SENSITIVITY OF PCDD/F FORMATION TO HAZARDOUS WASTE FIRING RATE AND COMBUSTION QUALITY

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Introduction

Industrial boilers that cofire hazardous waste will be receiving attention from the U.S. Environmental Protection Agency (EPA) as part of an effort to consider revising PCDD/F emission standards for hazardous waste combustors. Recent combustor work[1] has shown that combustion deposits became a sink and source for polychlorinated dibenzodioxins and dibenzofurans (PCDDs/Fs) and their precursors, respectively, and that byproduct emissions have species-specific response times[2] that result in varying pollutant concentrations long after fuel/waste or combustion conditions change. It is important to understand the PCDD/F emissions from hazardous-waste cofiring boilers as well as the impact of operating changes on emissions, such that accurate causality can be determined as well as appropriate conditions under which sampling can characterize emissions.

Methods and Materials

PCDD/F emissions were examined after changes in hazardous waste cofiring rate and combustion quality (fuel equivalence ratio, φ) with an industrial boiler. The boiler was a 732 kW (2.5 x 10^6 Btu/h), 3-pass, firetube boiler using #2 fuel oil cofired with a 1,2-dichlorobenzene (1,2-diClBz) and copper naphthenate (CuNA) dopant mixture (more details are available in Ref. 1). The boiler is fully instrumented with continuous emission monitors (CEMs) for oxygen, carbon dioxide, carbon monoxide, nitrogen oxides, sulfur dioxide, hydrogen chloride, water (O_2, CO_2, CO, NO_x, SO_2, HCl, H_2O, respectively), and total hydrocarbons (THCs) such as methane. This work used bioassay analyses[3] [chemically activated luciferase gene expression, or CALUX®] for fast and sensitive determinations of toxicity equivalents (TEQs) and traditional emission sampling/analysis (EPA Method 23, mono- to octa-chlorinated congeners)[4] for complete isomer quantification in order to determine the effect of varying dopant feed rate and φ (reflected by [O_2]) on PCDD/F emissions.

Initial tests characterized the boiler temperature profile, soot loading, and PCDDs/Fs in the soot deposits and gases during normal firing conditions after 5 h. Prior to this characterization, the boiler tubes were physically cleaned to remove any traces that remained in the boiler tubes after a previous, similar test program[1] that finished with 500 h of natural-gas-firing-only for facility decontamination. The boiler was then operated for over 30 h under alternating "good" and "poor" combustion conditions, effected by changes in the burner φ ratio (from 0.70 to 0.95). These conditions were meant to accumulate soot on the boiler tubes, and were not necessarily indicative of desired operating conditions. Earlier work had shown the need for buildup of a reactive soot surface followed by sufficiently oxidative combustion in order to form PCDDs/Fs. The O_2 concentration was monitored as an indicator of ö and combustion quality.

The first test phase consisted of varying combustion conditions while co-firing #2 oil and 1,2-diClBz with CuNA. This sequence of testing consisted of running 2 days under sooting conditions followed by 1 day of good combustion, the latter in which PCDD/F samples were taken. This alternating sequence was repeated until the CALUX technique indicated that PCDD/F concentrations had reached our Method 23 detection limits. At this point, the test program began with CALUX analysis of emissions under three φ ratios and three dopant feed rates (0, or no dopant; ½; and "full" rate (full rate is such that [HCl] ~ 400 ppm) followed by the same scenario with Method 23 sampling.

