SIMULTANEOUS MEASUREMENT OF DIOXINS AND ORGANIC HALOGENATED COMPOUNDS IN WORKING ENVIRONMENT AT WASTE INCINERATOR

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Abstract

Dioxins (PCDD/Fs and Dioxin Like PCB) and organic halogenated compounds (OHC) in working environment were simultaneously measured at the municipal solid waste incinerator while the incinerator stopped for periodic maintenance. OHC was automatically measured with an OHC continuous monitor (J-Power OHC-201). From the results, it was found that the relationship between dioxins and OHC had a positive correlation. The dioxins in working environment of incinerator originate from *de novo* synthesis as well as that in flue gas. The various organic halogenated compounds, not only dioxins, are also formed by the mechanism. Therefore, the correlation of OHC with dioxins was shown in not only flue gas but also working environment. It was considered that OHC was desirable surrogate for dioxins in working environment, and the continuously measurement of OHC was effective in working environmental management at waste incinerator. On the other hand, as OHC was almost gaseous compound, it was more possible to exist in working environment at the room temperature than dioxins. Therefore, it was thought that the correlation of OHC with dioxins lowered with a fall in a temperature. It should be noted that the correlation between dioxins and OHC depends upon the temperature at sampling point.

Introduction

The analysis of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) costs a lot of time and expense because of many steps required, e.g. sampling, extraction, clean-up and HRGC-HRMS operating, which make daily gas monitoring difficult to perform. Therefore, a more cost- and time-efficient measurement technique is strongly needed. Various organic halogenated compounds have been already proposed such as an indicator or substitute for PCDD/Fs in flue gas from municipal solid waste incinerator (MSWI), and many data have been accumulated[1 - 15]. Watanabe and coworkers have reported the measurement of lower chlorinated hydrocarbons (HC-Cln) in flue gas from MSWI[1]. In the report, they have observed that HC-Cln in flue gas have a good relationship with PCDD/Fs and suggested that the concentration of HC-Cln in flue gas may be index of PCDD/Fs emission in some cases. Recently, Takakura and Watanabe have investigated the middle and low volatile organic chlorine (M/LVOCl) as an indicator of PCDD/Fs in flue gas at various MSWIs[16]. In the investigation, they have pointed out that LVOCl give an excellent correlation with total PCDD/Fs concentration in flue gas.

Although many studies on relationship between dioxins (PCDD/Fs and Dioxin Like PCB) and organic halogenated compounds in flue gas have been reported in this way, there are few reports about that in working environment. In this paper, we have reported the simultaneous measurement of dioxins and organic halogenated compounds (OHC) in working environment at MSWI, and investigated the relationship between them.

Materials and Methods

Sampling

Measurement of working environment was carried out at North Fujisawa Incineration Plant in Japan on October 23 and 30 in 2006. The incinerator No. 1 and No. 2 of the plant have stoker type furnaces and incinerate 150 tons of municipal waste per 24 hours respectively. The incinerator No. 1 has a dust collector with an electric precipitator, and No. 2 with a bag filter (BF). Air sampling in the working environment was performed 5 times (A, B, C, D and E) while the incinerators stopped for periodic maintenance. **Fig. 1** shows the principal equipment of the plant and the sampling points. The sampling at point A or B was performed at the inside of the furnace of incinerator No. 2 and point C was at incinerator No. 1, where the sampling at point A was conducted

on cleaning of furnace (Furnace-2 on cleaning), and at point B and C were done after cleaning of that (Furnace-2 and -1 after cleaning). The sampling at point D was in duct between BF and stack (Duct of BF outlet). Sampling E was in the room installed the dust collector (Dust collector room).

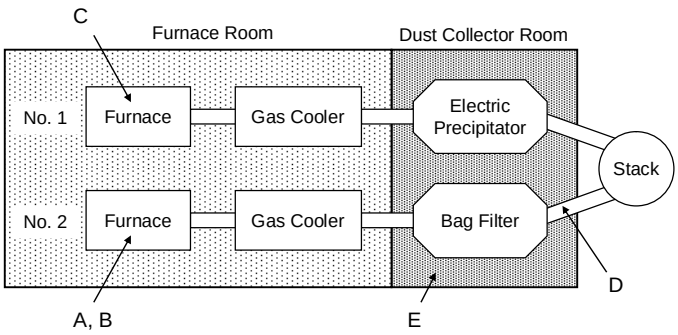

Fig. 1 Principal equipment of North Fujisawa Incineration Plant and sampling points (A, B, C, D and E)

Measurement

Dioxins (PCDD/Fs and Dioxin Like PCB) in air at working environment were sampled with a high volume sampler (Shibata HV-500FD) attaching a filter and polyurethane foam, and then analyzed with a GC/MS (JEOL JMS-700D) in accordance with a notice of Ministry of Health, Labour and Welfare of Japan.

