

Effect of Facility Design on Dioxin Formation and Emissions from Power Boilers Burning Salt-Laden Wood Waste

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ABSTRACT

Industrial research has been carried out to investigate dioxin formation and emissions from power boilers burning salt-laden wood waste. Eight full scale hog fuel power boilers at BC coastal pulp mills participated in the study. Experimental results indicated that some boilers had consistently higher PCDD/F emissions than the others. The general emission performance of each boiler was evaluated in terms of average emission levels and variability. The predominating dioxin formation mechanism was suggested by examining the congener profiles of both the ash captured in the electrostatic precipitation or scrubber and the final flue gas emissions.

Boiler G, followed by Boiler C, had the highest dioxin emissions together with poor performance consistency. Boiler A also had a poor performance consistency, while Boilers D, E, H had the lowest dioxin emissions and excellent performance consistency. The most likely predominating formation mechanism for the boilers having higher dioxin emissions was precursor reactions in Boilers A and G and a combination of precursor and de novo formation in Boilers C and F. These differences were attributed primarily to the different boiler designs. Poor combustion performance would be expected if the furnace is too thin, too wide, or too short. Firing auxiliary fuel in the upper furnace may cause delayed combustion and increased flue gas temperatures in the post combustion zones. Methods to improve combustion and reduce dioxin formation and emissions are discussed.

Higher flue gas temperatures in the post-GB (generating bank) processes promote dioxin formation by both de novo and precursor reactions. Based on average values for the eight hog boilers, stack dioxin emissions increased with air heater inlet temperatures above 370° C. Stack dioxin emissions, as well as ash dioxin contents, increased also with average temperature to scrubber/stack above 190° C. The optimum range of hog steam load was roughly between 65% and 80% of the hog MCR in terms of both stack dioxin emissions and fly ash concentrations. The actual optimum range is very much boiler specific.

INTRODUCTION

Toxic polychlorinated dibenzo dioxin and furan (PCDD/F) species are emitted in trace quantities from various thermal processes involving chlorine or chlorides. Their formation in the incineration of municipal solid waste (MSWI) is well known and incinerators used to be the dominating emission sources [1]. As PCDD/F emissions from incinerators are now reduced by advanced abatement techniques, such as activated carbon injection [2], much attention has been paid to other combustion sources, e.g. iron sintering processes, coke-making ovens, iron-making blast furnaces, steel-making basic oxygen furnaces, electric arc furnaces, wood waste combustion processes, and hog fuel power boilers [3-5]. Few facilities of these categories have installed dioxin control devices

other than high efficiency particulate separators like electrostatic precipitators (ESP). Despite extensive research and development efforts, effective, reliable and affordable control techniques specifically for these sources are not commercially available for industrial applications. We have investigated dioxin emissions from pulp mill power boilers burning salt-laden hog fuel, with a focus on approaches that minimize formation at source [6].

Our experiments were conducted on 9 full-scale power boilers and one pilot plant combustor [7]. Over the past three years, a total of 105 stack tests and 165 ash tests were carried out on the 9 power boilers and 22 ash tests were carried out on the pilot combustor. Only one power boiler (2 stack tests on it) burned interior wood waste containing no chlorides and the rest are coastal mill boilers burning salt-laden hog fuel. The coastal mills are all located in the same region of Western Canada with a similar climate and the hog fuels they receive contained similar moisture contents. Although dioxin emissions varied significantly between individual tests on a given boiler and between boilers at different coastal pulp mills, some boilers showed consistently higher average emissions than the others [6]. These observations suggest that, in addition to fuel properties and operating parameters, which could cause variations in dioxin emissions, the facility design may determine its average dioxin emissions or contribute to the propensity for dioxins formation.

