North Carolina Department of Environment and Natural Resources
Division of Air Quality

Michael F. Easley, Governor

William G. Ross, Jr., Secretary
B. Keith Overcash, P.E., Director

MEMORANDUM

TO: Section Chiefs
Regional Supervisors

FROM: Keith Overcash

DATE: June 11, 2008

SUBJECT: Emission Factor for Wood-fired Industrial Boilers for 1,2,3,6,7,8-HxCDD

The Air Quality Committee requested the Division of Air Quality (DAQ) to develop additional information on how reliable the 1,2,3,6,7,8-Hexachlorodibenzo-p-dioxin (1,2,3,6,7,8-HxCDD, CAS # 57653-85-7) emission factor (EF) is for wood boilers. Review of the EPA AP-42 spreadsheet revealed that the HxCDD EF of 1.6 E-6 lb/MMBtu in AP-42 Table 1.6.3 was actually for 'Total HxCDD' (CAS# 34465-46-8) and not 1,2,3,6,7,8-HxCDD.

Another EPA published report (Dioxin Inventory Report) with a 1,2,3,6,7,8-HxCDD EF for wood combustion was found.[1] It is a peer reviewed final report representing EPA's assessment of all major dioxin emission sources. The Dioxin Inventory Report presented the EF data in units of ng dioxin /kg wood, and DAQ converted the data into units of lb/MM Btu (pounds per million British thermal units). The new 1,2,3,6,7,8-HxCDD EF for wood boilers is 1.79 E-11 lb/MMBtu for dry wood (8,000 Btu/lb), and 3.18 E-11 lb/MMBtu for wet wood (4,500 Btu/lb).

Staff in several DAQ sections and regions reviewed the attached technical document on the basis of the recommended update of the subject EF and found it acceptable. The new 1,2,3,6,7,8-HxCDD EF should be used for permitting and compliance determinations of wood-fired industrial boilers.

Any questions regarding the technical aspects of the emission factor update should be directed to Mr. Steve Schliesser at (919) 715-2694 or Mr. Todd Pasley at (919) 733-2014.

Attachment

Cc: Brock Nicholson
Steve Schliesser
Todd Pasley

[1] U.S. EPA (Environmental Protection Agency). (2006) An inventory of sources and environmental releases of dioxin-like compounds in the United States for the years 1987, 1995, and 2000; EPA/600/P-03/002F. Available in May 2008 from http://cfpub.epa.gov/ncea/cfm/recordisplay.cfm?deid=159286.

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North Carolina Department of Environment and Natural Resources
Division of Air Quality

Michael F. Easley, Governor

William G. Ross, Jr., Secretary
B. Keith Overcash, P.E., Director

April 28, 2008

MEMORANDUM

TO: Emission Inventory Work Group

THROUGH: Lori Cherry, Supervisor
Toxics Protection Branch

FROM: Steve Schliesser, Environmental Engineer II
Todd Pasley, Environmental Engineer I
Toxics Protection Branch

SUBJECT: Review and Recommended Update of the DAQ Emission Factor for 1,2,3,6,7,8-Hexachlorodibenzo-p-dioxin from Wood Combustion

Introduction

The Air Quality Committee (AQC) requested the Division of Air Quality to develop additional information on how reliable and representative the 1,2,3,6,7,8-Hexachlorodibenzo-p-dioxin (1,2,3,6,7,8-HxCDD) emission factor (EF) is for wood boilers. The basis driving AQC's interest included the following:

