# USE OF MERCURY EMISSION TEST DATA FOR SETTING MACT EMISSION LIMITS FOR INDUSTRIAL BOILERS

## Background

We understand EPA plans to use emission test data to set limits for various hazardous air pollutants (or surrogates), including mercury, in the current Boiler MACT rulemaking. If EPA follows the same methodology as was used to establish emission limits for Hospital, Medical, and Infectious Waste Incinerators (HMIWI), the most critical test data will be from the "best performing" units, i.e. the 12% of the units in a subcategory with the lowest emission rates as determined from actual test results.

EPA plans to draw on two sources of emission test data for the Boiler MACT, one being the 2008 EPA survey responses, and the other being 2009 emission test results from units selected by EPA for sampling. Units were selected for 2009 sampling either to fill critical information gaps for certain subcategories or to generate additional emissions data that could be used to examine variability for some "best performing" units. For the latter, "best performing" units were identified from the 2008 survey responses.

If EPA assembles a combined emissions data set from the 2008 survey responses and the 2009 test data and then applies the HMIWI methodology to develop emission limits, there are some potential problems, at least for some pollutants. NCASI believes mercury will present significant problems for the reasons discussed below.

Most of the mercury emission test results in the 2008 survey data base are for boilers burning solid fuels, and were obtained using EPA Method 29. Method 29 was also extensively used for the mandated 2009 sampling. Thus a critical examination of results obtained with this method is needed to ensure the 2008 and 2009 data are consistent and compatible.[1]

## Method 29 Overview

In EPA Method 29, stack gas is drawn isokinetically through a sampling probe. An external heated filter captures all the particulate mercury. The gases leaving the filter pass through a series of impingers which capture gaseous mercury. The probe, filter and impinger contents are recovered by transferring the captured material, including the filter catch, wash solutions, and impinger contents, to several containers for digestion and further processing for analysis. This processing of the samples results in five sub-samples which are identified as sub-samples 1B, 2B, 3A, 3B and 3C. These samples are analyzed separately using cold vapor atomic absorption spectroscopy. A series of reagent blanks are also analyzed. The blank-corrected mercury concentrations ($\mu$g/L) in the five sub-samples are multiplied by the amount of sample liquid, and the calculated masses are summed. The sum is divided by the volume of stack gases sampled to calculate the mercury concentration in $\mu$g/m$^3$ in the stack gas. This concentration is multiplied by

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[1] Note this paper takes no position on the legal or policy issues surrounding the methods used by EPA to develop MACT emissions limitations. The purpose of this paper is simply to explain technical concerns related to the possible use of the 2008 and 2009 data in development of the Boiler MACT regulation.

the appropriate fuel F-factor, corrected for the stack gas oxygen (or $CO_2$) content, to obtain the mercury emission rate in $lb/10^{12}$Btu.

A critical aspect of Method 29 is the need to sum five different measurements (1B, 2B, 3A, 3B and 3C), each with its own detection limit, to obtain the total mass of mercury in the sample being analyzed.  In reporting results, Method 29 does not require reporting of mercury masses in each of the five sub-samples, nor does the method provide guidance as to how any non-detect values should be handled when calculating the total mass of mercury in the samples.  In the absence of such guidance, testing companies have used a variety of different procedures in summing detect and non-detect sub-samples of mercury to obtain the total mercury content of the sampled gases.

However, for the mandatory 2009 sampling, EPA wanted the mercury content of each sub-sample reported and instructed that values below the analytical detection limit should be assigned the detection limit value when the total amount of mercury in the five samples was computed.  When a calculated emission rate included a non-detect from one or more of the five sub-samples, it was to be identified with a less than (<) sign preceding the numerical value.

Thus, there is certainly the potential for reporting inconsistencies between the Method 29 results for the 2009 sampling versus the pre-2009 sampling results in the EPA survey data base.  To evaluate this possibility, NCASI obtained and reviewed a number of Method 29 sampling reports for solid fuel boilers.  The following discussion is limited to pre-2009 reports; the 2009 reports are still under review.

**Review of Pre-2009 Mercury Test Results**

NCASI obtained full sampling reports, including associated laboratory reports, for several solid fuel boilers at forest products industry facilities that had reported very low mercury emission rates, generally under 1 $lb/10^{12}$Btu heat input, in their 2008 EPA survey responses.  Reports from facilities listed in Table 1 are included in this review (some mills provided test reports for more than one boiler).