Both proposed dioxin formation theories and reported experimental results available in the literature seem to support this view. In a comprehensive review, Kilgroe [8] reported that stack PCDD/F emissions from incinerators could range from <0.01 to more than 400 ng TEQ/m^3 , depending on the combustion and control technologies used. Kilgroe [8] indicated that PCDD/Fs may be formed at high temperatures and/or low temperatures ($600\text{-}200^\circ \text{C}$) through three primary mechanisms, all involving products of incomplete combustion (PICs):

1. Gas-phase reactions involving chemically similar (chlorinated) precursors (PICs), such as chlorobenzenes (CBs), chlorophenols (CPs), or polychlorinated biphenyls (PCBs)
2. Condensation, adsorption and desorption reactions involving gas-phase precursors (PICs) and fly ash
3. Solid-phase reactions on the surface of fly ash involving metal chlorides and unburned carbon (a PIC), or the so called “de novo” formation.

Gas-phase precursors are mainly formed at high temperatures. It is increasingly accepted [8] that gas-phase reactions cannot result in the high PCDD/F levels found in incinerator flue gases and therefore mechanisms 2 and 3, both involving solid surfaces, would be predominating. Mechanism 2 is thus frequently referred to as precursor formation and mechanism 3 as de novo formation. Altwicker [9] studied the relative rates of precursor and de novo formation and concluded that the precursor reactions tended to be much faster and could occur in a wider temperature range (up to 600°C) than de novo formation. Further, both PCDDs and PCDFs could be formed by precursor reactions but in different regions at different temperatures. Precursors led to forming predominantly PCDFs at higher temperatures (e.g. $>485^\circ \text{C}$), while at lower temperatures precursor reactions would produce more PCDDs. Other information available in the literature may, however, lead to an opposite conclusion. Huang and Buekens [10] showed that the de novo synthesis was the dominant mechanism of PCDD/F formation in actual combustion processes. Maximum formation occurred at about 300°C with little formation below 250°C and above 400°C . For de novo formation, the typical ratio of PCDDs to PCDFs was 1:1.6

and the phase distribution of PCDD/Fs was about 0.7%, 37%, and 94% in the gas phase at 250, 300, and 350° C, respectively.

Unburned “carbon”, a PIC, is never pure carbon. It contains some hydrocarbons, such as PAHs, at least a thin layer adsorbed on the surface of “carbon” particles. Iino et al. [11] defined de novo synthesis as the breakdown reaction of the carbon matrix. They suggested that PAHs were one of the possible major carbon sources for de novo formation of PCDFs but PCDDs were not formed from the PAHs. Though possible, it is not clear how PCDDs are formed by de novo. Our experimental results showed a good correlation between dioxin and PAH emissions for some of the full scale power boilers but poor or no correlation for others [12], possibly reflecting the role of PAHs in PCDD/F formation in the specific processes.

Assuming the literature results obtained with incinerators can be applied to hog fuel boilers, the boiler design and air system would affect combustion performance, leading to different quantities and species of PICs such as chlorinated precursors and/or fly ash unburnt carbon. The design and arrangement of downstream heat exchanger banks, namely the air heater and economizer, would affect the temperature and residence time distribution for precursor and de novo reactions and adsorption and desorption of PCDD/Fs in the heat exchangers, ductwork, and particulate removal devices. The design and performance of the particulate removal device would affect stack particulate emissions and consequently dioxin emissions. This paper discusses the effect of facility design on dioxin formation and emissions based on our experimental results obtained on the 8 coastal mill hog boilers [6].

EXPERIMENTAL FACILITIES

The general design information for the participating boilers is described in a separate paper [6]. The same letter as in [6] is also assigned to label the mill and its boiler in this paper. In addition to the design features presented in [6], major dimensions of the tested hog fuel power boilers at the 8 participating coastal mills are given in Table I.

RESULTS AND DISCUSSION

Table I provides a summary of the operating parameters and test results extracted from the data presented in [6]. A qualitative comparison of the dioxin emission performance of the 8 coastal boilers is given in Table II, as a further summary of the data in Table I and Ref [6] (Table II).