OHC was automatically measured with an OHC continuous monitor (J-Power OHC-201). **Fig. 2** shows an outline of the monitor. The monitor continuously collected only gaseous sample through a filter at the speed of 2 L min^{-1}. The moisture in the sample was eliminated with an electronic cooler, and inorganic halogens were removed through a column filled with 20 g of silver granules (5.11 m^2 g^{-1} in specific surface area, 0.42 to 0.85 mm in diameter). OHC in the sample was adsorbed and concentrated on 0.1 g of graphite carbon adsorbent (100 m^2 g^{-1} in specific surface area, 0.4 to 0.6 mm in diameter) kept at 100 °C, and then desorbed by heating at 450 °C with nitrogen as the carrier gas. The desorbed OHC was combusted at 800 °C under oxygen gas, and decomposed into hydrogen halide. The halide was guided into a titration cell with silver electrode, and then titrated by electrolytically generated silver ions as below.

$$HX + Ag^+ \rightarrow H^+ + AgX\downarrow \quad \text{(Titration)}$$

$$Ag \rightarrow Ag^+ + e^- \quad \text{(Electrolysis)}$$

where, X is halogen. From the quantity of electricity determined by titration, the halogen amount (m) was calculated based on Faraday's law as below, and presented as a chlorine equivalent value (g-Cl).

$$m = QM / zF$$

where, Q is the charge required to deposit the halogen, M the relative ionic mass, z the charge of the ion and F the Faraday constant (9.648×10^4).

The temperature and pressure of sample were converted into 0 °C, 101.3 kPa.

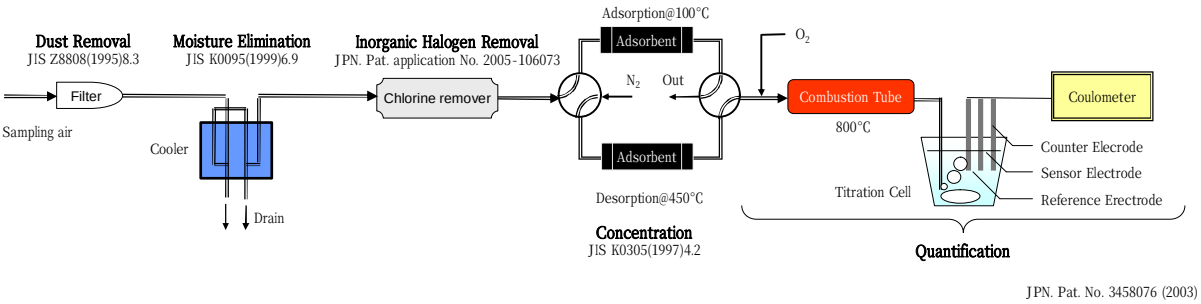

Fig. 2 Outline of OHC continuous monitor (J-Power OHC-201)

Results and Discussion

Homologues of PCDD/Fs

PCDD/Fs in the working environment were measured. The measured homologues of PCDD/Fs are shown in **Fig. 3**. From the results, it was found that the homologues of PCDFs at sampling point A (Furnace-2 on cleaning) and D (Duct of BF outlet) decreased with increase in the degree of chlorination. In other words, PCDFs with high volatility more existed than that with low volatility in working environment. The distribution of the homologues may result from the memory effect.

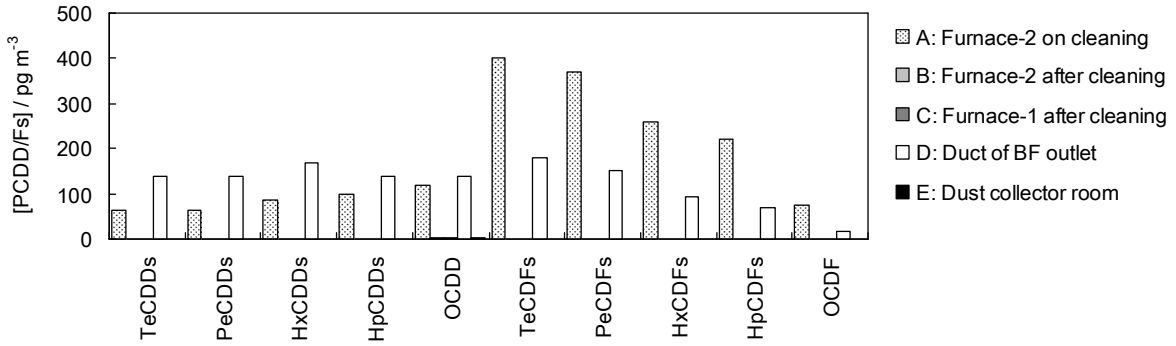

Fig. 3 Homologues of PCDD/Fs in working environment at MSWI

Dioxins and OHC in working environment

Dioxins and OHC in the working environment were simultaneously measured. These results are shown in **Table 1**, where TEQ is Toxic Equivalency Quantity.

