

## Comparison of the Measurement Methods for Dioxins and Coplanar PCB in Soil and Ambient Air between the U.S. and Japan

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### Introduction

An opportunity arose to examine the concentrations of dioxins in ambient air and soil by employing both the Japanese measurement methods<sup>1,2</sup> and the U.S. methods<sup>3,4,5</sup>. Japanese and the U.S. high volume air samplers were set side by side for taking practically the same air. Soil samples were collected from the same spots at each location by following a five-point sampling method<sup>2</sup>. This paper examines the methodology used for sampling and laboratory analysis for dioxins and coplanar PCB in the two countries and the comparability of dioxin concentrations resulting from the respective country's method. The aims of this paper are to discuss major differences between the two countries' measurement methods for dioxins in ambient air and soil, and to investigate whether those differences cause a significant impact on measured concentrations.

### Design of the Comparative Study

In ambient air, a dioxin concentration varies not only with location but also with time. Therefore, the present study was conducted for an 8-week long period to determine if any, a concentration difference attributable to the measurement methods<sup>1,3</sup>. A pair of two dioxin-specific high volume (HV) air samplers, the U.S. method-specified and the Japanese method-specified, was placed at two different sites, one in residential area and the other impacted by a nearby source. At each site, the two samplers were placed side by side only about a half-meter apart at a position, which was well exposed to stack-gas plume from the source.

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Soil samples were taken at 6 locations, of which a pair of samples was taken at each location by following the Japanese sampling method and the U.S. sampling method. The sixth location was a background site. To minimize an artifact difference in the sampling, 5 sub-samples were taken at every site to form one composite sample. At every sub-sampling point, a pair of samples was taken by making two attached holes 5cm deep using a Japanese soil-sampling device.

For air samples, double measurements were made using the Japanese method, while the U.S. method was employed for a double measurement of one soil sample.

### Features of the Japanese Methods and those of the U.S. Methods

Both countries use a dioxin-specific HV air sampler. It has a metal tube containing polyurethane forms (PUF) inside, which is attached to the space between the filter paper holder and the blower motor. The Japanese sampler employs a 200-by-250mm square filter paper and then a 90mm diameter PUF, and normally draws air at a rate of 700 l/min. The U.S. sampler employs a 4" circular filter paper and a 2" diameter PUF, and normally draws air at a rate of 200 l/min. Laboratory-cleaned PUF was housed in glass cartridge, which was then slid into a metal tube at sampling site in both countries.

The soil sampling method in Japan recommends taking a soil sample 5cm deep from 5 sub-sampling points. Both sides followed this sampling scheme. In the Japanese method, each sub-sample is air-dried until no weight change with time is observed. Only then, an equal amount is measured out of each sub-sample to form a composite sample. On the other hand, the U.S. method recommends placing an equal amount of the 5 sub-sample in a stainless-steel bowl and thoroughly mixing them until the sample soil becomes uniform. This operation was done in the field.

The laboratory analysis methods for dioxins and coplanar PCB are similar in the two countries, but some details differ. In Japan, one method covers both dioxins and coplanar PCB<sup>1</sup>, whereas in the U.S., Method 1613 covers dioxins and Method 1668 does coplanar PCB<sup>4,5</sup>. For air samples, the Japanese method recommends the use of acetone for filter extraction and toluene for PUF

extraction, whereas the U.S. method recommends using toluene for extracting both filter and PUF. For soil samples, the Japanese method is stringent for dryness of soil prior to solvent extraction while the U.S. method recommends using Dean-Stark moisture-trap apparatus in extraction.

Clean-up procedures differ in the type of solvent to be used between the two countries. In general, the Japanese method recommends using a greater amount of solvent and multiple types of solvents in clean-up extraction. Both countries use an isotope dilution method to minimize the effects of incomplete extraction, clean-up loss, and instrument condition on the calibration curve.

