incinerator.

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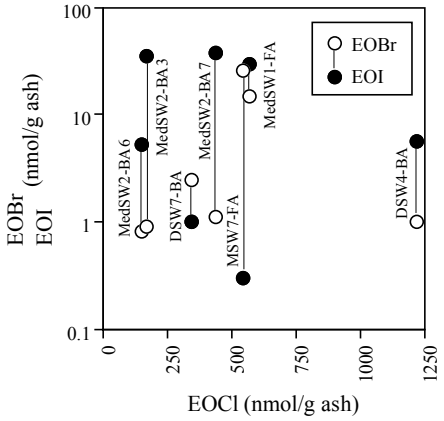

Fig. 1 Relationships between EOI or EOBr versus EOCl

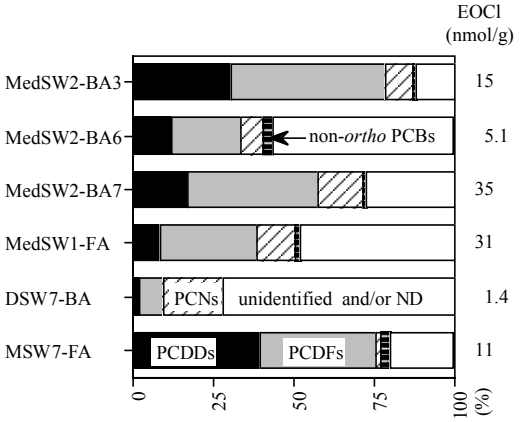

Fig. 3 Cl content (%) binding with PCAHs determined in EOCl in Al-2 Fr.

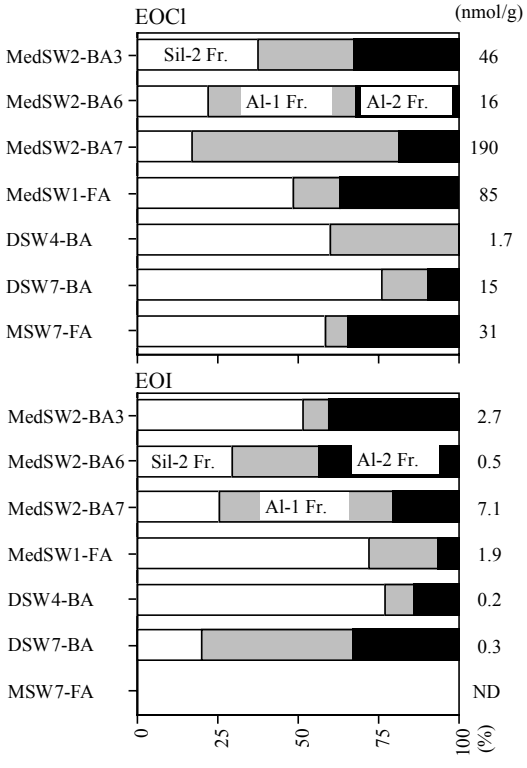

Fig. 2 EOCl and EOI (%) in fractions separated by column chromatography

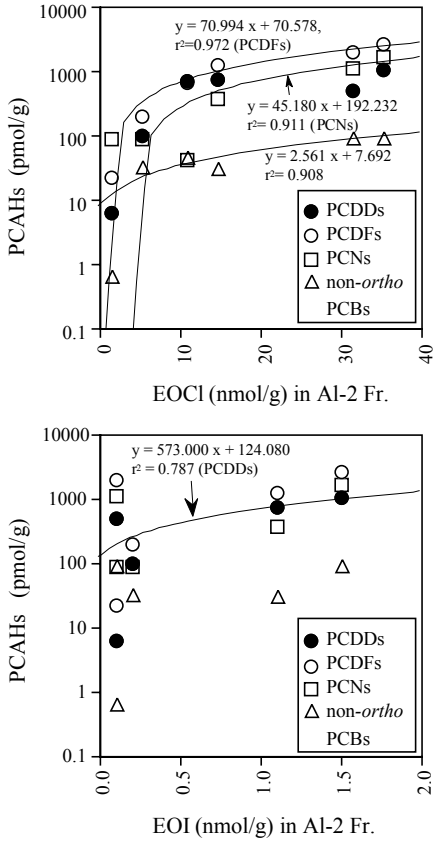

Fig. 4 Relationships between PCAHs versus EOCl or EOI in Al-2 Fr.