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Abstract

The effect of the injection of brominated powdered activated carbon (Br-PAC), on the emission of brominated and chlorinated dioxins and furans in coal combustion flue gas has been evaluated. The sampling campaigns were performed at two U.S. Department of Energy (DOE) demonstration sites where brominated PAC was being injected for control of mercury emissions. The results of the sampling campaigns showed that injection of the brominated PAC upstream of the electrostatic precipitator (ESP) did not increase the emissions of total and Toxic EQuivalent (TEQ) chlorinated and brominated dioxin compounds. Rather, the data suggested the sorbent may capture these compounds and reduce their concentration in the flue gas stream. This effect, when seen, was small, and independent of the type of plant emission controls, temperature at the point of injection, or fuel-chlorine content. The addition of the brominated PAC sorbent resulted in slight increases the total content of chlorinated dioxins and furan in the particulate matter (ash) collected in the ESP, but did not increase its overall toxicity.

1. Introduction

A wide variety of studies have been undertaken to understand the formation and to measure the extent of emissions of polychlorinated dibenzo-*p*-dioxins and furans (PCDDs/Fs) from thermal processes, such as municipal solid waste combustion and medical waste incineration (Everaert and Baeyens, 2002). In contrast, a relatively small number of studies have been conducted to measure such emissions from coal-fired utility boilers (Riggs et al., 1995; Cleverly et al., 1999; Fernandez-Martinez et al., 2004). Those studies have reported that, although the reactants for PCDD/F formation are present during coal-combustion, very low levels of PCDD/F emissions are measured compared to other thermal processes. In fact, PCDD/F emissions from coal-fired power plants are estimated to account for only about 3% of the total U.S. dioxin inventory, compared to 37% from municipal solid waste (MSW) combustion (Cleverly et al., 1998). Co-combustion of small amounts of coal with MSW has been shown to be an effective means to limit PCDD/F emissions (Raghunathan and Gullett, 1996; Ogawa et al., 1996).

Experiments have shown that the sulfur content of the coal acts to suppress the formation of PCDDs/Fs. This effect was found to be influenced by the S/Cl ratio within the flue gas (Raghunathan and Gullett, 1996; Gullett and Raghunathan, 1997). In pilot-scale tests, an S/Cl ratio of 1:1 produced a consistent inhibitory effect, with dramatically decreased PCDD/F formation (Raghunathan and Gullett, 1996). This suppression is likely due to an inhibition of metal chloride formation (especially copper and iron) due to the competition between HCl and SO_2 (Ryan et al., 2006). Such metal chlorides have been found to be essential for PCDD/F formation, specifically those homologues with isomers contributing to the toxic compounds (Stieglitz, 1998; Ryan and Altwicker, 2004). Briefly, formation of PCDDs/Fs involving metal

chlorides and particulate carbon (such as native carbon in fly ash and soot deposits) has been proposed to include the chlorination and oxidation of the carbon via the dual role of the metal chlorides (Stieglitz et al, 1994; 1996; Ryan, 2001).

Activated carbon has been identified as one of the most reactive particulate carbons in the formation of PCDDs/Fs via the de novo synthesis (Stieglitz et al., 1993; Ryan and Altwicker, 2000; Milligan and Altwicker, 1995). Experiments with pre-chlorinated carbons, before exposure to the metal chlorides within the PCDD/F formation temperature window of 200-550 ^{o}C, have shown incorporation of the carbon-bound chlorine in PCDD/F formation (Addink and Altwinker, 1998).

The addition of a source of bromine to waste has been observed to lead to increased emissions of PCDDs/Fs into the flue gas, in addition to the emissions of PBDDs/Fs and PBCDDs/Fs (polybromo- and polybromochloroDDs/Fs) (Lemieux and Ryan, 1998a; 1998b; Lemieux et al., 2002). While little is known about the brominated and mixed chloro/bromo homologues (relative to the thousands of published works on the health effects of the chlorinated dioxins/furans), the available literature suggests that the brominated compounds have similar toxicity profiles to their chlorinated homologues (Birnbaum et al., 2003).