- DAQ performed a risk assessment study for the AQC in response to the combustion sources exemption from NC Air Toxics rules under 2Q .0701 during 2005 – 2007.
  - From the 1800 permitted combustion sources in the state, the original risk assessment showed 62 units posed risks levels of concern, and 53 of those were wood-fired boilers. These wood boilers presented the highest exposure results in the Asheville and Winston-Salem areas and the risks were driven primarily (> 90%) on exposure to 1,2,3,6,7,8-HxCDD. Emissions for this toxic compound were calculated from an AP-42 emission factor, with its toxicity potency factor being much higher than other toxic pollutants (except for 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD).
  - Review of the 1,2,3,6,7,8-HxCDD AP-42 EF data shows it to be three orders of magnitude greater than other dioxin compound EFs and that five of the six AP-42 tests used to derive dioxin EFS were from wet wood fired boilers.
  - The 1,2,3,6,7,8-HxCDD AP-42 EF has a high standard deviation (>2 times the average), with two of the six tests accounting for the high degree of variability, and the data from two tests eligible for consideration as outliers.
  - Given the above, DAQ found compound-specific EF data for NC burned woodwaste from a different, credible EPA source compiled from industry and state agency test data.

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Basis and Recommendation for Revised 1,2,3,6,7,8-HxCDD EF for Wood Combustion

Statement of the Problem

The DAQ Toxics Program specifically identifies 1,2,3,6,7,8-HxCDD (CAS # 57653-85-7) as one of the two dioxin compounds for the control of toxic air pollutants listed in 2D .1104 for acceptable ambient levels. However, a thorough review of the AP-42 test data details spreadsheet revealed that the HxCDD EF of 1.6 E-6 lb/MMBtu in AP-42 Table 1.6.3 was actually for "Total HxCDD" (CAS# 34465-46-8), as Table 1.6.3 identifies it as simply "Hexachlorodibenzo-p-dioxins." While both compounds have the same molecular weight, there is a small but profound difference in their compound structure, emission factor, toxicity potency, and CAS (chemical abstract service) numbers. In simple terms, 1,2,3,6,7,8-HxCDD is only one of several specific isomers that are contained in Total HxCDD—along with 1,2,3,4,7,8- (CAS # 39227-28-6) and 1,2,3,7,8,9-HxCDD (CAS # 19408-74-3) to name a few.

The AP-42 "total HxCDD" EF was conservatively applied to 1,2,3,6,7,8-HxCDD, the specific TAP compound of interest. The non-controversial solution is to apply pollutant-specific data for 1,2,3,6,7,8-HxCDD available in other EPA literature.

Statement of the Solution

A 677-page EPA published report (Dioxin Inventory Report) with a 1,2,3,6,7,8-HxCDD EF for wood combustion was found.[1] It is a peer reviewed and final report representing EPA's assessment of all major dioxin sources and their air emissions. To the extent practical, the inventory is a comprehensive analysis of all major dioxin sources, including wood combustion in industrial boilers. Over 800 references were reviewed and cited in the preparation of this report. The citations reflect publications up to the year 2003, with the final report peer-reviewed by an expert panel. David Cleverly, one of the report's primary authors, sent a workable spreadsheet file containing the EF data and discussed it with DAQ staff. The file contained the EPA EF data in units of ng dioxin /kg wood and allowed DAQ to convert the data into our units of lb/MM Btu (pounds per million British thermal units).

Section 4.2.2 of the the Dioxin Inventory Report contains information on industrial wood combustion emissions collected largely by CARB (California Air Resources Board) at 4 facilities and by NCASI (National Council of the Paper Industry for Air and Stream Improvement) at 5 facilities. Both CARB and NCASI conducted tests with a variety of permitted types of wood waste as fuel, including bark, coarse wood waste, sawdust, urban wood waste, wood chips, wood residue, and agriculture waste. The tests were performed on electric generating and wood products boilers with either multicyclones and/or electrostatic precipitators (ESPs) for emission controls. The dioxin emission factors are based on tests conducted at nine facilities in two industries (paper and allied products, and lumber and wood products) that account for 97% of total industrial wood fuel combustion. The remaining 3% of industrial wood combustion may not be well represented by these emission factors, particularly if poorly controlled combustors or treated wood (e.g., treated with pentachlorophenol or plastics) are burned.

