

**SOURCES OF UNCERTAINTIES IN THE DIOXINS INVENTORY
FOR AMBIENT AIR EMISSIONS UNDER THE DIOXINS
COUNTER-MEASURE LAW AND JIS K 0311**

Yuji Horie

Green Blue Corporation, 5-4-11 Higashi Koujiya, Ohtaku, Tokyo 144-0033, Japan

Introduction

Air emissions of dioxins defined as the sum of PCDD, PCDF, and coplanar PCB decreased dramatically in the past three years according to the government report³. The issuance of the formal measurement method, JIS K0311 in late 1999, and the enforcement of the law concerning special measures against dioxins (hereafter called, "counter-measure law") in January 2000 seem to have provided an impetus for dioxins emission reduction and improvement for measurement accuracy^{1,2}. This paper examines the methodology used for national dioxins inventory and uncertainties in the inventory estimates. The aim of this paper is to provide Japanese experience in light of the United Nations effort to develop a worldwide dioxins emission inventory.

Méthodology for Air Emissions Inventory for Dioxins

Compilation of an emission inventory usually requires: 1) a list of emitting sources, 2) emission rate, and 3) source activity data. Under the counter-measure law, a list of dioxins emitting sources increased from waste incineration sources alone to include other sources such as crematory, electrical furnace and sintering process for steel manufacturing, aluminum manufacturing, zinc recovery industry, other manufacturing, cigarette smoke, and auto exhaust. The law requires, at a minimum, one emission test per annum for every subject facility.

Air emissions from dioxins emitting facility are estimated using the following generic equation:

$$E = C \times V \times Q \qquad \text{Eq. 1}$$

where E = Dioxins emissions in nano-gram per year, ng/y.,
 C = Dioxins concentration in toxic equivalent quantity (TEQ), ng-TEQ/m³,
 V = Exhaust gas constant, m³/ton of incinerated material or product manufactured, and
 Q = Annual amount of incineration or production, ton/y.

In the above equation, the exhaust gas constant for general municipal incinerator is given as 5000 m³/ton, while the one for industrial waste incinerators is varied with types of the material burned. The exhaust gas constants for production categories are given for a few characteristic production processes. Data for the dioxin concentration and the annual amount of incineration or production were obtained from actual measurements and actual operation records of each subject facility. Table 1 summarizes national air emissions of dioxins in g-TEQ/y in the past three years, 1997, 1998, and 1999.

Table 1. National Dioxins Inventory for Air Emissions³, g-TEQ/y

(Based on WHO-1998 TEF)

| Source Category | 1997 | 1998 | 1999 | %Reduction (1997-1999) |
|--|------|------|------|---------------------------|
| General waste incineration facility | 5000 | 1550 | 1350 | 73 |
| Industrial waste incineration facility | 1500 | 1100 | 690 | 54 |
| Small-scale waste incinerator | 591 | 591 | 481 | 19 |
| Crematory | 5 | 5 | 5 | 0 |
| Steel production electrical furnace | 228 | 140 | 142 | 38 |
| Steel production sintering process | 135 | 114 | 101 | 25 |
| Zinc recovery industry | 42 | 20 | 18 | 57 |
| Aluminum alloy production | 21 | 19 | 14 | 33 |
| Other manufacturing | 26 | 26 | 18 | 31 |
| Cigarette smoke | <1 | <1 | <1 | 0 |
| Auto exhaust gas | 1 | 1 | 1 | 0 |
| Total | 7549 | 3566 | 2820 | 63 |

Results and Discussions

Dioxins emission inventories were developed and reported for several countries and by different organizations. However, very few inventories addressed uncertainties in the emission estimate. An emission inventory can be produced from a back-of the envelope calculation or from a compilation of actual data, which usually consist of emitting facilities, measurements of dioxins emission, and operation records. The dioxins inventory reported above was produced from actual data. Even so, there are many sources of uncertainties in the emission estimate.

To improve a reliability of dioxins emission inventory, this paper examines potential sources of uncertainties in the input data for and the calculation method of dioxins inventory in Japan.

