ONE-YEAR MONITORING OF DIOXINS USING BIOASSAYS AT TWO WASTE INCINERATION PLANTS IN JAPAN

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Introduction

Dioxin monitoring was conducted throughout a year at two waste incineration plants. Incineration gas, fly ash and bottom ash samples were regularly taken and analyzed by high resolution GC/MS as a golden standard and two bioassay methods (i.e., the dioxin responsive-chemical activated luciferase gene expression (DR-CALUX) and flow-through kinetic exclusion immunoassay (Immuno-sensor)). The two bioassays were newly included in the official simple and low cost bio-analytical methods specified by the Ministry of the Environment of Japan in March 2010[1], which are available for monitoring dioxins in flue gas and incineration ash from waste incinerators. The obtained bioassay results were compared to World Health Organization toxic equivalent (WHO-TEQ) values to verify the applicability of the two bioassays as a semi-quantitative approach for dioxins.

Materials and methods

Incineration samples. Flue gas and incineration ash were sampled during September 2007 and September 2008 at a batch-type industrial waste incinerator (incinerator A, incineration capacity: 1,800 kg/h) and a mechanical stoker type municipal solid waste incinerator (incinerator B, incineration capacity: 80 metric tons/day) in Japan. From each plant, six untreated and treated gas samples (> 1.5 m^3), twelve fly ash and twelve bottom ash samples (> 1 kg) were taken regularly throughout a year.

Analytical method. The PCDD/DFs and dl-PCBs were determined using a high-resolution GC/MS system. Toxicity equivalent concentrations (TEQ) were calculated using TEF values according to the latest WHO recommendations[2].

Bioassays. As for DR-CALUX (BioDetection Systems BV, The Netherlands), the recombinant rat hepatoma H4IIE cell line, stably transfected with the aryl hydrocarbon receptor (AhR)-controlled luciferase–cDNA construct was used and the assay was carried out as previously described[3]. Immuno-sensor (DXS-600, Kyoto Electronics Manufacturing Co., Ltd., Japan) adopts a kinetic exclusion assay and a monoclonal anti-dioxin antibody[4]. Automated sample cleanup devise (SPD-600, Kyoto Electronics Manufacturing Co., Ltd., Japan) was applied to sample preparation for the bioassays. The sample extracts (Soxhlet toluene extracts) were replaced with *n*-hexane. The extract was cleaned-up by multi-layer silica gel column jointed with alumina column. The PCDD/DFs and dl-PCBs were eluted from the alumina column by toluene, which were further replaced with smaller volume of dimethylsulfoxide (DMSO, bioassay solvent). Mean of the determinations for quantification (> LOQ) was less than 30% for the two bioassays (DR-CALUX: n =3, Immuno-sensor: n =2).

Results and discussion

Conversion of measured variables. Conversion of measured concentrations (2,3,7,8-TCDD equivalents) is necessary to compare these values with WHO-TEQs calculated by the GC/MS results. Correlation between the 2,3,7,8-TCDD equivalents and WHO-TEQs was determined for each bioassay (for each medium). For DR-CALUX, site- and media-specific conversion factors (i.e., slope of the regression line) were calculated in this study and they were used to convert 2,3,7,8-TCDD equivalents to WHO-TEQ estimates. For Immuno-sensor, empirical media-specific conversion factors calculated using the accumulated (not site-specific) data in the past (the same sample cleanup method was used), were adopted.

Incineration gas. At the incineration A, WHO-TEQs for four incineration gas samples exceeded the Japanese emission standard (5 ng-TEQ/m^3N) for small scale waste incinerators (treatment capacity < 2 metric tons/h),

though the samples were all taken at the “non-legal” points before final emission. On the other hand, at the incineration B, the WHO-TEQ level was sub ng/m^3 level in the inlet gas to bag filters, and far below the emission standard (0.1 ng-TEQ/m^3 for large-scale waste incinerators) in the final emission gas. WHO-TEQ estimates obtained by the two bioassays were in good agreement with WHO-TEQs. Their accuracy (discrepancy from WHO-TEQs) was less than 30% for the most quantified samples.

Fly ash. WHO-TEQs and the bioassay TEQ estimates in fly ash are shown in Figure 1. Japanese control standard value for waste incineration ash is 3 ng-TEQ/g. The level at the incinerator A varied with the samples, which depends on the waste quality and incineration conditions of each batch. The highest WHO-TEQ showed 9.0 ng/g and the concentrations of six samples exceeded 3 ng-TEQ/g. In this plant, the incineration ash was further treated and processed by high-temperature melting operation. WHO-TEQ level in fly ash in the incinerator B was in the range of 0.1 – 0.7 ng/g, which seems to be relatively lower in variations. Here also, WHO-TEQ estimates obtained by the two bioassays agreed well with WHO-TEQs. False-negative bioassay results were not observed at the standard of 3 ng-TEQ/g.