Average results for the 4 CARB and 5 NCASI tests with non-detected results set to one-half the detection limit are presented in Table 4-14 of the Dioxin Inventory Report. Specific values for 1,2,3,6,7,8-HxCDD average results for the CARB and NCASI tests are presented in Table 1 below

[1] U.S. EPA (Environmental Protection Agency). (2006) An inventory of sources and environmental releases of dioxin-like compounds in the United States for the years 1987, 1995, and 2000. National Center for Environmental Assessment, Washington, DC; EPA/600/P-03/002F. Available from: National Technical Information Service, Springfield, VA, and online at http://epa.gov/ncea, and in April 2008 from http://cfpub.epa.gov/ncea/cfm/recordisplay.cfm?deid=159286.

for both sets of units (ng dioxin/kg wood and lb/MMBtu). The overall average results for dioxins and furans in the CARB tests are approximately twice that of the NCASI results, while the 1,2,3,6,7,8-HxCDD average results for the CARB and approximately half the NCASI tests. Both sets of data are considered to be in reasonable agreement with the other. Table 2 summarizes the process conditions of the dioxin tests reported by CARB and NCASI.

Table 1. Emission Factors from Dioxin Inventory Report

Congener 1,2,3,6,7,8-HxCDD	**4 CARB tests**	**5 NCASI tests**	**Average of 9 tests by CARB and NCASI**
EF, ng dioxin / kg wood			
Various forms of wood wastes – independent of heat content	0.096	0.193	0.143
EF, lb/MMBtu			
Dry wood of 8,000 Btu/lb.	1.20 E-11	2.41 E-11	1.79 E-11
Wet wood of 4,500 Btu/lb.	2.13 E-11	4.29 E-11	3.18E-11

Units conversion from ng dioxin/kg wood to lb dioxin/ MMBtu wood = 1E-6/ X Btu/lb

- Example Dry wood with 8,000 Btu/lb: 1E-6 / 8 E3 Btu/lb = 1.25 E-10

Table 2. Summary of CARB and NCASI Dioxin Emission Tests

Test	**Industry**	**Type of Wood Fired**	**Boiler Type**	**Particulate Emission Controls**	**Average Dioxin TEQ EF, ng I-TEQ_{DF}/kg wood**
4 CARB tests					
1	Electric generator	Course wood waste & sawdust	Quad-cell	Multicyclone	0.64
2	Electric generator	Wood waste & urban wood waste	Spreader stoker	ESP	0.82
3	Electric generator	Wood waste & agricultural waste	Fluidized bed	Multicyclone & ESP	1.32
4	Unspecified	Wood chips & bark	Quad-cell	Multicyclone & ESP	0.5
5 NCASI tests					
1	Wood products, pulp and paper	Bark & wood residue	Unspecified	Multicyclone	0.46
2			Unspecified	ESP	
3-5			Spreader stoker	Multicyclone or ESP	

Average Dioxin TEQ EF, ng I-TEQ_{DF}/kg wood: TEQ = toxicity equivalence. I-TEQ refers to the international TEF scheme adopted by EPA in 1989. TEQ covers the mixture of dioxin and furan compounds, derived from a toxicity weighting system that converts all mixture components to a single value normalized to the toxicity of 2,3,7,8-TCDD.

Table 3 presents the AP-42 EF for Total HxCDDs from AP-42 and the Dioxin Inventory of Sources Report Proposed EF for 1,2,3,6,7,8-HxCDD in the same units. The AP-42 EF is approximately 50,000 to 90,000 higher than the Dioxin Inventory Report EF for wet wood and dry wood respectively, and is clearly not in reasonable agreement with the other EPA emission factors.

Table 3. Emission Factor Comparison between AP-42 and Dioxin Inventory of Sources Report

Wood	**AP-42 EF for Total HxCDD**	**Proposed EF for 1,2,3,6,7,8-HxCDD**	**Ratio of Total HxCDDs / 1,2,3,6,7,8-HxCDD**
	lb dioxin/ MMBtu wood		
Dry wood	1.6 E-6	1.79 E-11	89239
Wet wood		3.19 E-11	50197

Recommendation

It is recommended to change the Woodwaste Combustion EF for 1,2,3,6,7,8-HxCDD to be aligned with the Dioxin Inventory of Sources Report rather than the AP-42 EF for Total HxCDDs. It is expected that these emission factors would apply to 97% of woodwaste burned in NC.

