## PCDD/PCDF Emissions from Coal-Fired Power Plants

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## 1. Introduction

Measurement of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/PCDF) emissions from coal-fired power plants has been limited. <sup>1,2)</sup> In addition, the few previous studies which have been conducted did not use currently-accepted methodology for measuring PCDD/PCDF from stationary sources. <sup>3)</sup> Consequently, previous measurements may not have had the detection limits, isomer specificity, or other necessary parameters to comprehensively assess PCDD/PCDF emissions from this source.

The U.S. Department of Energy (DOE) sponsored a project in 1993 to assess emissions of hazardous air pollutants (HAPs) from several coal-fired power plants. The HAPs measured on this project included a variety of inorganic and organic compounds. At most plants, PCDD/PCDF were also measured.

The purpose of this paper is to summarize the PCDD/PCDF data collected under the DOE project. Included in this paper is a listing of the plants tested, a description of the sampling and analysis procedures used to measure PCDD/PCDF emissions, a compilation of the results, and conclusions derived from the data.

## 2. Experimental

<u>Plants Tested</u> Eight plants were tested as part of the DOE project in 1993. At seven of the eight plants, PCDD/PCDF were measured at the stack (i.e., as emissions were exhausted to the ambient air). At some plants, PCDD/PCDF were also measured in gas streams entering pollution control devices. This paper focuses on PCDD/PCDF emissions measured at the stack only.

Parameters which may affect the production and release of PCDD/PCDF from combustion systems include fuel type, presence/absence of pollution control devices, and temperature. 4,5,6) A summary of some of these parameters for the seven coal-fired power plants is provided in Table 1.

Sampling and Analysis Procedures. Sampling was conducted according to general procedures in EPA Method 23<sup>3)</sup> at all plants. The Method 23 sampling train consists of a heated filter followed by a water-cooled sorbent trap containing XAD-2 resin. The sample is withdrawn

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isokinetically from the gas stream. Sample fractions recovered from the Method 23 sampling train include the particulate filter, XAD-2 resin, and a solvent rinse of the sampling probe and filter holder.

Sampling volumes of approximately 6 normal cubic meter (Nm<sup>3)</sup>) were collected. Typically, three replicate Method 23 samples were collected on three separate test days at each plant. Train blanks were also collected at all plants.

Table 1. Characteristics of Coal-Fired Power Plants Tested

| ····· | <br> |                    |
|-------|------|--------------------|
|       | Coal | Temperature (°C) a |

|               | Coal Type     | Coal<br>Chlorine<br>Content<br>(µg/g) | Temperature (°C) at: |     |     |       |  |
|---------------|---------------|---------------------------------------|----------------------|-----|-----|-------|--|
| Plant         |               |                                       | Pollution            |     |     |       |  |
|               |               |                                       | ESP                  | Bag | FGD | Stack |  |
| Baldwin       | Bituminous    | 800                                   | 160                  |     |     | 160   |  |
| Niles         | Bituminous    | 1,400                                 | 130                  |     |     | 130   |  |
| Boswell       | Subbituminous | 300                                   |                      | 150 | -   | 150   |  |
| Springerville | Subbituminous | 390                                   |                      | 70  | 130 | 75    |  |
| Yates         | Bituminous    | 1,400                                 | 130                  | -   | 120 | 40    |  |
| Coal Creek    | Lignite       | 400                                   | 170                  |     | 170 | 110   |  |
| Cardinal      | Bituminous    | 1,000                                 | 150                  |     | -   | 150   |  |

<sup>&</sup>lt;sup>a</sup>ESP = Electrostatic precipitator, Bag = Baghouse, FGD = Flue gas desulfurization system.

Samples were analyzed for PCDD/PCDF according to general EPA Method 23 procedures. The Method 23 sample fractions were solvent extracted and processed through multiple cleanup columns to remove compounds that may interfere with PCDD/PCDF analysis. After cleanup, the samples were analyzed for PCDD/PCDF using gas chromatography/high resolution mass spectrometry. Concentrations for total PCDD/PCDD congener classes and individual 2,3,7,8-substituted PCDD/PCDF isomers were determined.

# 3. Results

The concentrations of the 2,3,7,8-substituted PCDD/PCDF isomers and total PCDD/PCDF by congener class are presented in Table 2. These data represent the average of the replicate measurements (typically three) at the plant stack. The numbers with a "<" are detection limits for PCDD/PCDF that were not detected. All data have been corrected for train blanks.

