

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

Takigami H¹, Honda M¹, Kitamoto H², Nakamura T³, Oka M⁴

¹National Institute for Environmental Studies, Onogawa 16-2, Tsukuba, Ibaraki, Japan; ² Hyogo Prefectural Institute of Environmental Sciences, Japan; ³ Miyagi Prefecture, Japan; ⁴Gifu Prefectural Research Institute for Health and Environmental Sciences, Japan

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 2010¹, 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 m³), 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 recommendations².

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 described³. Immuno-sensor (DXS-600, Kyoto Electronics Manufacturing Co., Ltd., Japan) adopts a kinetic exclusion assay and a monoclonal anti-dioxin antibody⁴. Automated sample cleanup device (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/m³N) 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/m³ level in the inlet gas to bag filters, and far below the emission standard (0.1 ng-TEQ/m³ 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.

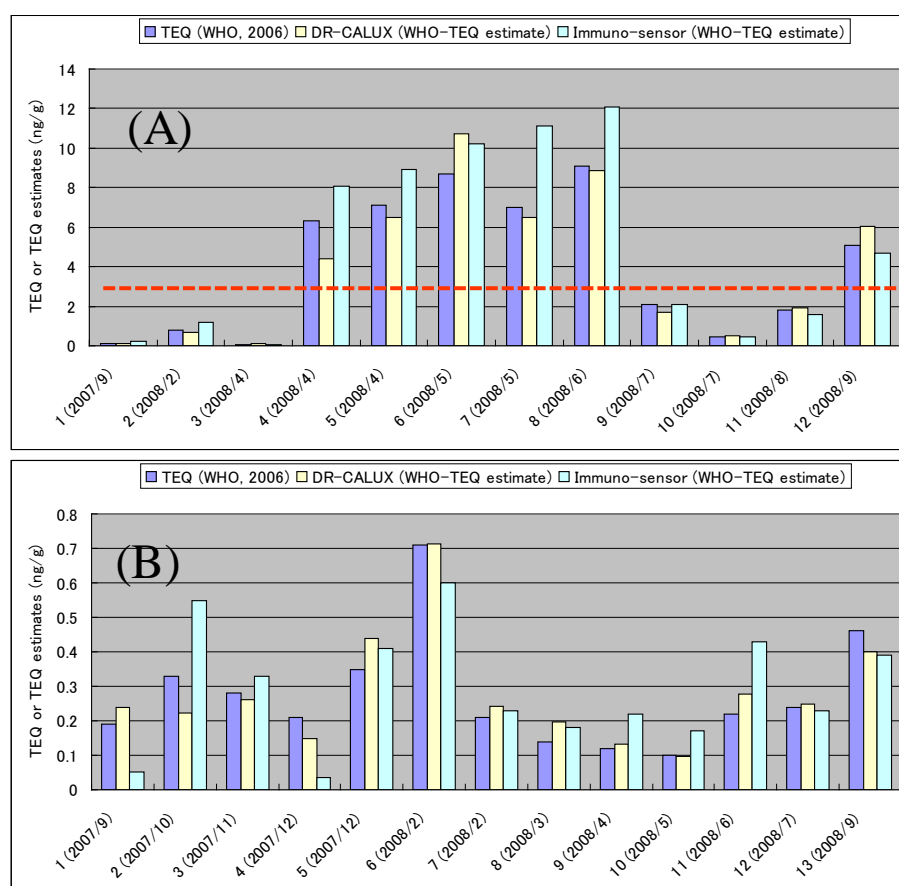


Fig. 1 Comparison of WHO-TEQ and TEQ estimates obtained by the two bioassays for fly ash samples. (A): incinerator A, (B): incinerator B. The dashed line shows a control standard for dioxins for waste incineration ash (3 ng-TEQ/g).

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.

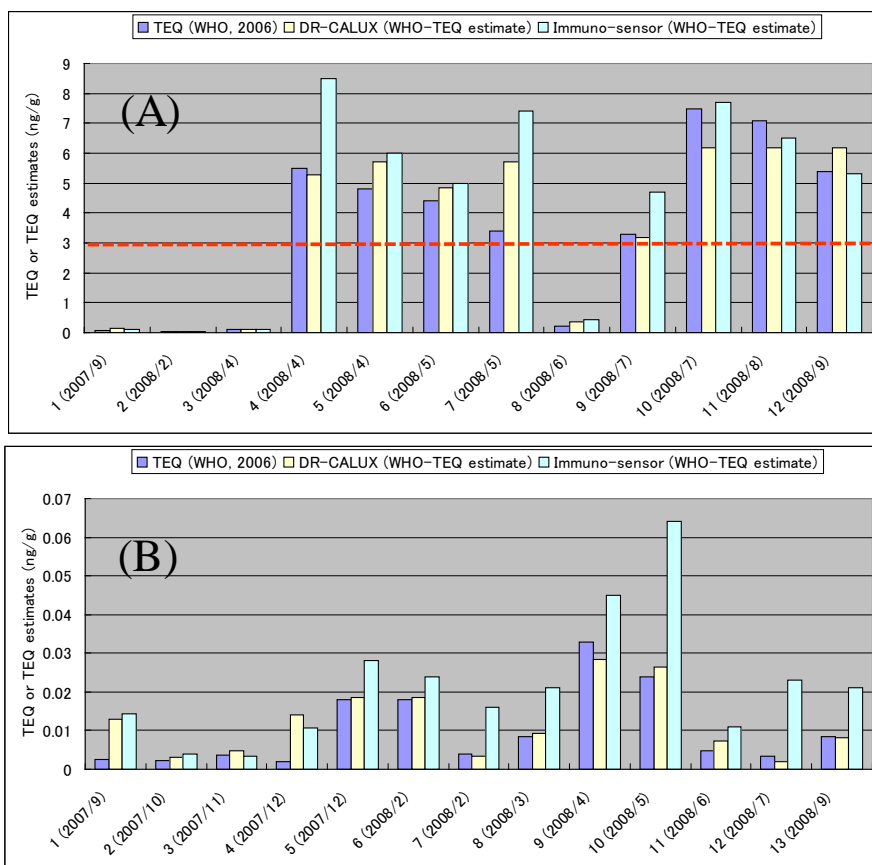


Fig. 2 Comparison of WHO-TEQ and TEQ estimates obtained by the two bioassays for bottom ash samples. (A): incinerator A, (B): incinerator B. The dashed line shows a control standard for dioxins for waste incineration ash (3 ng-TEQ/g).

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.

Acknowledgements

This study was supported by Global Environment Research Account for National Institute of the Ministry of the Environment, Japan (FY 2007-2009). We thank Prof. Bram Brouwer of BioDetection Systems BV (Amsterdam, The Netherlands) and Dr. Kazuyuki Sawadaishi of CBST LLC (Kyoto, Japan) for providing the testing materials.

References:

1. The Ministry of the Environment of Japan (2010); <http://www.env.go.jp/press/press.php?serial=12338> (in Japanese), last accessed 14/05/2011.

2. Van den Berg M, Birnbaum LS, Denison M, De Vito M, Farland W, Feeley M, Fiedler H, Hakansson H, Hanberg A, Haws L, Rose M, Safe S, Schrenk D, Tohyama C, Tritscher A, Tuomisto J, Tysklind M, Walker N, Peterson RE. (2006); *Toxicol Sci.* 93(2): 223-41.
3. Takigami H, Suzuki G, Sakai S. (2010); *J Environ Monit.* 12(11): 2080-7.
4. Fujita H, Hamada N, Sawadaishi K, Honda K. (2004) ; *Organohalogen Compounds.* 66 : 677-81