Table 1 Concentration of dioxins and OHC in working environment at MSWI

Sampling Point	Temperature / °C	Dioxins / pg m^{-3}	Dioxins / pg-TEQ m^{-3}	OHC / μg-Cl m^{-3}
A: Furnace-2 on cleaning	24.3	1,900	35	1.308
B: Furnace-2 after cleaning	22.0	15	0.03	0.102
C: Furnace-1 after cleaning	22.4	17	0.02	0.310
D: Duct of BF outlet	26.2	1,300	16	3.432
E: Dust collector room	21.4	12	0.03	1.679

Although the concentration of dioxins in working environment of furnace was high on cleaning (Point A), that was low after cleaning (Point B and C). From these results, it was found that dioxins in furnace evidently decreased through the cleaning. The concentration of dioxins in working environment at duct of BF outlet was comparatively high, and at dust collector room was relatively low.

Correlation between Dioxins and OHC

Fig. 4 shows the correlation of OHC with dioxins (converted into TEQ) in working environment. For comparison, previously measured data[14] were also shown in this figure. From the results of furnace and duct of BF outlet, it was found that dioxins and OHC had roughly positive correlation. Especially, OHC in working environment of incinerator was high concentration on cleaning as dioxins. The dioxins in working environment of incinerator originate from *de novo* synthesis as well as that in flue gas. The various organic halogenated compounds, not only dioxins, are also formed by the mechanism[17]. Therefore, the correlation of OHC with dioxins was shown in not only flue gas but also working environment. It was considered that OHC was desirable surrogate for dioxins in working environment, and the continuously measurement of OHC was effective in working environmental management at waste incinerator.

However, in the results of the dust collector room, although the concentration of dioxins was low, that of OHC was relatively high. The reason was thought in terms of vapor pressure as follows. Yoshioka and coworkers have

investigated the gas-particle partitioning of dioxins in the atmosphere, and found that the particle ratios of dioxins decreased with increase in temperature[18] (**Fig. 5**). It meant that gaseous dioxins decreased with decrease in temperature. As the temperature of the dust collector room was lowest in the all sampling points, compounds with low vapor pressure, such as dioxins, were hardly present in gaseous phase at the room temperature. On the other hand, as OHC was almost gaseous compound, it was more possible to exist in working environment at the dust collector room than dioxins. It should be noted that the correlation between dioxins and OHC depends upon the temperature at sampling point.

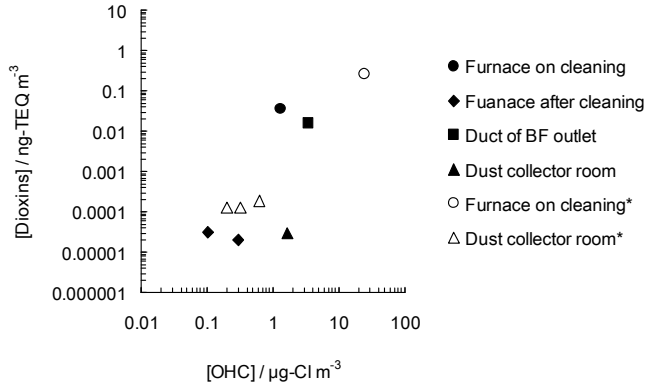

Fig. 4 Correlation of TEQ dioxins with OHC at various working environments, where ○ (Furnace on cleaning*) and △ (Dust collector room*) are previously reported data[14]

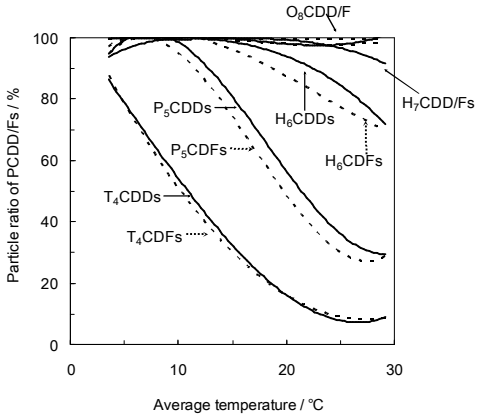

Fig. 5 Particle ratio of PCDD/Fs in atmosphere as a function of average temperature during sampling[18]

Acknowledgements

The work was carried out under the grant of New Energy and Industrial Technology Development Organization (NEDO), Japan.

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