Boiler	Stack Dioxin Emissions	Consistency
<i>G</i>	<i>Highest</i>	<i>Poor</i>
<i>C</i>	<i>2nd Position</i>	<i>Fair</i>
<i>F</i>	<i>3rd Position</i>	<i>Good</i>
<i>A</i>	<i>4th Position</i>	<i>Poor</i>
<i>B</i>	<i>Low</i>	<i>Good</i>
<i>D,E,H</i>	<i>Lowest</i>	<i>Excellent</i>

In Table I, the results are presented in three groups for Mill A, in two groups for Mills B, C, F, and G, and in one group for Mills D, E, and H. Dioxin emissions from boilers D, E, and H were consistent and the lowest (0.01-0.14 ng TEQ/m³ @11% O₂), compared with those from the other

boilers. These three mills did not deliberately vary their operating practices and conditions for trial purposes during the stack dioxin tests over the past three years. The other five mills either substantially changed operating practices and conditions for research purposes or tried new control techniques proposed to reduce dioxin emissions. As a result, significant variations in dioxin emissions were observed from these 5 mills. The grouping employed in Table I, and in presenting the test results for the 8 mills, is to better demonstrate the effect of these operating changes.

For Mill A, the tests conducted in 2000 and 2001 were under normal operating conditions, while the 2002 tests were performed during a coal co-firing trial. The steam load for test ID July24-01 was much lower than for any other tests and the combustion conditions were very poor. As a result, both stack dioxin emissions and ash dioxin concentrations were the highest tested on all the participating boilers. This result is not considered to be typical and is not included in any of the correlations. For Mill B, the earlier tests (in the year 2000) were conducted with an on-line hog dryer operating and the later tests were conducted after the hog dryer was removed. Since the hog dryer cooled the flue gas, the stack temperatures in the 2000 tests were significantly lower than in the later tests. For Mill C, the majority of the tests were carried out under normal operating conditions. The two April 2001 tests were conducted at an elevated steam pressure, and consequently at higher air heater, ESP and stack temperatures. The May 23, 2002 test was performed at lower than normal ESP and stack temperatures, which was accomplished by opening several man-doors on the flue gas ducting. Although the stack dioxin/furan emissions are lower than normal for this boiler, the result is confounded by the fact that CNCG's were also burned in the boiler during the test. For Mill F, four of the 2002 tests were conducted with water spraying in order to lower the flue gas temperature in the ESP. Consequently, the ESP temperature became significantly lower than that observed in the earlier tests. For Mill G, some of the important operating data, namely the GB exit and air heater inlet temperatures, were not available for the pre-2002 tests and the boiler was better stabilized during the 2002 tests.

Boiler G – The poor consistency in dioxin emission performance suggests that precursor reactions provided the main dioxin formation mechanism in this boiler. This conclusion is supported by the PCDD/Fs congener profiles which indicated a very high ratio of PCDDs to PCDFs at lower grate temperatures, whereas a lower PCDD/PCDF ratio was found at higher grate temperatures [12]. Since the precursors are PICs, precursor dioxin formation means that the level of PCDD/Fs depends on the combustion performance. This is supported by the observations that dioxin emissions decreased exponentially with increasing fuel bed temperature in this boiler and can be impacted by the sludge moisture content [12] and variability in the sludge feed rates [6]. The conclusion is that periodically high dioxin emissions from this boiler were caused by poor combustion.

The poor combustion performance is, to a great extent, attributed to the boiler design. Table I indicates that this boiler is short, less than a half of the height of the tallest boiler. A short boiler cannot provide sufficient residence time for air-fuel mixing, gas-phase combustion, and residual particulate carbon burnout. Although the cross-sectional area is large compared to its steam capacity, the furnace volume is relatively small. As shown in Figure 1, the ratio of the boiler volume to its hog MCR is the second lowest, at only 68% of the 8 boiler average. It is therefore difficult to maintain good combustion efficiency in this boiler at either high or low load. The

boiler is too short and small to handle the high throughput associated with high steam loads, while the combustion temperature would be too low at low loads. The combustion performance was further downgraded by the fact that no over-fire air was used during the tests conducted in the past 3 years. The above analysis suggests that in order to improve the combustion performance and reduce dioxin emissions from this boiler, the mill could investigate the following options:

- Add a hearth burner
- Use good quality hog and reduce sludge moisture content
- Operate the boiler around the optimum steam load
- Optimize the air system, including relocation of the over-fire air nozzles
- Install some combustion performance indicators, such as a stack CO monitor

Boiler C – The fair consistency of dioxin emission performance and relatively high emissions suggest that PCDD/Fs may be formed by a combination of precursor reactions and de novo synthesis in this boiler. Again, significant precursor formation of PCDD/Fs means poor combustion performance. The boiler height is around the 8 boiler average. The ratio of cross-sectional area to its hog MCR is slightly below the average for the 8 boilers (93% if the average is normalized to 100%), while the ratio of volume to hog MCR is lower (89% of the 8 boiler average), as shown in Figure 1. However, this boiler was not able to operate even at a reasonably high hog steam load (e.g. 80% of the hog MCR) during the tests in the past three years. The hog steam load ranged from 32 to 67% of the hog MCR, the lowest utilization of boiler capacity for all 8 boilers, and frequently natural gas had to be fired to meet the mill steam demand. Even at such low hog steam loads, the boiler still experienced significant carryover and plugging. For example, the average fly ash carbon content was 44%, as shown in Table I, also the highest of all the tested boilers. Firing natural gas did not help reduce carbon carryover or dioxin emissions, as shown in Figure 2. The effect of firing auxiliary fuels was similar to that observed in Boiler A (to be discussed later).

Such poor behavior may be attributed to a number of factors. First of all, the boiler height is still not sufficient and consequently the boiler volume is too small. This cannot be seen by direct comparison of the face values of the participating boilers. Six of the 8 boilers were designed to generate lower pressure steam (400° C and 600-625 psig) than this boiler was (480° C and 1300 psig). The temperature and pressure of generated steam were 440-451° C and 970-1139 psig for this boiler, as compared to 344-410° C and 530-677 psig for those six boilers. Only Boiler E had similar steam quality (444-479° C and 861-909 psig). However, Boiler E has a much higher ratio of volume to hog MCR (200% of the 8 boiler average). Secondly, since this boiler does not have an economizer and consistently had the highest stack temperature, its thermal efficiency must be lower. This requires higher fuel input for a given steaming rate. Thirdly, as reported in [6], the combustion air temperature was the highest (over 100° C higher than the average of the other boilers), due to the high flue gas temperature and the absence of an economizer. Hotter combustion air helps dry the hog fuel on the grate, which is positive, but also helps entrain dry solid particles leading to high carryover. Fourthly, the cross-section of this boiler is rectangular with a long width and short depth (14x6.5 m²). As discussed later with Boiler A, the utilization of grate area with such a grate shape is relatively low. Finally, this boiler has a vibrating grate and vibrating actions would enhance carryover.

The above boiler characteristics also resulted in the observed high temperatures in the air heater (ca. 200-400° C), multicyclones, ESP, and stack (ca. 200-250° C). These levels of the flue gas temperature are ideal for de novo reactions, suggesting that a substantial portion of the PCDD/Fs was formed in this boiler by the de novo mechanism. A good correlation between stack dioxin emissions and stack temperature is presented in [17], while the effect of air heater temperature will be discussed later in this paper. A significant reduction in dioxin formation by firing CNCGs [13] is another indication of de novo formation in Boiler C. It was believed that the sulfur content in the CNCGs inhibited de novo reactions for PCDD/F formation [14].

Boiler F – The good consistency but above average levels of dioxin emissions, as shown in Table II, suggest that PCDD/Fs may be formed by a combination of precursor reactions and de novo synthesis but the relative contribution by the precursor mechanism may not be as great in this fluidized bed boiler as in Boilers G and C. A fluidized bed combustor can usually maintain a better combustion performance than a grate furnace. In particular, this boiler is tall, the second tallest of all the participating boilers, while its hog MCR is the fifth highest (Table I). As a result, the normalized ratio of furnace volume to hog MCR is also the second highest (128% of the 8 boiler average), as shown in Figure 1. The relatively good combustion performance of this boiler is also evident from the low unburned carbon content in the fly ash (<10%) even though the boiler was running at very high hog steam loads (95% of its hog MCR on average).