Table 2 provides detailed results of Method 29 mercury tests carried out at the facilities listed in Table 1.  It lists the laboratory detection limits (DLs) for the five different sub-samples of mercury for each test or individual test runs, when the run-by-run values were provided.  For each run, the amount of mercury measured in each sub-sample is provided.  Under the title "Total Hg in Samples, µg," the column under "Reported" shows the total µg of mercury reported as being present in the five samples and used for calculating the Hg emission rate.  The numbers in the "Protocol" column show the total µg of mercury that would be obtained if the mercury content of the samples was calculated using EPA's 2009 reporting instructions indicating values less than the detection limit should be treated as being equal to the detection limit.  It should be noted that at facilities 705 and 709, Fraction 3C was not collected and is reported as "nc." Although the current version of Method 29 allows a visual observation determination to be made as to whether Fraction 3C should be collected, not collecting Fraction 3C can result in an underestimate of the total mercury captured and introduce unnecessary errors in emission rates, even though the method detection limit is lower when Fraction 3C is not analyzed.

**Table 1**  Identification and Location of Facilities

| Facility ID | Facility |
|:---:|:---|
| 705 | Cogen South, N. Charleston, SC |
| 707 | Bowater, Catawba, SC |
| 708 | SAPPI/SD Warren, Westbrook, ME |
| 709 | Bowater, Grenada, MS |
| 710 | MeadWestvaco, N. Charleston, SC |
| 711 | SAPPI/SD Warren, Skowhegan, ME |
| 713 | Potlatch, Lewiston, ID |
| 724 | Georgia-Pacific, Phillips, WI |
| 732 | Bowater, Calhoun, TN |
| 750 | Wausau,  Rhinelander, WI |
| 754 | Masonite, Laurel, MS |
| 756 | International Paper, Ticonderoga, NY |

Note:  The North Charleston facility (ID 705 and 710) changed ownership from
MeadWestvaco to CoGen South

The results in Table 2 show that for all of the test runs (i) one or more sub-samples was at or below the method detection limit, (ii) there was a large variation in the mercury detection limits achieved by the different analytical laboratories, and (iii) the reported total mercury content of the samples was often less, and sometimes significantly less, than what was obtained using the 2009 EPA instructions for handling data below the detection limit.

Table 3 provides a summary of the Hg detection limits in µg that were achieved during the tests reported to EPA.  A histogram of these results is plotted in Figure 1.  The results show that a detection limit of ≤1.25 µg was achieved by 75 percent of the facilities and nearly 90 percent of the facilities achieved a detection limit of ≤2.0 µg.