Mercury (Hg) is present in coal in trace amounts (approximately 0.1 ppm on average) and coal-fired power plants are known to be the major source of anthropogenic Hg emissions in the U.S. To address this, the EPA has recently suggested a regulatory approach to achieve reductions in emissions of Hg from these plants. While some Hg reductions are expected to come as a co-benefit of other control technologies (e.g., wet SO_2 scrubbers), deep Hg reductions will likely require the addition of Hg-specific control technologies (Srivastava et al., 2006). Injection of powdered activated carbon (PAC) into the flue gas stream has been successfully

demonstrated on several full-scale systems. It is thought that chlorination of the carbon surface is the first step in the Hg oxidation and binding process. As such, the effectiveness of standard PAC may be limited when inadequate free chlorine is available in the flue gas (for example, during combustion of sub-bituminous coals). Pre-halogenated PAC sorbents have been developed to overcome this limitation. Several pre-brominated PAC sorbents have been evaluated in full-scale field tests and have been shown to be quite effective in flue gases containing both Hg^0 and Hg^{2+} vapor species (Srivastava et al., 2006).

The exchange of a chlorine atom from gas-phase HCl with a carbon-bound bromine atom is faster than the chlorination of the carbon via hydrogen exchange. Such a pathway may counteract the proposed PCDD/F reduction mechanism of metal sulfide formation, favored over metal chloride formation, by reducing the dependency on the need for metal chlorides for the carbon chlorination step in the PCDD/F formation processes. These factors, and the high HCl: HBr ratio in the flue gas, may lead to increased PCDD/F emissions due to the addition of the brominated carbon. The presence of the brominated carbon and halogen acid gases (HBr, HCl) has led to questions regarding the possibility of increases in the formation of brominated and/or chlorinated organic compounds (e.g., PCDDs/Fs and PBDDs/Fs). The objective of this work was to collect flue gas samples during normal boiler operation with and without brominated PAC injection to determine if there are corresponding increases in the emissions of PCDDs/Fs and/or PBDDs/Fs.

2.   Methods and materials

Plant Descriptions

The U.S. Department of Energy (DOE) has sponsored or co-sponsored several large-scale demonstrations to evaluate the use of brominated PAC injection for control of Hg emissions. As

part of this current work, flue gas sampling for dioxin/furan emissions took place at two of the DOE demonstration sites, Plant A and Plant B. The plant configurations with the sorbent injection and sampling locations, for both Plant A and Plant B, are shown in Figure 1. A summary of the plant characteristics is given in Table 1. Each of the flue gas sampling campaigns took place over a 2 – 3 day period during the approximately 1-month Hg control demonstration at each of the facilities. While these sampling locations were selected in order to coordinate with mercury control demonstrations, the two dissimilar power plants also provided the opportunity to sample for halogenated organics at varying temperatures (both cold-side and hot-side ESPs) and with different chlorine-to-sulfur ratios in the fuel (as shown in Table 1).

The first sampling campaign (Plant A) took place at a 160 MW unit burning a mixture of western sub-bituminous (85%) and eastern bituminous coal (15%). The mixed coal had a sulfur content of 0.78 wt% (dry) and a chlorine content of 150 ppm (dry), resulting in an S/Cl ratio of 52. The duct configuration was such that the flue gas from the boiler was evenly split after the economizer and directed into two parallel cold-side electrostatic precipitators (CS-ESPs). A brominated PAC (B-PAC™, Sorbent Technologies) was injected upstream of one of the CS-ESPs for Hg control. Mercury emissions were effectively reduced by approximately 94% during the month-long demonstration. The flue gas temperature at the point of sorbent injection was approximately 140 °C. Although this is below the typical PCDD/F formation temperature window, it was felt that the potential for increased emissions of PCDD/Fs and/or PBDDs/Fs should be addressed due to possible anomalies in the formation processes due to plant conditions and/or operation.

The second sampling campaign (Plant B) was at a 140 MW unit burning a low sulfur Appalachian bituminous coal blend. The coal had a sulfur content of 0.75 wt% (dry) and a

chlorine content of 1400 ppm (dry) resulting in an S/Cl ratio of 5. The unit was equipped with a hot-side ESP (HS-ESP) for PM control and separated over-fired air (SOFA) for NO_X control. The flue gas stream from the boiler was split prior to entering the HS-ESP, which was bisected so that there were two independent gas streams flowing through each section of the HS-ESP. The gas streams then exited through separate stacks. A brominated PAC (B-PAC™, Sorbent Technologies) was injected upstream of one side of the bisected HS-ESP. Mercury emissions were reduced by 50 – 70% (depending on the injection rate and boiler load) during the month-long demonstration. The flue gas temperature at the point of sorbent injection was approximately 340 °C, which falls well within the typical PCDD/F formation temperature window of 250 – 500 °C.