Enclosure

cc: Person A
Person B
Person C w/o enclosures

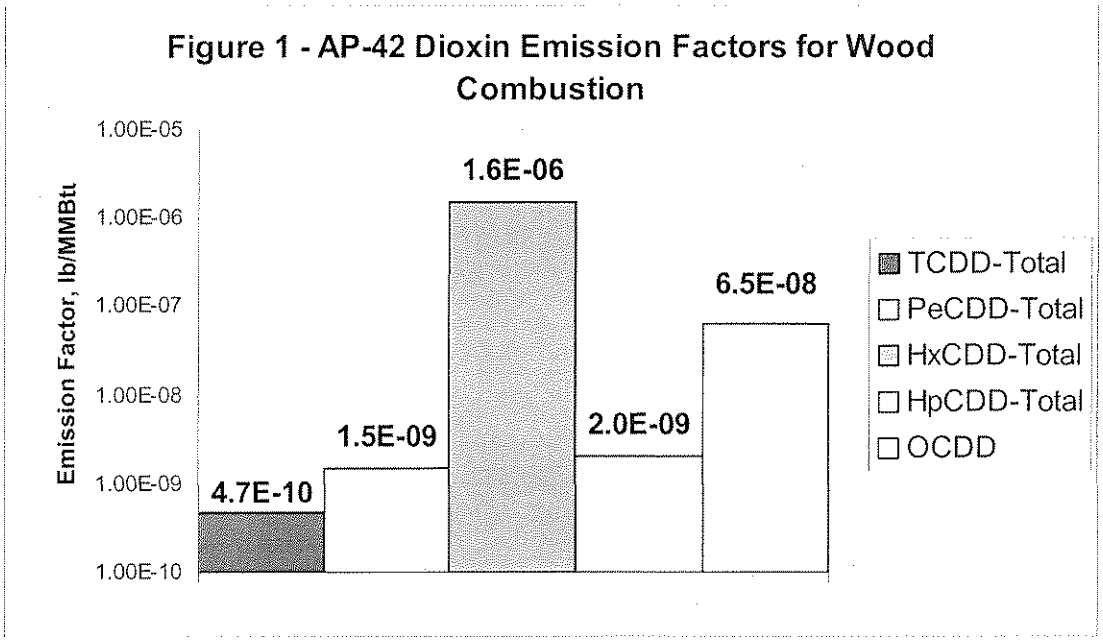
ATTACHMENT
Wood-fired Boilers Emission Factors for Dioxins

The Attachment is an excerpt from the March 2007 report to the AQC, and provides the basis for the AQC's request to further investigate the 1,2,3,6,7,8-HxCDD EF issue. It discusses and illustrates the points mentioned in the Introduction, namely:

- Risk were driven primarily (> 90%) on exposure to 1,2,3,6,7,8-HxCDD based on an AP-42 EF.
- Review of 1,2,3,6,7,8-HxCDD AP-42 EF data shows it to be 3 orders of magnitude greater than other dioxin EFs, and 5 of the 6 AP-42 tests used to derive dioxin EFs were from wet wood fired boilers.
- The 1,2,3,6,7,8-HxCDD AP-42 EF has a high standard deviation, with 2 of the 6 tests accounting for the high variability and eligible for consideration as outliers.

Excerpt from March 2007 Report to the Air Quality Committee

"The last bullet point, representativeness, was one issue raised at the September 13, 2006 AQC meeting regarding emission factors for dioxins from wood-fired boilers. To address this issue, the background test data used to develop these emission factors was analyzed. Figure 1 shows the EPA emission factors for five poly-chlorinated dioxin homologues, grouped according to the number of chlorine atoms in each compound. The graph shows the HxCDD emission factor is one to three orders of magnitude (10 to 1000 times) greater than other dioxin compound emission factors.