**Table 2**  Method 29 Mercury Analysis Results, μg

| Facility ID | Boiler | Date Tested | Run No. | Fraction 1B | Fraction 2B | Fraction 3A | Fraction 3B | Fraction 3C | Total Hg in Sample, μg | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | Reported* | Protocol** |
| **705** | **Main** | | **DL** | **0.1** | **0.56** | **0.2** | **0.5** | **nc** | | **1.36** |
| 705 | Main | 11/3/2005 | 1 | <.1 | <.56 | <.2 | <.5 | nc | 0 | 1.36 |
| **705** | **Main** | | **DL** | **0.1** | **0.66** | **0.2** | **0.5** | **nc** | | **1.46** |
| 705 | Main | 11/3/2005 | 2 | <.1 | <.66 | <.2 | <.5 | nc | 0.6 | 1.46 |
| **705** | **Main** | | **DL** | **0.1** | **0.63** | **0.2** | **0.5** | **nc** | | **1.43** |
| 705 | Main | 11/3/2005 | 3 | <.1 | <.63 | <.2 | <.5 | nc | 0.5 | 1.43 |
| **705** | **Main** | | **DL** | **0.01** | **0.4** | **0.2** | **0.5** | **nc** | | **1.11** |
| 705 | Main | 11/25/2003 | 1 | 0.11 | <.4 | <.2 | 0.685 | nc | 0.8 | 1.39 |
| 705 | Main | 11/25/2003 | 2 | 0.04 | <.4 | <.2 | 0.53 | nc | 0.57 | 1.17 |
| **705** | **Main** | | **DL** | **0.01** | **0.3** | **0.2** | **0.5** | **nc** | | **1.01** |
| 705 | Main | 11/25/2003 | 3 | 0.06 | <.3 | <.2 | 0.6 | nc | 0.66 | 1.7 |
| **707** | **1** | | **DL** | **0.03** | **0.01** | **0.01** | **0.05** | **0.05** | | **0.15** |
| 707 | 1 | 4/21/2004 | 1 | 0.035 | <.42 | <0.01 | <0.05 | 0.14 | 0.15 | 0.655 |
| 707 | 1 | 4/21/2004 | 2 | 0.037 | <.48 | <0.01 | <0.05 | 0.15 | 0.19 | 0.73 |
| **707** | **2** | | **DL** | **0.03** | **0.01** | **0.01** | **0.05** | **0.05** | | **0.15** |
| 707 | 2 | 4/21/2004 | 1 | 0.086 | <.44 | <0.01 | <0.05 | 0.15 | 0.24 | 0.740 |
| 707 | 2 | 4/21/2004 | 2 | 0.074 | <.43 | <0.01 | <0.05 | 0.11 | 0.18 | 0.67 |
| **709** | **Bark Boiler** | | **DL** | **0.02** | **0.3** | **0.02** | **0.08** | **nc** | | **0.42** |
| 709 | Bark Boiler | 2/23/2007 | 1 | 0.02 | 0.3 | 0.02 | 0.89 | nc | 0.89 | 1.23 |
| 709 | Bark Boiler | 2/23/2007 | 2 | 0.02 | 0.3 | 0.02 | 0.92 | nc | 0.92 | 1.28 |
| 709 | Bark Boiler | 2/23/2007 | 3 | 0.02 | 0.3 | 0.02 | 0.85 | nc | 0.85 | 1.21 |
| **711** | **Power Boiler 2** | | **DL** | **0.015** | **0.45** | **0.005** | **0.05** | **0.05** | | **0.57** |
| 711 | Power Boiler 2 | 4/15/2008 | 1 | <0.015 | <0.45 | 0.007 | <0.05 | 0.77 | 0.78 | 1.292 |
| 711 | Power Boiler 2 | 4/15/2008 | 2 | <0.015 | <0.45 | <0.005 | <0.05 | 0.83 | 0.83 | 1.35 |

**Table 2 (Cont'd)**   Method 29 Mercury Analysis Results, μg

| Facility ID | Boiler | Date Tested | Run No. | Fraction 1B | Fraction 2B | Fraction 3A | Fraction 3B | Fraction 3C | Total Hg in Sample, μg | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | Reported* | Protocol** |
| 711 | Power Boiler 2 | 4/15/2008 | 3 | <0.015 | <0.45 | 0.017 | 0.05 | 0.93 | 0.95 | 1.462 |
| **711** | **Power Boiler 2** | | **DL** | **0.015** | **0.48** | **0.005** | **0.05** | **0.05** | | **0.6** |
| 711 | Power Boiler 2 | 4/22/2008 | 1 | <0.015 | <0.45 | <0.005 | 0.1 | 0.61 | 0.71 | 1.18 |
| 711 | Power Boiler 2 | 4/22/2008 | 2 | <0.015 | <0.47 | <0.005 | <0.05 | 0.7 | 0.75 | 1.24 |
| 711 | Power Boiler 2 | 4/22/2008 | 3 | <0.015 | <0.48 | <0.005 | 0.14 | 0.62 | 0.76 | 1.26 |
| **711** | **Power Boiler 2** | | **DL** | **0.015** | **0.48** | **0.005** | **0.05** | **0.05** | | **0.6** |
| 711 | Power Boiler 2 | 4/23/2008 | 1 | <0.015 | <0.48 | <0.005 | <0.05 | 0.78 | 0.79 | 1.33 |
| 711 | Power Boiler 2 | 4/23/2008 | 2 | <0.015 | <0.45 | 0.01 | <0.05 | 0.4 | 0.41 | 0.925 |
| 711 | Power Boiler 2 | 4/23/2008 | 3 | <0.015 | <0.45 | <0.005 | <0.05 | 0.42 | 0.42 | 0.94 |
| **713** | **4** | | **DL** | **0.030** | **0.100** | **0.010** | **0.050** | **0.050** | | **0.24** |
| 713 | 4 | 8/16/2006 | 1 | 0.07 | 0.1 | ND | ND | 0.33 | 0.5 | 0.56 |
| 713 | 4 | 8/16/2006 | 2 | 0.08 | 0.1 | ND | 0.06 | 0.47 | 0.71 | 0.72 |
| 713 | 4 | 8/16/2006 | 3 | 0.11 | 0.2 | ND | 0.08 | 0.36 | 0.75 | 0.76 |
| **724** | **Boiler Dump** | | **DL** | **0.03** | **0.08** | **0.02** | **0.1** | **0.1** | | **0.33** |
| 724 | Boiler Dump | 10/2/2003 | 1 | 0.03 | 0.08 | 0.02 | 0.04 | 0.1 | 0.4 | 0.48 |
| 724 | Boiler Dump | 10/2/2003 | 2 | 0.02 | 0.08 | 0.02 | 0.05 | 0.41 | 0.41 | 0.53 |
| 724 | Boiler Dump | 10/2/2003 | 3 | 0.02 | 0.14 | 0.02 | 0.11 | 0.39 | 0.64 | 0.68 |
| **732** | **Boiler 1** | | **DL** | **0.03** | **0.35** | **0.01** | **0.05** | **0.05** | | **0.49** |
| 732 | Boiler 1 | 10/5/2005 | 1 | ND | 10.5 | 0.18 | ND | 1.41 | 0.03 | 12.17 |
| 732 | Boiler 1 | 10/5/2005 | 2 | ND | 10.2 | 0.14 | ND | 1.36 | 0.03 | 11.78 |
| 732 | Boiler 1 | 10/5/2005 | 3 | ND | 9.46 | 0.19 | ND | 1.22 | 0.03 | 10.95 |
| **732** | **Boiler 2** | | **DL** | **0.03** | **0.33** | **0.01** | **0.05** | **0.05** | | **0.47** |
| 732 | Boiler 2 | 10/4/2005 | 1 | 0.04 | 7.54 | 0.13 | ND | 1.45 | 0.04 | 9.21 |