Sampling

The sampling plan for this work was in accordance with a modified EPA Method 23a. This protocol is specifically for the sampling of chlorinated dioxins and furans – no EPA method currently exists for prescribed sampling of brominated dioxins and furans. However, the similarity of the brominated and chlorinated dioxins and furans, in terms of both chemical and physical properties, suggests that Method 23a should be an appropriate sampling protocol.

At Plant A, simultaneous samples were taken from the rectangular duct downstream of each of the CS-ESPs. The samples taken from the duct downstream of the CS-ESP with brominated PAC injection were designated as the "test" samples. Those taken simultaneously downstream of the CS-ESP with no sorbent injection are referred to as the "control" samples. Over a 2-day period, three sequential samples were taken at sample ports located downstream of the "test" CS-ESP. Simultaneously, three samples were taken downstream of the "control" CS-

ESP. During one of the test periods, a complete sampling train was assembled, but not used for sampling. This train was later recovered and analyzed as the field blank. The sampling time for each sampling period was 4 hours.

At Plant B, simultaneous samples were taken from the two exhaust stacks downstream of the bisected HS-ESP. The samples taken from the stack containing flue gas with the brominated PAC injection are designated as the "test" samples while those taken from the stack with sorbent injection are referred to as the "control" samples. The first two sampling periods were for a total of 8 hours each. This sampling time was longer than is typically done and was based upon the recommendations of the Electric Power Research Institute (EPRI) for improvements in stack testing methods for coal-fired power plants (EPRI, 2004). The final sampling period was reduced to 4 hours due to time constraints.

During each sampling period the sample volume, duct/stack temperature at the sampling location, and total sampling time (min) were recorded by the sampling crew. Plant operation data including inlet and outlet temperatures of the ESPs, ESP operational parameters (i.e., voltage and amperage), and unit continuous emission monitoring (CEM) data (NO_X, SO_X, CO_2, O_2 and opacity) were collected by the plant operations group. Before the start of flue gas sampling, the ESP ash hoppers were evacuated by the facility operators. Ash was then allowed to accumulate in the hoppers and was sampled.

Extraction and clean-up of samples

The extraction and cleanup procedures followed EPA Method 23a/8290 (available at *www.epa.gov/epawaste/hazard/testmethods/sw846/online/index.htm)* and a modified Method 23a (as discussed below). Following completion of each sampling period, each sampling train was

transported and recovered in a clean area as soon as the probe was removed from the sample source location. During transportation between the test facility and the designated recovery area, both ends of the heated probe and openings of the impinger assembly were sealed with aluminum foil or glass caps. The filters for all samples were recovered and placed in a Petri dish. The cyclone ash was added to the top of the filter, rather than in the front-half rinse (as called for in Method 23a). Particles not freely removed from the cyclone were incorporated into the front-half acetone/dichloromethane rinse. The Petri dishes were sealed with Teflon tape to prevent spillage and stored in a way such that the fly ash would not be disturbed. This fraction of the train was called the filter sample. The probe, cyclone, and front half of the filter housing were then rinsed with acetone followed by dichloromethane. The solvents were collected in a single, 250 mL amber jar. This was called the acetone/dichloromethane front-half rinse sample. The probe and filter were then rinsed with toluene. The toluene was collected in a separate 250 mL amber jar and this sample was called the toluene front-half rinse sample. This collection of rinses into separate sample bottles was also a modification to EPA Method 23a.

The XAD-2 cartridges were kept refrigerated prior to use and during transport to the facility to prevent evaporation of the pre-sampling surrogates. The XAD-2 resin cartridge from each train after sampling was capped at both ends and wrapped in aluminum foil during transport. As with all sample fractions, the XAD-2 resin cartridges remained refrigerated during storage and transport. This sample was called the XAD-2 fraction of the sampling train. The back half of the filter housing, glass connection, and condenser were rinsed with acetone followed by dichloromethane. The solvents were collected in a single 250 mL amber jar. This was the acetone/dichloromethane back-half rinse sample. This glassware was rinsed with

toluene and the solvent was collected in a separate 250 mL amber jar. This sample was the toluene back-half rinse sample.