EPA developed each dioxin emission factor by:

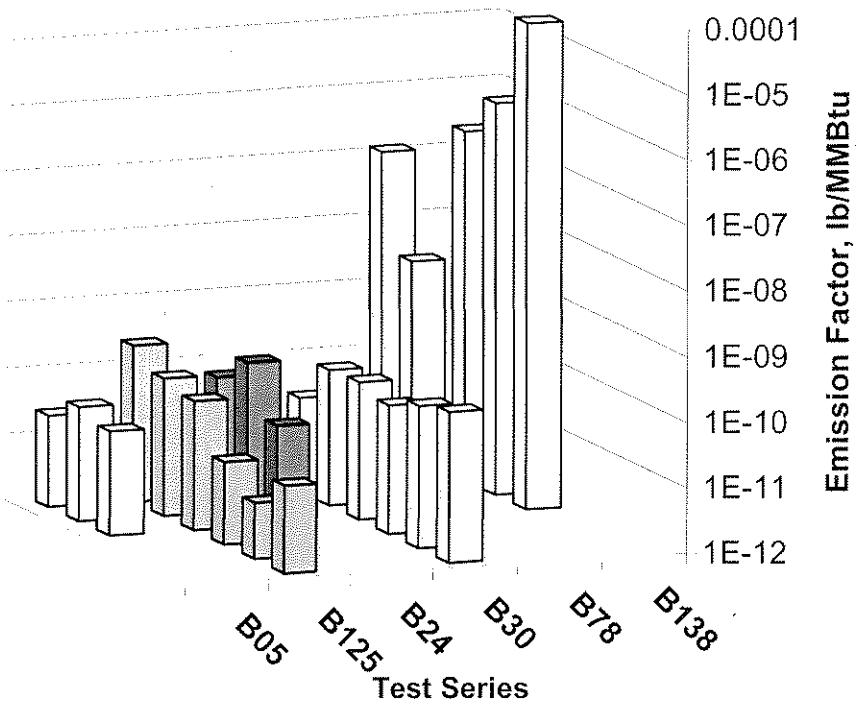
- Measuring the dioxin emission rates and boiler heat rates at several different wood-fired boilers, featuring several different combinations of wood type (wet wood, dry wood), burner configurations, and pollution control equipment, and
- Calculating an average emission factor for each dioxin homologue, applicable across all wood-fired boiler operation scenarios.

Table 1 shows the test data, from six different test series (one test series for each boiler tested), used to calculate the average HxCDD emission factor. First, individual emission factors for each test series were averaged. To determine the overall HxCDD emission factor, the test series averages were then averaged again, giving an emission factor of 1.6 $x10^{-6}$ lb/MMBtu with a standard deviation of 3.8 $x10^{-6}$ lb/MMBtu.
Such a high standard deviation (~2.4 times the average) reflects a high degree of variability in the data. This can be seen in Figure 2, which presents the data graphically. Figure 2 shows the number of results in each test series and how the results from the first four test series (B05, B125, B24, and B30) are more comparable than the last two series (B78 and B135). Note there is a larger body of data (18 runs) in the first four test series forming a more similar pattern than the smaller body of data (5 runs) in the last two test series.