1. Uncertainty in Facility Population

It is important to identify all-inclusive population of emitting facilities for an inventory calculation. In the earlier stage of Japanese dioxins inventory, several categories of production related dioxins emissions were not included. In addition, the population of small waste incinerators with capacity less than 200 kg/hr was not known well. The knowledge of these sources was improved considerably after the passage of counter-measure law, which subjected all those source for a mandatory emission test.

2. Uncertainty in Operation Record

It is necessary for an inventory estimate to have an operation record such as incineration (or production) amount, type of material burned, and days (or hours) of operation per year. The extent of operation record utilized for an inventory calculation more or less depends on the availability of such data and the methodology adopted for an inventory calculation. It is customary to use only the most available record such as incineration amount, and then to develop an emission factor (or emission base-unit) for that quantity. Although this emission factor method is convenient for an inventory calculation, it should be cautious of using it without examining its validity. In many cases, an emission factor for a large class of emitting facilities turns out no correlation between the calculated emissions and the actual emissions.

3. Uncertainty in Test Condition

ORGANOHALOGEN COMPOUNDS

Under the counter-measure law, every subject facility must have a source test at least once a year. Therefore, no inference error will be introduced into the population of dioxins emitting facilities. However, a problem of non-representative test arises from a difference between the actual operating conditions and the plant operating condition under which a source test is conducted. Every facility subjected to the law must demonstrate that the resulting concentration from its source test (after normalized for the residual oxygen) is below the law-specified rate. Namely, 0.1 ng-TEQ/m³ for new municipal incinerators with hourly capacity >4000 kg, and 1 ng-TEQ/m³ for existing incinerators; and for industrial waste incinerators, 80 ng-TEQ/m³ until December 2002, and 5 ng-TEQ/m³ thereafter.

An official test method prescribed in JIS K 0311 simply states that 3 to 10 m³ of exhaust gas must be sampled during a source test. The test method recommends sampling to start after the facility reaches a stable burning condition. It is totally silent about the type of combustion material or the level of plant load. This allows a facility owner to manipulate the condition under which a source test is performed. In some case, the owner asks the test provider to re-test it when results of the initial test are unsatisfactory for him.

4. Uncertainty in Sampling Process

In addition to the possible non-representative source test described above, conducting a source test has many technical problems. A set-up arrangement of the Japanese sampling device is more similar to the U.S. method than to the European method. The set-up order is sampling probe, cylindrical filter, the first impinger with water, XAD-2 absorbent, the second impinger with di-ethylene glycol, and pump. The key factors for sampling are: 1) to maintain the temperature of the filter below 120 deg. C all the time, and to prevent an occurrence of break-through in the XAD-2 absorbent. The importance of these points was examined in a cooperative study done by two environmental measurement/analysis associations and city of Yokohama⁴. The same study also revealed that TEQ concentrations of the same incinerator change as much as 3 times within a normal range of the operating condition. This study indicates that a control of the exit gas temperature of boiler and the gas temperature of electric precipitator can be effective to minimize dioxins formation.

5. Uncertainty in Laboratory Analysis

Proliferation of dioxin analysis laboratories in Japan was very rapid. Now, some 80 laboratories provide dioxins analysis based on high resolution GC/MS instrument. The analysis method given by JIS K 0311 is quite complete of the quality assurance and quality control requirements for laboratory analysis of dioxins. However, the method allows two options for the position of clean-up spike: either into the sample prior to extraction or into the extract solution of the sample. Therefore, the correction using a recovery of clean-up spike means two different things under the same method: complete correction for the entire process of extraction through clean-up; and a partial correction for the clean-up process only. Furthermore, most laboratories are silent about where the clean-up spike was added in the analysis.

6. Overall Uncertainty in the Dioxins Inventory

Arithmetic for combining individual uncertainties into an overall uncertainty depends on both the type of uncertainties (errors) and the propagation characteristics of errors in each estimation process into a final estimate. Uncertainties, which are given by a combination of systematic errors (bias) and random errors, can be combined, using a statistical formula for error propagation. In general, random errors in individual measurements are decreased quickly in the sum or the mean, whereas biases tend to be added up in the final estimate. In this sense, systematic errors such as the partial correction for clean-up spike recovery and the difference in gas temperature

between during the source test and the normal operating condition must be minimized so as to obtain an unbiased estimate for dioxins inventory.

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