The solvent rinse jars were capped with Teflon lined caps and sealed with Teflon tape to prevent leakage and evaporation during transport. The recovered sample trains were identified with unique sample IDs for each test run and stored in a refrigerated space before they were sent for analysis. During transportation, storage and shipment, the samples were kept in a refrigerated space. The impinger series were weighed before and after the sampling in order to determine the amount of water collected in the train. The weight of the solids (fly ash, unburned carbon, sorbent) that were collected on the filter and in the cyclone was measured for each sample.

Sample analysis

The recovered samples were shipped for analysis to Alta Analytical Laboratory (El Dorado Hills, CA), an accredited independent laboratory chosen for analytical support to this project. At the time, there was no EPA reference method for the analysis of the PBDD/Fs of interest. However, their similarity, in terms of chemical and physical properties, to the PCDD/Fs suggests that Method23a/8290 can be applied by adding the appropriate internal standards for the PBDDs/Fs target compounds. No analyses were conducted for mixed chloro/bromo-dioxins/furans due to the complexity of the analysis and the lack of analytical standards. There is a legitimate concern that mixed chloro/bromo PCDD/F compounds may be forming; however, the state of the art HRGC/HRMS technique cannot provide these mixed congeners. Considerable additional funding would be required to undertake this type of method development.

At Plant A, the second sampling period filter (plus cyclone catch) and front half rinses were extracted and analyzed separately from the XAD-2 resin and back-half rinses. The fly ash samples were stored in sealed amber jars in a refrigerated space prior to analysis.

Quality Assurance/Quality Control

An EPA Level II Quality Assurance Project Plan (QAPP) was followed for each sampling location. Utility representatives and other stakeholders were allowed to review and comment on the QAPP prior to initiation of sampling. External personnel with specific stack sampling expertise and EPA QA personnel conducted on-site audits of the sampling technique and quality assurance procedure implementation during sampling at both sites.

One complete sampling train (the field blank) underwent all normal set-up procedures except actual duct sampling. Analysis of this field blank filter, XAD-2 resin cartridge and rinses helped to determine if any target analytes could be attributed to sample handling in the field. In addition, the data quality for the sampling was verified by conducting leak determinations, volume/concentration measurements, weight/concentration measurements, velocity/flow measurements, and isokineticity.

3. Results and discussion

Results from Plant A

The overall PCDD/F and PBDD/F TEQ and total emissions for the sequential dual samples (control and test samples) taken from the rectangular duct downstream of each of the CS-ESPs are presented in Figure 2[*]. The PCDD/F TEQ were calculated using the World Health Organization's (WHO) TEFs (2005), and conversely the PBDD/F TEQ was also based on the chlorinated PCDD/F equivalent WHO TEFs. Overall, the PCDD/F totals and TEQ emissions for

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[*] All results have been corrected to 7% O_2.

all the samples were found to be below the laboratory reporting limits and at the levels of the field blanks. The results were one to two orders of magnitude lower than PCDD/F total emissions standards (13 ng/dscm[†] at 7% O_2) for hazardous waste combustors in the U.S. (EPA, 2005) and within an order of magnitude of PCDD/F TEQ emissions standard (0.13 ng/dscm at 7% O_2) in Europe (EN, 2000). The PCDD/F and PBDD/F compounds reported as ND (not detected) by the laboratory were treated as detections at one-half the detection limit, consistent with the data handling measurements of non-detects in the 1999 Maximum Achievable Control Technology (MACT) rule for Phase1 sources.

The differences between the test and the control samples were assessed using the values of the OCDD and OCDF congeners (octachloroDD/DF congeners) that are well above the field and laboratory blanks. The results for the two congeners, shown in Figure 3, suggest that the effect of the brominated PAC injection on the PCDD/F TEQ or total emissions was insignificant. No PBDD toxic isomers were detected above the detection limit for any of the sampling periods (control or test). Of the toxic PBDF isomers that were detected, the concentrations in the controls appear to have been slightly greater, but less than the reporting limit, than in the test. This may be due to the presence of injected activated carbon in the test case; activated carbon has been used in PCDD/F emission control. The results for test 3 fell below the field blank sample and, though reported, they appear to be unrealistic low.