Table 2. PCDD/PCDF Concentration in Stack Emissions (pg/Nm³)<sup>a</sup>

|                             | Baldwin | Niles | Boswll | Sprngvl | Yates  | CoalCrk | Cardinl |  |
|-----------------------------|---------|-------|--------|---------|--------|---------|---------|--|
| 2,3,7,8-Substituted Isomers |         |       |        |         |        |         |         |  |
| 2378-TCDF                   | <1.7    | 8.1   | 7.8    | <2.0    | <3.3   | 13      | 0.7     |  |
| 12378-PeCDF                 | <1.0    | <5.7  | 7.2    | < 10    | <3.2   | <5.7    | <1.1    |  |
| 23478-PeCDF                 | 2.4     | < 19  | 6.6    | < 10    | <3.2   | <4.8    | < 1.4   |  |
| 123478-HxCDF                | 3.3     | 16    | 8.4    | < 10    | <16.4  | < 5.1   | <1.8    |  |
| 123678-HxCDF                | 1.1     | <5.0  | 2.9    | < 10    | <5.8   | <4.0    | <1.3    |  |
| 123789-HxCDF                | < 0.44  | 11    | <1.8   | < 10    | < 8.8  | < 6.9   | <1.5    |  |
| 234678-HxCDF                | <2.0    | <4.2  | 3.0    | < 10    | < 16.4 | <2.5    | <2.0    |  |
| 1234678-HpCDF               | 2.0     | 29    | 6.0    | < 10    | <23    | <30     | <2.2    |  |
| 1234789-HpCDF               | < 0.63  | < 6.1 | <3.6   | < 10    | < 15.4 | <5.0    | < 2.1   |  |
| OCDF                        | 5.6     | 33    | 2.4    | < 20    | <131   | < 19    | 11.4    |  |
| 2378-TCDD                   | <3.5    | <3.5  | 1.0    | <2.0    | <3.3   | <2.6    | <1.7    |  |
| 12378-PeCDD                 | < 0.56  | <4.8  | <1.8   | < 10    | <4.7   | <3.2    | <1.8    |  |
| 123478-HxCDD                | < 0.56  | <5.7  | <3.6   | < 10    | < 15.4 | <2.7    | <2.0    |  |
| 123678-HxCDD                | < 0.44  | 5.0   | <1.8   | < 10    | < 9.9  | <4.2    | <1.4    |  |
| 123789-HxCDD                | < 0.56  | 4.9   | <1.8   | < 10    | < 12.1 | <4.3    | <1.2    |  |
| 1234678-HpCDD               | <1.7    | 29    | < 1.8  | < 10    | < 26.4 | 4.3     | 2.4     |  |
| OCDD                        | <12     | 32    | < 14   | < 20    | < 131  | 20      | 21.6    |  |
| Total Congener Class        |         |       |        |         |        |         |         |  |
| TCDF                        | <5.2    | 29    | 78     | <2      | <3.3   | 88      | <37     |  |
| PeCDF                       | 5.4     | 33    | 61     | <10     | < 6.6  | 14      | 3.0     |  |
| HxCDF                       | 7.6     | 39    | 29     | < 10    | < 16.4 | <5.0    | <27     |  |
| HpCDF                       | 4.3     | 34    | 9.0    | < 10    | <29.5  | <20     | 2.9     |  |
| TCDD                        | 1.8     | 12    | 12     | C,      | 6.7    | <2.6    | < 55    |  |
| PeCDD                       | <1.0    | 4.4   | 6.0    | <10     | <4.7   | <3.2    | <32     |  |
| HxCDD                       | 1.3     | 18    | 2.7    | <10     | <26.3  | <4.0    | <24     |  |
| HpCDD                       | 3.4     | 45    | <2.4   | <10     | <26.4  | <14     | < 8.1   |  |

Shaded numbers represented detected PCDD/PCDF; unshaded numbers are detection limits for nondetected PCDD/PCDF.
 Suspected contamination problem.

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### 4. Conclusions

In most cases, PCDD/PCDF were not detected in coal-fired power plant emissions. For some plants, levels ranging from 1 to 33 pg/Nm³ for 2,3,7,8-substituted isomers and from 1 to 88 pg/Nm³ for total congener classes were detected. In general, PCDF levels were higher than PCDD levels. Of the seventeen 2,3,7,8-substituted isomers, the 2,3,7,8-tetraCDF isomer was detected most often. Detected levels are significantly below the U.S. regulatory limit of 30 ng/Nm³ total PCDD/PCDF proposed for other types of incinerator systems.<sup>7)</sup> More PCDD/PCDF were detected in this study than in previous studies of coal-fired power plants<sup>1,2)</sup> due to a reduction in method detection limits rather than a recent increase in PCDD/PCDF emissions from this source type.

Variations in emission levels between plants could not be attributed to specific operating characteristics. The presence of particulate control devices on all seven plants is probably the primary contributor to the low PCDD/PCDF levels detected.<sup>6)</sup>

#### 5. References

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