### Results of the Comparative Study

For ambient air, 16 pairs of ambient air samples were obtained at each of the two monitoring sites. Figure 1 shows a scatter plot and a regression line for all 32 ambient air samples, whose dioxin concentrations were determined by the Japanese method and the U.S. method. The regression exhibits a relatively good correlation between the two methods with a high  $R^2$  value of 0.81. A correlation between the measured concentrations for 6 soil samples was even better with  $R^2 = 0.99$ . In the air samples, some of the 32 paired samples exceeded 30 % in relative percent difference (RPD), which is adopted in the Japanese manuals as the maximum allowable difference in double measurements. In the soil samples, none of the paired samples exceeded this threshold.

### Discussions and Conclusion

The mean concentrations at the two monitoring sites were measured by the Japanese method as 8.0 and 0.64 pg-TEQ/m<sup>3</sup> whereas by the U.S. method, they were 7.3 and 0.51 pg-TEQ/m<sup>3</sup>. RPD in the two means are 9.2% at the high concentration site and 22.6% at the low concentration site. Four double measurements were taken at each site using the Japanese method. The mean concentrations of original sampling at the two sites were 6.6 and 0.26 pg-TEQ/m<sup>3</sup> whereas those of duplicate sampling were 7.2 and 0.31 pg-TEQ/m<sup>3</sup>. RPD values of the double measurements were 9.1% at the high concentration site and 17.5% at the low concentration site. Therefore, the Japanese method and the U.S. method yield a comparable result in ambient air samples, despite the vastly different configuration in the dioxin-specific HV samplers of the two countries.

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Analysis results of the soil samples by the two methods were so consistent each other. None of the 6 paired samples exceeded 30% in RPD. This is remarkable, given the fact that the Japanese method requires an elaborate preparation for making a composite sample and a complete air dry prior to solvent extraction, whereas the U.S. method allows a mixture of the collected sub-samples on site and no requirement for air dry prior to extraction.

### Acknowledgements

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### References

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3. U.S. EPA Method TO9-1: Method for the Determination of Polychlorinated Dibenzo-p-Dioxins (PCDDs) in Ambient Air using High-Resolution Gas Chromatography/High-Resolution Mass Spectrometry (HRGC/HRMS), Revision 1.1, June 1988.
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Figure 1. Comparison of the dioxin concentrations for ambient air samples measured by : Japanese method vs. U.S. method.  
(PCDD + PCDF + Co-PCB, Used 1998 WHO TEF, n = 34)

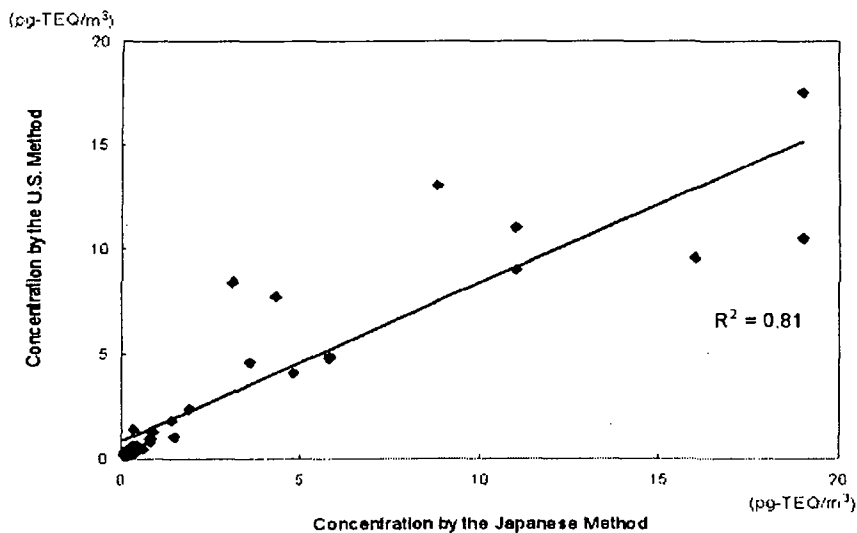


Figure 2. Comparison of the dioxin concentrations for soil samples measured by : Japanese method vs. U.S. method.  
(PCDD + PCDF + Co-PCB, Used 1998 WHO TEF, n = 6)