Results and Discussion

PCDD/F emissions during the initial (5 h) boiler characterization (#2 fuel oil and full dopant rate) were 394 ng/dscm (11.76 ng TEQ/dscm) as sampled by EPA Method 23. After the 30 h of subsequent alternating sooting and good combustion conditions, emissions were 2,360 ng/dscm (14.93 ng TEQ/dscm). Under subsequent good combustion conditions, the dopant levels were increased from 0 to ½ to full levels with 20-40 min equilibration time between tests. Sampling and analyses via the CALUX assay showed TEQ values of 14.83, 12.73, and 15.46 ng TEQ/dscm at cumulative run times of 31 h 20 min, 32 h 40 min, and 33 h 35 min, respectively. The similarity in Method 23 and CALUX results (≈15 ng TEQ/dscm) suggests that the absence of dopant for over an hour (0 dopant rate) had little effect on emissions, confirming the role of deposits in PCDD/F formation and suggesting that both measures are reasonably equivalent. The subsequent tests that examined the effect of ½ and full dopant amounts for 35-40 min firing periods saw no effect of the dopant levels on the TEQ measure. This suggests that increased hazardous waste firing did not result in prompt changes (in the order of 1-2 h) in PCDD/F levels, reinforcing the role of boiler deposits in effecting emissions.

The following tests varied burner φ (as reflected by measured $[O_2]$) with full dopant level and measured PCDD/F TEQ via CALUX. «High» $[O_2]$ (5.0 %, j = 0.70), «low» $[O_2]$ (1.8 %, j = 0.89), and «lowest» $[O_2]$ (0.6 %, j = 0.95) yielded 123.20, 22.59, and 35.17 ng TEQ/dscm, respectively. The distinction in PCDD/F emissions between higher and lower $[O_2]$ conditions confirms the role of oxidative (versus fuel-rich, or sooting) conditions for formation[5]. However, the increase of PCDD/F at the lowest $[O_2]$ suggests a minimum for PCDD/F formation; limited data preclude further speculation, however. In contrast to the previous tests varying dopant level, variation of burner ö (hence, $[O_2]$) had a prompt effect upon PCDD/F levels. A CALUX sample after only 35 minutes of high $[O_2]$ showed a substantial increase in PCDD/F TEQ (from 15 to 123 ng TEQ/dscm). Similarly, subsequent alteration of the $[O_2]$ level by varying φ resulted in PCDD/F variations with only 15-20 min between sampling periods.

The effects of dopant feed rate and varied burner φ were further verified in a second round of testing; Method 23 sampling and analysis was used to obtain additional information on PCDD/F species. About 8 h of alternating #2 fuel oil firing (only) and #2 fuel oil with dopant under sooting conditions preceded 4 h and 10 min of #2 fuel oil firing (only). At the end of this period, test and sampling intervals were initiated in which the dopant level was 0, ½, and full loads, as indicated by increasing levels of [HCl]. Conditions were allowed to equilibrate for 10 to 30 min between condition changes prior to sampling. Method 23 samples showed 0.01, 1.07, and 8.82 ng TEQ/dscm for the 0, ½, and full dopant feed rates, respectively (Figure 1). Unlike the earlier, varied j CALUX results, raising dopant feed rates about every 2 to 2 ½ h showed a significant increase in PCDD/F emissions. This discrepancy is possibly due to an "induction" period, or lagging response, that was longer than the duration of the CALUX-sampled runs – with lower detection limits, CALUX-sampled run conditions were altered about every 1 h whereas the Method-23-sampled run conditions were changed about every 2 – 2 ½ h. This induction period is consistent with the role of deposits as a sink and source for reactants and PCDD/F[1] and a lag timeframe of 1-5 h noted in a different system[6]. Further evidence for induction periods and accompanying emission hysteresis or "memory" effects has been noted[2,7] albeit at much shorter times which seem to be a function of system and pollutant type.

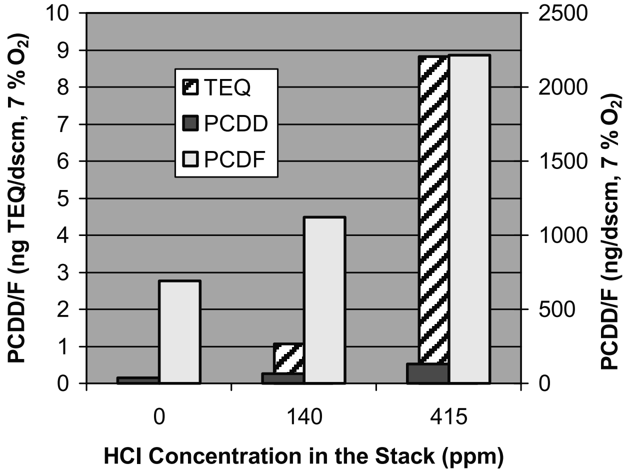

Figure 1. Effect of increased dopant level (0, ½, and full), as indicated by increased [HCl], on PCDD/F levels.