As mentioned earlier, separate analyses were done for samples collected during the second sampling period to ensure that combining the filter plus cyclone ash (plus rinses) with the XAD-2 resin cartridge (plus rinses) into a single sample did not impact recoveries. The results from separate analysis of these portions of the sampling train are illustrated in Figure 4 as

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[†] dscm = dry standard cubic meters, all results have been corrected to 7% O_2.

PXDD/F (X = C for chlorinated compounds, and X=B for brominated compounds) homologue group concentrations as the "front half" (filter plus cyclone ash plus rinses) and "back half" (XAD-2 resin cartridge plus rinses). The homologue concentrations PXDDs/Fs were found mainly in the back half sample, and there appears to be little difference between the control sample and test sample results for the PCDD/F compounds. Combining the front-half (particle-bound) and the back-half (volatile phase) fractions apparently did not affect the sample recovery. However, for the PBDD/F compounds, their concentrations seem to be higher, but not statistically significant, for the control than those observed for the test samples. These results may suggest an added role of the brominated PAC in the apparent removal of the PXDD/F compounds from the flue gas stream.

The TEQ and total concentrations of PCDD/Fs and PBDD/Fs, for samples taken from Plant A, are given in the top half of Table 2. There is no clear indication of an effect due to the injection of the brominated PAC, and the observed variations between the control and the test samples may be within the normal variations due to sampling, analytical uncertainties, and other inhomogeneities in the flue gas stream.

Results from Plant B

The overall PCDD/F and PBDD/F TEQ and total emissions for the three sequential dual samples (control and test samples) taken from the two exhaust stacks downstream of the bisected HS-ESP are illustrated in Figure 5. Similar to the results from Plant A, the overall PCDD/F totals and TEQ emissions for all the samples were found to be one to two orders of magnitude lower than PCDD/F emissions standards for hazardous waste combustors in the U.S. and Europe. During this sampling campaign, the field and laboratory blanks were all below detection limits.

The PCDD/F homologue distributions (the percentage of the total yield) for all the runs and for both the control and the test samples are presented in Figure 6. The overall distributions are almost identical, and suggest that the effect of the brominated PAC on the overall emissions is minimal or non-existent. Further, the PCDD/F isomer distributions shown in Figure 7 show no trend or effect on the relative concentrations of the 17 toxic PCDD/F isomers that can be directly attributed to injection of brominated PAC. No PBDD isomers were detected in any of the control or test sample runs; and only 1,2,3,4,6,7,8-HpBDF was detected during the third sampling period with almost the same concentrations for both the control and test samples.

The TEQ and total concentrations of PCDD/Fs and PBDD/Fs for samples taken at Plant B are given in the bottom portion of Table 2. Overall, they are in the same order as the emissions from Plant A, and are at least one order of magnitude lower than the PCDD/F emissions standards for hazardous waste combustors in the U.S. and Europe.

Analysis of brominated PAC and ash samples

The brominated PAC sorbent, and the ashes from the control and test lines of the Air Pollution Control system (APCS) were analyzed for chlorinated and brominated PXDD/F contents and the results are presented in Table 3. All the toxic PXDD/F compounds were either non-detects or were detected at the detection limit levels. The total PCDD/F concentrations were found to be higher in the brominated PAC samples than in the ash samples, and slightly higher in the ash test samples than in the control samples. The relatively higher PCDD/F concentrations in the test samples may be due primarily to the added brominated PAC sorbent in the ash, with the removal of these compounds from the flue gas stream by the brominated PAC sorbent being a secondary impact.

Acknowledgments

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LIST OF FIGURES AND TABLES

[‡] dscm = dry standard cubic meters, all results have been corrected to 7% O_2.