**Table 2 (Cont'd)**   Method 29 Mercury Analysis Results, µg

| Facility ID | Boiler | Date Tested | Run No. | Fraction 1B | Fraction 2B | Fraction 3A | Fraction 3B | Fraction 3C | Total Hg in Sample, µg | |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| | | | | | | | | | Reported* | Protocol** |
| 732 | Boiler 2 | 10/4/2005 | 2 | ND | 8.5 | 0.11 | ND | 1.17 | 0.03 | 9.86 |
| 732 | Boiler 2 | 10/4/2005 | 3 | ND | 8.58 | 0.13 | ND | 1.01 | 0.03 | 9.8 |
| **732** | **Boiler1 TDF** | | **DL** | **0.03** | **0.35** | **0.01** | **0.05** | **0.05** | | **0.49** |
| 732 | Boiler1 TDF | 10/6/2005 | 1 | 0.04 | ND | ND | ND | 0.05 | 0.03 | 0.5 |
| 732 | Boiler1 TDF | 10/6/2005 | 2 | ND | ND | ND | ND | ND | 0.03 | 0.56 |
| 732 | Boiler1 TDF | 10/6/2005 | 3 | 0.1 | ND | ND | ND | ND | 0.05 | 0.59 |
| **732** | **Boiler 1 Bark** | | **DL** | **0.03** | **0.45** | **0.01** | **0.05** | **0.05** | | **0.59** |
| 732 | Boiler 1 Bark | 10/7/2005 | 1 | 0.05 | ND | 0.03 | ND | 0.27 | 0.05 | 0.85 |
| 732 | Boiler 1 Bark | 10/7/2005 | 2 | 0.04 | ND | 0.02 | ND | 0.33 | 0.04 | 0.94 |
| 732 | Boiler 1 Bark | 10/7/2005 | 3 | 0.04 | ND | 0.04 | ND | 0.18 | 0.04 | 0.75 |
| **732** | **Boiler 2 TDF** | | **DL** | **0.03** | **0.46** | **0.01** | **0.05** | **0.05** | | **0.6** |
| 732 | Boiler 2 TDF | 10/6/2005 | 1 | ND | ND | ND | ND | ND | 0.05 | 0.6 |
| 732 | Boiler 2 TDF | 10/6/2005 | 2 | 0.05 | ND | ND | ND | ND | 0.03 | 0.61 |
| 732 | Boiler 2 TDF | 10/6/2005 | 3 | 0.03 | ND | ND | ND | 0.06 | 0.04 | 0.58 |
| **732** | **Boiler 3** | | **DL** | **0.03** | **0.36** | **0.01** | **0.05** | **0.05** | | **0.5** |
| 732 | Boiler 3 | 10/5/2005 | 1 | ND | 3.21 | 0.02 | ND | 0.83 | 0.04 | 4.14 |
| 732 | Boiler 3 | 10/5/2005 | 2 | ND | 2.91 | 0.02 | ND | 0.71 | 0.03 | 3.72 |
| 732 | Boiler 3 | 10/5/2005 | 3 | 0.05 | 3.18 | 0.01 | ND | 0.79 | 0.1 | 4.08 |
| **732** | **Boiler 2 Bark** | | **DL** | **0.03** | **0.5** | **0.01** | **0.05** | **0.05** | | **0.64** |
| 732 | Boiler 2 Bark | 10/7/2005 | 1 | 0.05 | ND | 0.03 | ND | 0.28 | 0.03 | 0.91 |
| 732 | Boiler 2 Bark | 10/7/2005 | 2 | ND | ND | 0.02 | ND | 0.33 | 0.05 | 0.91 |
| 732 | Boiler 2 Bark | 10/7/2005 | 3 | ND | ND | 0.02 | ND | 0.22 | 0.03 | 0.82 |