Still, the combustion efficiency of Boiler F is not as good as that of Boiler E, another BFB boiler. The average unburned carbon content in the fly ash of Boiler E was less than 3% (Table I). The different performance of these two BFB boilers is partially attributed to differences in boiler design. Boiler E is the tallest of all the boilers, and has the largest cross-section area and the largest furnace volume relative to hog MCR ratio. The cross-section area of Boiler F is, in contrast, relatively small and the normalized ratio of cross-section area to hog MCR is the lowest of all of the 8 boilers (77% of the 8 boiler average). These differences imply that if both BFB boilers were operated at the full hog MCR under the best conditions, the solid and flue gas residence times in Boiler F would be much shorter than in Boiler E. The flue gas velocity would be much higher in Boiler F, which would enhance particulate entrainment, leading to increased carryover. In addition to the boiler design characteristics, operating parameters further amplified the performance difference. As shown in Table I, the hog steam load for Boiler E ranged from 53-73% of its hog MCR during stack tests over the past three years, as compared to the average of 95% for boiler F. It should be noted that the steam load is just one of the influential parameters. Some of the lowest dioxin emission results for this boiler were obtained at the highest steam loads when tire derived fuel (TDF) was being co-fired together with flue gas quenching.

The air system designs of the two boilers are also different, as described in a separate paper [6]. A combustion process analysis was carried out to examine the profiles of excess air and flue gas velocity in the two BFB boilers. The estimated results based on two tests, one for each boiler, are compared in Table III. Although the two BFBs had similar fluidizing air velocities, the flue gas velocity in the main body of Boiler F was much higher than in the main body of Boiler E. This is due to the special design of Boiler F with an enlarged cross-section of the fluidized bed relative

to the main body of the furnace. The higher flue gas velocity largely explains the higher particulate carryover and higher unburned carbon content in the fly ash of Boiler F.

The lower furnace of Boiler F had stronger reducing conditions. Operating conditions recorded in the stack tests over the past few years indicated that 43-53%, averaging 48%, of the total combustion air was used as the fluidizing air, with 9-16% of the total as the secondary air. These levels of primary air are considered to be reasonable, although the optimum level is not determined with respect to PCDD/F formation and emissions. However, the combined primary and secondary (including start burners) air flow seemed to be low, averaging only 64% of the total air flow. In particular, the balance of the combustion air is introduced very late through the load burners and tertiary air nozzles, which are located about 7.8 and 10.6 m, respectively, above the secondary air nozzles. It is expected that increasing the combined primary and secondary air flow would improve the combustion performance in the lower furnace. However, the impacts of more primary air would be complicated, including more bed and freeboard burning, increased carryover and higher bed temperatures. It is therefore recommended to increase the secondary air flow and reduce or close the tertiary air flow. However, the ability to increase the secondary air flow was limited for Boiler F due to the small size of the secondary air nozzles. In addition, the forced draft (FD) fan was already running at its full capacity at those very high boiler loads.

For Boiler F, as mentioned above, the burner and tertiary air flow rates were too high and so are the locations for the burners and tertiary air nozzles. Table III indicates that a 13 m high section in the lower furnace was used for pyrolysis, while only 5 to 6 m in the upper furnace was available for combustion. In particular, there is only a very short distance of 2 to 3 m before the tertiary air reaches the bull nose. For comparison, while a 3 m long section in Boiler E was performing pyrolysis, there was an 18 m long section available for combustion. This is a big difference.

Because of the shorter combustion section with a higher flue gas velocity, combustion would be less complete in Boiler F. The delayed and incomplete combustion would result in the formation of more dioxin precursors in Boiler F. This is consistent with the observation that the unburned carbon content in the fly ash increased with increasing steam load for Boiler F [15]. In addition, both stack and ash samples from Mill F had higher PAH levels and greater variability [6] than those from Mill E.