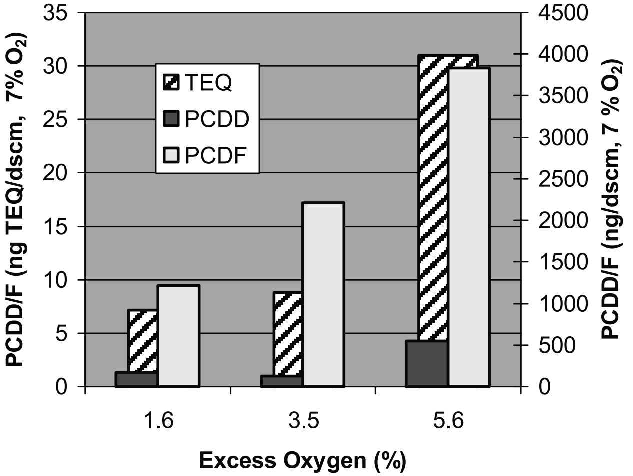

Figure 2. Effect of decreased j level, as indicated by increasing [O_2], on PCDD/F levels.

The multiple order of magnitude increases in the PCDD/F TEQ values are also accompanied by an increase in total PCDD/F, albeit only 3-fold (730 to 2343 ng/dscm). The primary effect of higher dopant feed rate is to shift the homologue profile to more highly chlorinated, and TEQ-related, congeners (not shown). The PCDDs shifted from a mass-weighted, average chlorine number of 1.7 to 3.9 and the PCDFs from 1.2 to 1.8. Thus, total PCDD/F production appears to be only a weak function of dopant (1,2-diClBz + CuNA) levels whereas the degree of chlorination and, hence, TEQ, is more affected by changes in loading rates. Both PCDF and PCDD levels are equally affected by changing dopant levels, and the PCDF/PCDD ratio, » 20/1, is not affected. The effect of dopant level on degree of chlorination does not result from changes in the thermal conditions of the boiler: temperatures remain relatively constant (± 3 C° for Passes 1 and 2, ± 10 C° for Pass 3) throughout the three dopant rates.

Tests varying φ and accompanied by Method 23 sampling (full dopant level) showed TEQ and total PCDD/F levels (Figure 2) that were affected by changes in operating conditions. Increases in burner ö (as reflected by lowered O_2, 1.6%) showed lower TEQ and total PCDD/F values, similar to the CALUX results. Low burner φ (as reflected by high O_2, 5.6 %) resulted in an increased TEQ value, 30.97 ng TEQ/dscm, and total PCDD/F value, 4,383 ng/dscm. These observations are consistent with earlier results[1] in which improved combustion conditions following periods of soot formation and deposition led to significant increases in PCDD/F formation. The role of these deposits as a sink and source for reactants is consistent with experimental results[8] and studies[9] on polycyclic aromatic hydrocarbons (PAHs) as PCDD/F precursors. Resultant theories have been summarized in Ref. 7.

These results demonstrate that PCDD/F emissions may take hours to stabilize after changes in operating conditions, a period that appears to be a function of system type. With sufficient time (≈ > 1 h), changes in dopant levels in this industrial boiler can promote increased TEQ levels, primarily through effecting a shift toward higher chlorinated congeners and less so through effecting greater formation. Improved combustion, reflected by lower burner ö and higher [O_2], resulted in higher PCDD/F emissions when the boiler was “seasoned” by periods of marginal combustion.

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