**Table 2 (Cont'd)**   Method 29 Mercury Analysis Results, µg

| Facility ID | Boiler | Date Tested | Run No. | Fraction 1B | Fraction 2B | Fraction 3A | Fraction 3B | Fraction 3C | Total Hg in Sample, µg | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | Reported* | Protocol** |
| **750** | **26** | | **DL** | **0.1** | **0.5** | **0.2** | **0.6** | **0.4** | | **1.8** |
| 750 | 26 | 9/7/2007 | 1 | <0.1 | <.5 | <0.2 | <.6 | 1.93 | 1.93 | 3.33 |
| 750 | 26 | 9/7/2007 | 2 | <0.1 | <.5 | <0.2 | <.6 | 0.826 | 0.826 | 2.226 |
| 750 | 26 | 9/7/2007 | 3 | <0.1 | <.5 | <0.2 | <.7 | 1.1 | 1.1 | 2.6 |
| **750** | **20-23** | | **DL** | **0.1** | **0.5** | **0.2** | **0.7** | **0.4** | | **1.9** |
| 750 | 20-23 | 9/7/2007 | 1 | <0.1 | 0.902 | <0.2 | <.7 | 0.667 | 1.57 | 2.569 |
| 750 | 20-23 | 9/7/2007 | 2 | <0.1 | 1.36 | <0.2 | <.7 | 0.492 | 1.85 | 2.852 |
| 750 | 20-23 | 9/7/2007 | 3 | <0.1 | 2.05 | <0.2 | <.7 | 0.506 | 2.56 | 3.556 |
| **754** | **15** | | **DL** | **0.2** | **0.95** | **0.4** | **1** | **nc** | | **2.55** |
| 754 | 15 | 3/4/2005 | 1 | <.2 | <.95 | <.4 | <1 | nc | 2.55 | 2.55 |
| 754 | 15 | 3/4/2005 | 2 | <.2 | <.92 | <.4 | <1 | nc | 2.55 | 2.52 |
| 754 | 15 | 3/4/2005 | 3 | <.2 | <1 | <.4 | <1 | nc | 2.55 | 2.6 |
| **756** | **Power Boiler** | | **DL** | **0.03** | **0.01** | **0.01** | **0.05** | **0.05** | | **0.15** |
| 756 | Power Boiler | 9/15/1999 | 1 | 0.0395 | 0.64 | <0.01 | <0.05 | 0.61 | 1.04 | 1.3105 |
| 756 | Power Boiler | 9/15/1999 | 2 | 0.16 | 0.8 | <0.01 | <0.05 | 0.43 | 1.13 | 1.411 |
| 756 | Power Boiler | 9/15/1999 | 3 | 0.1 | 0.78 | 0.13 | <0.05 | 0.49 | 1.11 | 1.511 |
| 756 | Power Boiler | 9/15/1999 | 4 | 0.05 | 0.83 | <0.01 | <0.05 | 0.62 | 1.02 | 1.521 |
| 756 | Power Boiler | 9/20/1999 | 5 | 0.03 | 0.67 | <0.01 | 0.16 | 0.28 | 0.83 | 1.111 |
| 756 | Power Boiler | 9/22/1999 | 1 | 0.03 | 0.67 | <0.01 | 0.068 | 1.4 | 1.86 | 2.139 |
| 756 | Power Boiler | 9/22/1999 | 2 | 0.03 | 0.75 | <0.01 | <0.05 | 1 | 1.52 | 1.801 |
| 756 | Power Boiler | 9/22/1999 | 3 | 0.064 | 0.84 | <0.01 | 0.14 | 1.8 | 2.53 | 2.815 |
| 756 | Power Boiler | 9/22/1999 | 4 | 0.0455 | 0.77 | <0.01 | 0.11 | 0.8 | 1.42 | 1.6965 |
| 756 | Power Boiler | 9/22/1999 | 5 | 0.03 | 0.69 | <0.01 | 0.13 | 1.4 | 1.94 | 2.221 |