De novo formation of PCDD/Fs is also considered to be significant for Boiler F because of the favorable flue gas temperature profiles in the air heater, economizer, multicyclones, and ESP. Since the economizer is located downstream of the air heater, the temperature in the air heater would be ideal for de novo reactions. The temperature and residence time available in the MC and ESP were also suitable for de novo formation. However, when the ESP temperature was lowered by spraying water into the flue gas, lower dioxin formation and emissions were measured. The effect of TDF co-firing on dioxin formation and emissions is another indication of de novo reactions [15]. It was believed that the sulfur content in the TDF inhibited PCDD/F formation by a de novo mechanism, thereby reducing the PCDD/F levels on ash and in stack emissions [14].

Boiler A – The high variability of dioxin emission performance, as shown in Table II, suggests that precursor reactions should be the main formation mechanism in this boiler. Poor combustion conditions caused high dioxin emissions. For example, one test with a very low steam load showed 2.57 ng TEQ/m³ @11% O₂, the highest of all the tests on all of the boilers, while another test with a “poor quality” salty hog and natural gas co-fired showed 0.513 ng TEQ/m³ @11% O₂.

Table I indicates that except for the two smallest boilers, this boiler is the shortest. The cross-section area is adequate compared to its steam capacity. Although the ratio of the boiler volume to hog MCR is slightly below the 8 boiler average, its value at 92% of the 8 boiler average is still the highest of all the grate boilers, as shown in Figure 1. This boiler was operated at relatively high hog steam loads (86% of the MCR on average) during stack tests over the past three years. The average levels of dioxin emissions were moderate, 0.12 ng TEQ/m³ @11% O₂ if the above highest emission result is excluded or 0.27 ng TEQ/m³ @11% O₂ if it is included.

The above analysis suggests that in order to improve the combustion performance and reduce dioxin emissions from this boiler, given the relatively short furnace, introducing fuel at high furnace levels should be consciously avoided. Therefore, co-firing coal (or TDF) on the grate should be preferred to firing gas or oil in the upper furnace. This was well demonstrated by the test results in the coal co-firing trials; co-firing coal with salty hog generated 0.034-0.036 ng TEQ/m³ @11% O₂, as compared to 0.113-0.513 ng TEQ/m³ @11% O₂ when co-firing natural gas and 0.190-0.193 ng TEQ/m³ @11% O₂ when co-firing fuel oil. A good correlation between stack PCDD/F emissions and PAH emissions for this boiler [12] also supports the precursor mechanism of dioxin formation in this boiler.

Given the large grate area relative to its hog MCR, operating at low hog steam loads should be avoided. An adequate hog load is necessary in order to maintain good combustion temperatures on the grate.

De novo formation of PCDD/Fs may not be significant in this boiler. This argument is based on the following observations:

- Relatively low air heater temperatures due to the presence of an economizer before the air heater
- The absence of a dry ESP, an important place for de novo formation at suitable temperatures (>200°C). The wet scrubber and wet ESP were operated at 60-70° C, a temperature too low for de novo formation
- Higher dioxin emissions with co-firing fuel oil than co-firing the low sulfur coal. As the sulfur content in the coal (ca. 0.25%) was lower than in the oil (ca. 1%), the effect of coal addition should not be attributed to the sulfur in the coal. Instead, the addition of coal to the hog fuel improved the combustion conditions by increasing the heat content of the solid fuel on the grate.

Wet scrubbers and wet ESPs are generally not as efficient as dry ESPs for particulate removal. In agreement with this generality, particulate emissions from this boiler are relatively high. High particulate emissions may also result in high dioxin emissions.

Fly ash samples can only be collected from this boiler as slurries. It is more difficult to derive PCDD/F formation rate data for slurries than dry ash due to inaccuracies in estimating both slurry flows and slurry solids content.

Boiler B – The good consistency of dioxin emission performance, as shown in Table II, suggests that precursor reactions may not be the predominating formation mechanism in this boiler. This is a result of generally good combustion conditions in this boiler, as seen from a comparison with Boiler A.