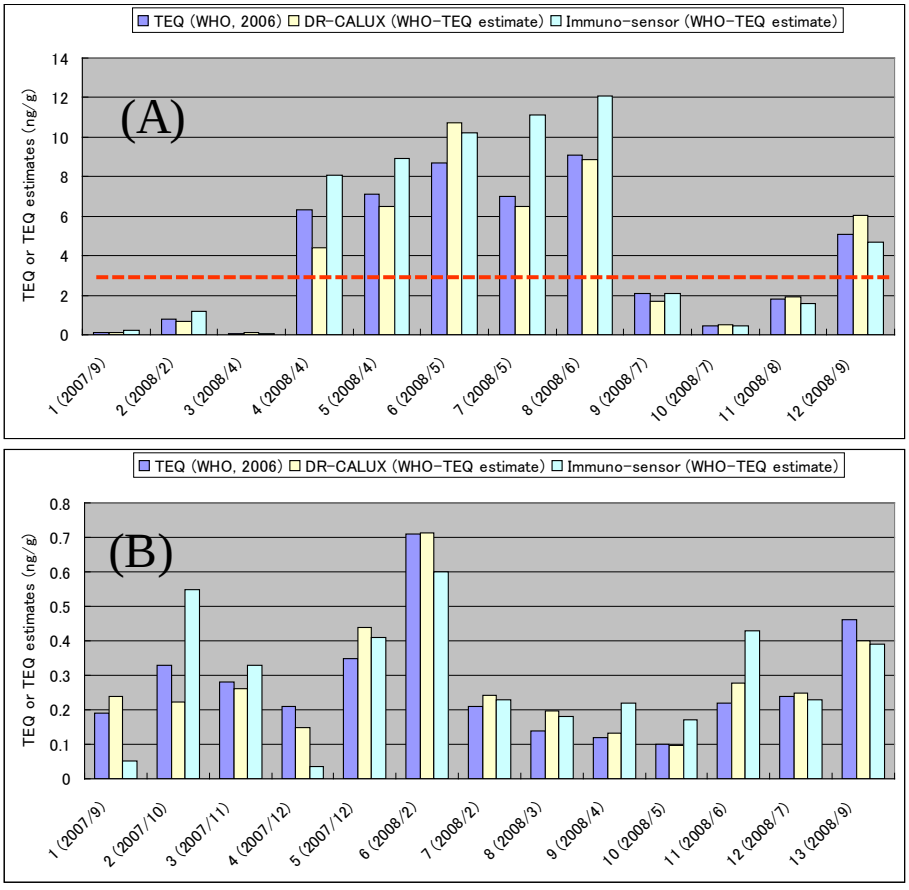

Fig. 1 Comparison of WHO-TEQ and TEQ estimates obtained by the two bioassays for fly ash samples. (A): incinerator A, (B): incinerator B. The dashed line shows a control standard for dioxins for waste incineration ash (3 ng-TEQ/g).

Bottom ash. WHO-TEQs and the bioassay TEQ estimates in bottom ash are shown in Figure 2. The level at the incinerator A varied with the samples, as seen in the fly ash samples. The highest WHO-TEQ showed 7.5 ng/g and the concentrations of eight samples exceeded the Japanese control standard. Bottom ash was also treated and

processed by high-temperature melting operation in this incineration plant. WHO-TEQ level in bottom ash in the incinerator B was up to 0.032 ng/g at maximum, which seems to be relatively lower in variations. WHO-TEQ estimates obtained by the two bioassays agreed well with WHO-TEQs. False-negative bioassay results were not observed at the standard of 3 ng-TEQ/g.

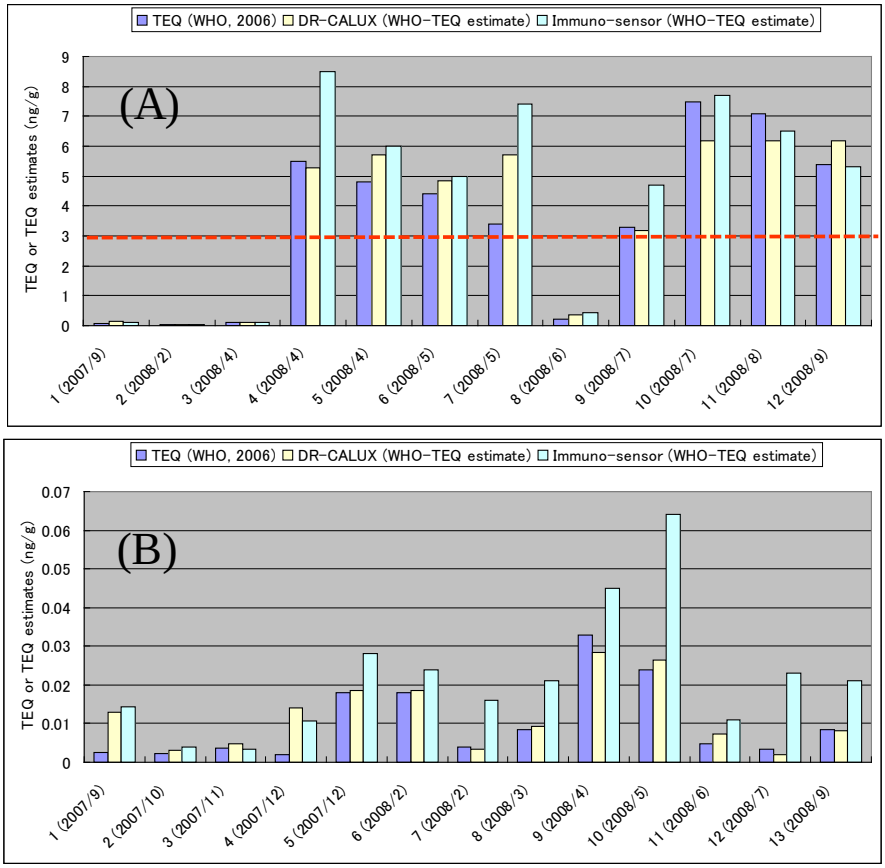

Fig. 2 Comparison of WHO-TEQ and TEQ estimates obtained by the two bioassays for bottom ash samples. (A): incinerator A, (B): incinerator B. The dashed line shows a control standard for dioxins for waste incineration ash (3 ng-TEQ/g).

The bioassays (DR-CALUX and Immuno-sensor) used in this study have been selected as Japanese official methods for monitoring dioxins in waste incineration samples. Those methods actually showed acceptably good accuracy results when compared to WHO-TEQs obtained by a golden standard GC/MS at two actual incineration plants throughout one-year monitoring.

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