**Table 2 (Cont'd)**   Method 29 2Mercury Analysis Results, µg

| Facility ID | Boiler | Date Tested | Run No. | Fraction 1B | Fraction 2B | Fraction 3A | Fraction 3B | Fraction 3C | Total Hg in Sample, µg | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | Reported* | Protocol** |
| 756 | Power Boiler | 9/22/1999 | 1 | 0.031 | 0.77 | <0.01 | <0.05 | 0.73 | 1.27 | 1.552 |
| 756 | Power Boiler | 9/23/1999 | 2 | 0.03 | 0.74 | <0.01 | <0.05 | 0.78 | 1.29 | 1.571 |
| 756 | Power Boiler | 9/23/1999 | 3 | 0.03 | 0.7 | <0.01 | <0.05 | 0.63 | 1.1 | 1.381 |
| 756 | Power Boiler | 9/23/1999 | 4 | 0.03 | 0.85 | <0.01 | <0.05 | 0.44 | 1.04 | 1.341 |
| 756 | Power Boiler | 9/23/1999 | 5 | 0.03 | 0.71 | <0.01 | 0.079 | 0.54 | 1.94 | 1.33 |

*Reported - µgs of mercury in the sample reported by the facility

**Protocol - µgs of mercury in the sample calculated according to EPA's protocol, i.e., treat all < values as actual

**Table 3** Hg Detection Limits Achieved at Tested Sources

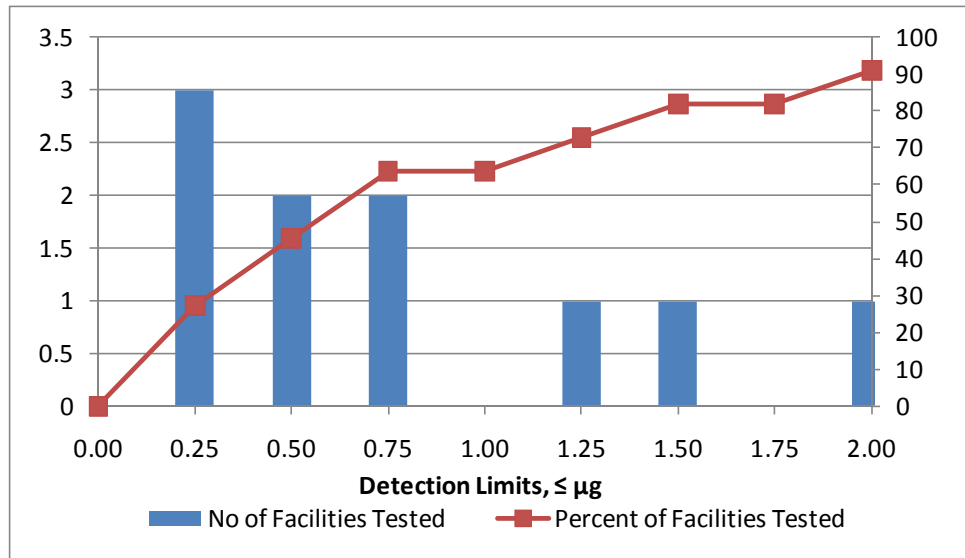| Detection Limit, µg | No. of Facilities | Cumulative Total | Cumulative Percent of Total |
|---|---|---|---|
| 0 | 0 | 0 | 0 |
| 0 - 0.25 | 3 | 3 | 27 |
| >0.25 - 0.5 | 2 | 5 | 45 |
| >0.5 - 0.75 | 2 | 7 | 64 |
| >0.75 – 1 | 0 | 7 | 64 |
| >1 - 1.25 | 1 | 8 | 73 |
| >1.25 - 1.5 | 1 | 9 | 82 |
| >1.5 - 1.75 | 0 | 9 | 82 |
| >1.75 – 2 | 1 | 10 | 91 |
| >2.0 | 1 | 11 | 100 |



**Figure 1** Detection Limit Histogram

Table 4 provides a comparison of the reported mercury emission rates to the emission rates that would be reported using the 2009 EPA instructions regarding data below method detection limits. The comparison shows all of recalculated emission rates have a less than (<) sign associated with them, but the numerical values are consistently higher than those in reported to EPA in the 2008 survey responses.