Table 1 - HxCDD Emission Factor Development Data

Test Series	Test ID	Sampling Method	Measured Emission Factor, lb HxCDD/MMBtu			# Sampling Runs In Test Series	Test Series Average
			Run 1	Run 2	Run 3		
B05	A008.001	EPA Method 23	2.51E-11	5.64E-11	3.96E-11	3	4.04E-11
B125	E521.004	EPA Method 23	2.42E-10	1.27E-10	9.48E-11		
	E522.004	EPA Method 23	1.85E-11	7.27E-12	2.21E-11	6	8.53E-11
B24	E28.001	CARB Method 428	6.55E-11	1.82E-10	3.32E-11	3	9.36E-11
B30	E833.003	CARB Method 428	2.65E-11	1.17E-10	1.27E-10		
	E833.004	CARB Method 428	9.37E-11	1.52E-10	2.04E-10	6	1.20E-10
B78	E625.002	Not Reported	1.24E-07	4.27E-09		2	6.41E-08
B138	E650.002	EPA Modified Method 5	2.13E-07	9.63E-07	2.67E-05	3	9.29E-06
						Min	4.04E-11
						Max	9.29E-06
						Average	**1.56E-06**
						Standard Deviation	**3.79E-06**

Figure 2 - HxCDD Emission Factor Development Data



While the TCDD toxicity potency is ten times that of HxCDD, the risk assessment results for wood-fired boilers are driven by HxCDD. From Table 1 it can be shown that the emission factor for HxCDD is 3400 times higher than TCDD. Table 2 presents the emission factor, potency factor, and the multiplication product of these two factors to illustrates why HxCDD drives the risk assessment so much more than TCDD.

Table 2 – TCDD and HxCDD Emission and Potency Factors

Dioxin Homologue	Emission Factor	Toxicity Equivalency Potency Factor [a]	Product of Emission and Potency Factors [b]
TCDD	4.7 E-10	1.0	4.7E-10
HxCDD	1.6E-6	0.1	1.6E -7

a – Obtained from the HAP library file used in EPA Human Exposure Model.
b – Multiplication product showing that HxCDD has a 300-fold stronger impact in risk assessment calculations than TCDD.

Furniture Industry Boiler Emission Factors

In the previous AQC meeting, DAQ reported the furniture manufacturers association was in the process of voluntarily planning to conduct emission tests related to dioxin emission factors. The

industry noted there is little information available about emission factor derivation for dioxins from burning different types of wood. Their standard practice is to burn wood that is kiln-dried and of small size, like shavings or saw dust. Such wood has more heating value and burns more completely than wet wood or wood of larger size. Given this advantage in combustion quality, there is reason to expect less products of incomplete combustion, such as dioxins, for furniture industry wood relative to wet wood combustion.

Table 3 includes information on the types of wood, boiler, and emission control for the data used to derive the EPA HxCDD emission factor. Note the dioxin emission factors are more representative of wet than dry wood, given 5 of the 6 tests used to derive emission factors were based on burning wet wood. Also note the highest emission factor test (ID B138) was from burning wet wood, and treating it as an outlier (removing it from the data set) would reduce the emission factor by a factor of 100. Instead of conducting an emission test, the industry now plans to develop technical arguments for more suitable furniture industry wood combustion dioxin emission factors for DAQ consideration.

Table 3. HxCDD Emission Factors with Process Information

Pollutant	ID	Wood type	Firing configuration	Control device	Number of test conditions	Run average	Average without B138
HxCDD	B05	Dry	Stoker	Mechanical Collector	1	4.04E-11	4.04E-11
HxCDD	B125	Wet	Not Reported	ESP	2	8.55E-11	8.55E-11
HxCDD	B24	Wet	Not Reported	Wet Scrubber	1	9.36E-11	9.36E-11
HxCDD	B30	Wet	FBC	Fabric Filter	2	1.20E-10	1.20E-10
HxCDD	B78	Wet	Stoker	Wet Scrubber	1	6.41E-08	6.41E-08
HxCDD	B138	Wet	Not Reported	Mechanical Collector	1	9.29E-06	
Arithmetic Average						1.56E-06	1.29E-08

In DAQ spreadsheet for woodwaste combustion, the AP-42 EF for total HxCDD (CAS# 34465-46-8) of 1.6 E-6 lb/MMBtu is used. This was meant to apply to 1,2,3,6,7,8-hexachlorodibenzo-p-dioxin (CAS # 57653-85-7). While both compounds have the same MW of 390.8646), there is a small but significant difference in their compound structure, emission factor, and toxicity potency.