Boiler B and Boiler A are both traveling grate boilers. As shown in Figure 1, both the furnace cross-sectional area and boiler volume to hog MCR ratios are smaller for Boiler B, implying that it could be more difficult for Boiler B to operate at full hog steam capacity than for Boiler A. This is indeed the case. During stack dioxin tests over the past three years, the average hog steam rate was 69.5% of the hog MCR for Boiler B, as compared to 86% for Boiler A. However, Boiler B is taller than Boiler A, as shown in Table I. Another positive factor for Boiler B is that it has a square furnace cross-section, while Boiler A is rectangular and much wider than it is deep (13.9x5.6 m²). This geometrical difference is significant, particularly for grate boilers:

- The square boiler has a less specific area of water-cooled walls in the lower furnace than the rectangular boiler and therefore absorbs less of the heat released on the grate. A lower heat removal rate would help maintain higher combustion temperatures in Boiler B.
- There is usually no combustion or pyrolysis in the front (ash discharge) areas of a traveling grate. The fraction of the “wasted” grate area should be significantly lower for the square furnace than for the rectangular furnace. Therefore, Boiler B would be expected to show better utilization of its grate than Boiler A.
- Both boilers have load burners installed on the sidewalls. For the same penetrating distance, the flames or air jets from the burners would better cover the furnace cross-section in Boiler B than in Boiler A (the central plane is too far from the side walls in Boiler A). Therefore, better mixing in Boiler B would improve its combustion performance.

In addition, the lower load burners of Boiler B are only 4.6 m above the grate, whereas those of Boiler A are 7 m above the grate. Since the load burners of Boiler A are installed above the lower furnace arches, the influence of the load burners on grate combustion conditions might be further reduced. These significant differences suggest that firing auxiliary fuel would likely increase the lower furnace temperature and hence help hog fuel combustion in Boiler B but cause delayed combustion and increased carryover in Boiler A. This was supported by the temperature profiles we measured during stack dioxin tests.

Except for, perhaps, at very high hog steam loads, de novo is considered as the main mechanism of PCDD/Fs formation in Boiler B because of the favorable flue gas temperature profiles in the air heater, MCs, economizer, and ESP. Since the economizer is currently located distantly downstream of the air heater and MC, the temperatures in the air heater and MC would be ideal for fast de novo reactions, and the temperature and residence time available in the ESP would also be suitable for de novo formation. Test results for the hog fuel boiler at Mill B indicate that stack PCDD/F emissions increased linearly with the air heater outlet temperature when it was

above 250° C, as shown in Figure 3. Below 250° C, PCDD/F emissions varied insignificantly with this parameter. These results are consistent with the report by Huang and Buekens [10] that little de novo formation would occur below 250° C, confirming the significance of de novo formation of PCDD/Fs in this boiler.

The formation mechanism may be further elucidated using the ash PCDD/F concentrations as the majority of the formed PCDD/Fs stay with the fly ash. As shown in Figure 4, the TEQ levels of PCDD/Fs in the ESP ash from Boiler B increased linearly with increasing ESP ash PAH concentrations. This is in agreement with the theory by Iino et al. [11] that PAHs were one of the major carbon sources for de novo formation. These authors also indicated, however, that no PCDDs, and only PCDFs, could be formed from the PAHs. In disagreement with their theory, our results (Figure 5) indicate that the level of PCDDs was much higher than that of PCDFs in the ESP ash from Boiler B, with the ratio of PCDFs to PCDDs ranging from 1:4 to 1:11. However, Figure 5 shows that the ratio of PCDFs to PCDDs did increase with increasing ESP ash PAH concentrations.

Boilers D, E and H – The excellent consistency of dioxin emission performance and very low stack emissions, as shown in Table II, suggests that neither precursor reactions nor de novo synthesis of PCDD/Fs were significant in these boilers. A detailed analysis is not provided for these boilers but a few most important factors are highlighted here.