This review of a limited number of pre-2009 stack tests shows the mercury analysis results data were not reported in a consistent manner, and the reported mercury emission rates will not be compatible with emission rates for the mandatory 2009 testing since these will be reported in accordance with EPA's specific instructions. Therefore, unless a thorough review of the pre-

2009 mercury stack test results is undertaken and appropriate adjustments are made to the reported emission rates, the pre-2009 survey responses cannot be combined with the 2009 test results.

**Table 4** Comparison of Mercury Emission Rates

| Facility ID | Boiler | Test Date | Hg Emission Rate, lb/$10^{12}$ Btu | |
| | | | Reported by Mill | Calculated by Protocol |
| --- | --- | --- | --- | --- |
| 705 | Main | 11/25/2003 | 0.166 | <0.349 |
| 707 | 1 | 4/21/2004 | 0.128 | <0.583 |
| 707 | 2 | 4/21/2004 | 0.243 | <0.812 |
| 708 | 21 | 11/28/2008 | 0.309 | <0.314 |
| 708 | 21 | 12/19/2007 | 0.104 | <0.158 |
| 709 | Bark | 2/23/2007 | 0.47 | <0.65 |
| 710 | Main | 11/3/2005 | 0.23 | <0.51 |
| 711 | PB2 | 4/15/2008 | 0.37 | <0.594 |
| 711 | PB2 | 4/24/2008 | 0.339 | <0.562 |
| 711 | PB2 | 4/22/2008 | 0.228 | <0.452 |
| 713 | 4 | 8/16/2006 | 0.249 | <0.25 |
| 724 | Bdump | 10/2/2003 | 0.393 | <0.456 |
| 732 | 1 | 10/5/2005 | 0.01790 | <6.9417 |
| 732 | 2 | 10/5/2005 | 0.02123 | <6.0538 |
| 732 | 3 | 10/5/2005 | 0.02566 | <2.7774 |
| 732 | NBFB | 10/5/2005 | 0.01822 | <0.3560 |
| 732 | SBFB | 10/5/2005 | 0.01493 | <0.3310 |
| 732 | NBFB | 10/5/2005 | 0.02831 | <0.2690 |
| 732 | SBFB | 10/5/2005 | 0.01568 | <0.2571 |
| 750 | 26 | 9/7/2007 | 0.4771 | <1.01 |
| 750 | 20-23 | 9/7/2007 | 1.602 | <2.405 |
| 754 | 15 | 3/4/2005 | 1.877 | <1.89 |
| 756 | | 9/15/1999 | 0.2518 | <0.425 |
| 756 | | 9/22/1999 | 0.4598 | <0.669 |
| 756 | | 9/23/1999 | 0.3436 | <0.479 |

This review of the pre-2009 survey responses for mercury also suggests the identification of "best performing" units for mercury will not be straightforward due to detection limit issues with Method 29.  Although we have not yet completed review of the 2009 sampling reports, the preliminary results strongly suggest there will be similar detection limit issues for boilers with very low mercury emission rates, which will be especially significant for a biomass subcategory. The problem will be compounded by the often significant differences in mercury detection limits

achieved by the different laboratories, which will lead to differences in emission rates identified as "non-detect." Further, application of the HMIWI methodology to address variability will be severely compromised when values which are either below the detection limit or close to the detection limit are present in the MACT pool of units with the lowest emission rates. This problem is caused by the problems associated with quantifying pollutants at or near detection limits, as explained below.

All measurements have errors associated with them. These errors consist of systematic errors, if the method is biased, and random errors. Thus, even in the absence of any systematic errors, random errors cause replicate measurements to vary from run to run, although the average of such random errors is zero when the number of replicates is high. In general, the magnitude of the random error decreases as a fraction of the measured value as the value of the measured parameter increases. In practice, when the measured value of a parameter is much higher than the potential for random error, there is a high degree of confidence in the measured value obtained from a single or a few runs. However, as the measured value decreases, the potential contribution of the random error to the measured value increases, thus decreasing the confidence level in the measured value from a single or a few runs until the point where the measured value cannot be distinguished from the random error.

Analytical chemists have for a long time been concerned about their ability to determine whether or not an analyte is present in a sample and, if it is present, what is its true level. This has given rise to two important concepts: limit of detection and limit of quantitation. In general terms, an analytical method detection limit is defined as the lowest concentration that can be distinguished from the blank at a defined level of statistical significance. The quantitation limit for a method is defined as the smallest concentration of the analyte which can be measured where the accuracy achieves the objectives of the measurement.