Table 1. Characteristics of coal-fired power plants (A and B)

	Plant A	Plant B
Location	Michigan	North Carolina
Coal type	sub-bit/bit blend	bituminous blend
Boiler Capacity, MW	160	140
Boiler Load*, MW	120	140
PM Control	CS-ESP	HS-ESP
Sampling location	duct	stack
S in coal, % (dry basis)	0.78	0.75
Cl in coal, ppm (dry basis)	150	1400
S / Cl ratio	52	5
Moisture in coal, %	22.8	8.1
SO$_2$, ppmv (dry)	260 - 285	370 - 420
Flue gas temp (sorbent inj.), °C	130 - 140	338
Flue gas temp (sample pt.), °C	127 - 138	155 - 167

* during sampling periods

Table 2. PXDD/F Total and TEQ emissions for Plants A and B (pg/dscm)

	Coal-fired Power Plant A					
	Sampling Period # 1		Sampling Period # 2		Sampling Period # 3	
Emissions (pg/dscm)	Control	Test	Control	Test	Control	Test[a]
Total PCDD/Fs (ND = 0, EMPC = 0)	515.8	1050.0	479.1	389.4	1749.0	28.0
Total PCDD/Fs (ND = DL/2, EMPC = EMPC)	531.0	1060.9	510.4	419.0	1792.4	38.0
PCDD/Fs TEQ (ND = 0, EMPC = 0)	2.4	3.6	2.0	0.2	20.3	0.0
PCDD/Fs TEQ (ND = DL/2, EMPC = EMPC)	3.7	7.9	5.0	3.3	20.4	2.7
Total PBDFs (ND = 0, EMPC = 0)	817.2	6167.4	688.8	159.8	110.0	85.7
Total PBDFs (ND = DL/'2, EMPC = EMPC)	850.7	6174.5	692.6	179.8	121.6	99.6
PCBD/Fs TEQ (ND = 0, EMPC = 0)	8.2	2.3	6.6	0.1	0.0	0.0
PCBD/Fs TEQ (ND =DL/2, EMPC = EMPC)	11.5	8.6	10.5	5.0	3.6	3.6

[a]Results for this test are below the field blank sample and do not seem to be realistic

	Coal-fired Power Plant B					
	Sampling Period # 1		Sampling Period # 2		Sampling Period # 3	
Emissions (pg/dscm)	Control	Test	Control	Test	Control	Test
Total PCDD/Fs (ND = 0, EMPC = 0)	389.4	1614.1	1805.9	1218.3	375.1	242.5
Total PCDD/Fs (ND = DL/2, EMPC = EMPC)	390.8	1614.9	1805.9	1221.3	390.3	248.9
PCDD/Fs TEQ (ND = 0, EMPC = 0)	9.1	40.6	41.4	27.2	8.5	1.8
PCDD/Fs TEQ (ND = DL/2, EMPC = EMPC)	9.1	40.6	41.4	27.2	8.6	4.8
Total PBDFs (ND = 0, EMPC = 0)	35.0	94.7	103.3	129.9	1018.8	1248.2
Total PBDFs (ND = DL/'2, EMPC = EMPC)	73.2	114.5	138.6	152.1	1078.5	1289.2
PCBD/Fs TEQ (ND = 0, EMPC = 0)	0.0	0.0	0.0	0.0	0.7	0.5
PCBD/Fs TEQ (ND =DL/2, EMPC = EMPC)	6.8	8.6	8.2	9.4	19.3	24.8

Values are expressed on a dry basis referenced to 25 °C, 101.3 kPa and corrected to 7% O2.   EMP = Estimated Maximum Possible Concentration.

Table 3. PXDD/F Total and TEQ concentrations for sorbent and ashes from Plants A and B

PXDD/F concentrations (pg/g)	Sorbent Analysis		Plant A Ash		Plar
	Sorbent	Method Blank 1	Control	Test	Control
Total PCDD/Fs (ND = 0, EMPC = 0)	12.4	0.0	0.9	1.1	2.3
Total PCDD/Fs (ND = DL/2, EMPC = EMPC)	14.5	2.6	2.2	10.0	2.7
PCDD/Fs TEQ (ND = 0, EMPC = 0)	0.0	0.0	0.0	0.0	0.0
PCDD/Fs TEQ (ND = DL/2, EMPC = EMPC)	0.4	0.5	0.2	0.1	0.2
Total PBDFs (ND = 0, EMPC = 0)	22.0	0.5	0.0	0.0	5.7
Total PBDFs (ND = DL/'2, EMPC = EMPC)	41.2	14.2	6.5	9.3	11.4
PCBD/Fs TEQ (ND = 0, EMPC = 0)	0.0	0.0	0.0	0.0	0.0
PCBD/Fs TEQ (ND =DL/2, EMPC = EMPC)	4.1	4.5	1.8	2.8	2.3