Low quantitation limits of a test method do not create measurement challenges when the pollutant concentration being targeted for measurement is well above the quantitation limit. However, when the concentration being measured is below the quantitation limit of the method, caution is required in interpreting the data. EPA's air program has not had many reasons to deal with this issue as most air emission standards have been set at levels well above such limits. However, EPA has faced this challenge in its water program for many years since the water quality standards for many pollutants in streams are well below the analytical capabilities of the methods to measure them. In a 2005 memorandum (EPA 2005) regarding effluent limits that are greater than zero but less than the minimum level, which is defined as "the concentration at which the entire analytical system must give a recognizable signal and an acceptable calibration point," EPA has stated the following:

> "The NPDES permit should state that any sample analyzed in accordance with a method having appropriate method detection limit (MDL) and minimum level (ML) and found to be below the ML will be considered in compliance with the permit limits unless other monitoring information indicates a violation."

Possible approaches for addressing the non-detect issues in the context of MACT emission limits are discussed in the next section.

**Setting Emission Limits When Test Methods Give Results Below or Close to Detection Limits**

As noted above, measurements below the quantitation limit of a test method cannot be reliably reproduced. Consequently, EPA needs to calculate the quantitation limits of all the tests which constitute the best performing 12 percent of the boilers to determine whether or not the reported value is above the quantitation limit. A number of different techniques are available for establishing analytical method quantitation limits (Coleman et al. 1997, Corley 2003, Currie 1999, Voightman 2008). In its October 2004 report EPA conducted a detailed review of detection and quantitation approaches (EPA 2004). In its simplest form the minimum level of quantitation of a method may be calculated by multiplying the method detection limit by 3.18 and rounding the results to the nearest whole number (EPA 2004, pp. 5-35). Unfortunately, at the present time EPA does not have the method detection limit data for the tests at facilities whose test results are in its database. Instead, EPA has information only on the analytical detection limits achieved by the analytical laboratories which analyzed the mercury samples. EPA could generate method detection and quantitation information through a multi-source, multi-laboratory study. It is reasonable to assume that the random errors associated with sampling would add to the currently reported laboratory analytical detection limits for the tests in EPA's database. EPA could account for this by raising the analytical detection limit multiplier to a higher value than 3.18 to estimate the method quantitation limit for the tests at each facility.

Once the quantitation limit of each of the lowest emitting 12 percent of the sources has been calculated, the reported emission rates can be compared to the quantitation limit for each emission test. If the emission rate is below the quantitation limit, the reported value would be replaced with the quantitation limit. Emission rates above the quantitation limit would not be changed. The revised set of emission rates would then be suitable for use in standard setting. Note that any standard that is based on such data should be set no lower than the highest quantitation limit from the emissions tests being used. As an alternative, it may be more appropriate to rank the quantitation limits for all the emission tests for the subcategory, not just the lowest 12%, and then pick the quantitation limit achieved by 95 percent of the laboratories, as recommended by the Federal Advisory Committee (Federal Advisory Committee 2007, p. 37).

**References**

Coleman, D., Auses, J., and Grams, N. 1997. Regulation – from an industry perspective or relationships between detection limits, quantitation limits, and significant digits. *Chemometrics and Intelligent Laboratory Systems* 37:71-80.

Corley, J. 2003. Best practices in establishing detection and quantification limits for pesticide residues in foods. *In* Handbook of Residue Analytical Methods for Agrochemicals. John Wiley & Sons Ltd.

Currie, L.A. 1999. Detection and quantitation limits: origins and historical overview. *Analytica Chimica Acta* 391:127-134.

Environmental Protection Agency (EPA). 2004. Revised assessment of detection and quantitation approaches. Washington, DC: Engineering and Analysis Division, Office of Science and Technology, Office of Water. EPA-821-B-04-005.

Environmental Protection Agency (EPA). 2005. Memorandum from Cindi Godsey, Michael Lidgard, and Kim Ogle to NPDES Permits Unit Consistency Book. Guidance on Water Quality Based Effluent Limits Set Below Analytical Detection/Quantitation Limits.

Federal Advisory Committee on Detection and Quantitation Approaches and Uses in Clean Water Act Programs. 2007. Final report to US EPA, submitted December 2007.

Voightman, E. 2008. Limits of detection and decision. Part 1. *Spectrochimica Acta Part B* 63:115-128.