Boiler D: Despite smaller cross-sectional area and boiler volume to hog MCR ratios, this boiler demonstrated better combustion performance than Boilers A and C. The good combustion performance may be attributed to the hearth burner [6], installed on the right hand sidewall, 3 m above the grate, and directed 30° toward the grate. As a reference, its load burners are located 7 m above the grate. The discussion regarding the lower load burners of Boiler B is also applicable to the hearth burner of this boiler. However, the hearth burner in Boiler D should be even more effective due to the downward direction, being closer to the grate, and the smaller size of the boiler. De novo formation of PCDD/Fs should also be limited due to the presence of an efficient economizer located upstream of the air heater which lowers the temperature in the air heater and further downstream equipment.

Boiler E: Excellent combustion performance was achieved because it is a fluidized bed furnace and the fact that Boiler E was the largest and tallest of all of the 8 participating boilers. More details were reviewed in the discussion on Boiler F. De novo formation of PCDD/Fs should also be limited due to the presence of an efficient economizer located upstream of the air heater which lowers the temperature in the air heater and ESP.

Boiler H: Good combustion performance is mainly attributed to the high quality hog fuel processed in the hog dryer. The moisture content of the hog fuel burnt in this boiler was 40-45% (wet based), or 15-20% lower than hog fuel burnt in the hog boilers at the other BC coastal mills. Suppose the generation of a certain amount of steam requires burning 100 tonnes of bone dry (BD) hog at a wet based moisture content of 40%. That 100 tonnes of BD hog would bring with it 67 tonnes of water into the boiler. In comparison, 100 tonnes of BD hog at a wet based moisture content of 60% would bring in 150 tonnes of water. Further, the generation of the same amount of steam would require burning more than 100 tonnes of BD hog at a moisture content of

higher than 40%. These differences would mean a higher hog combustion temperature and significantly lower fuel solids, vapor and combustion air throughputs in this boiler. High flame temperatures generated by oil firing is another positive factor for enhancing hog combustion, particularly with the burners only 3.5 m above the grate. In addition to the good combustion performance, de novo formation of PCDD/Fs should also be limited due to the presence of a substantial amount of sulfur from the co-fired sludge and fuel oil. Direct contact between the flue gas (at up to 1000°C) and hog fuel in the hog dryer may also help destroy PCDD/Fs already present in the flue gas.

CORRELATIONS BASED ON GROUP AVERAGES

The above discussion indicates that the emission levels and significance of each of the two major formation mechanisms depend, to a great extent, on the boiler system design. However, according to the literature, the most active temperature range is 600-200° C for both precursor and de novo formation of PCDD/Fs [8-10], which covers most of the downstream heat exchangers and particulate separators such as the generating bank, air heater, and ESP. Data for the eight power boilers was further examined to determine how the design and operating parameters affect the flue gas temperature profiles in the downstream processes and PCDD/F formation and emissions.

For a given boiler, the variation of hog steam load may affect the combustion performance. High steam loads, increased auxiliary fuel firing, and delayed combustion usually result in higher temperatures in the generating bank. However, as shown in Figure 6 based on the operating data contained in Table I, the average GB exit temperature depends little on the average ratio of the hog steam rate to the hog MCR. That is, the GB temperature is generally not set by operational parameters but by boiler design. This can be understood, given that the GB temperature is primarily a function of steam temperature and pressure, two key boiler design parameters.

Figure 7 shows that the average temperature of the flue gas to the stack (after a dry ESP) or wet scrubber tends to increase with increases in the average GB exit temperature. The significant data scattering reflects whether an economizer is present and how effective the economizer and air heater are in the eight different power boilers.

While the average stack PCDD/F emissions correlate poorly with the average GB exit temperature (not shown here), the average air heater inlet temperature appears to correlate well with stack PCDD/F emissions. The retention time for the flue gas in the air heater is usually much longer than in the economizer and the flue gas temperature in the air heater is in the 300-400° C range where dioxin and furan formation by de novo synthesis is maximized. A higher temperature in the air heater might, therefore, be expected to increase dioxin and furan formation. As shown in Figure 8, the average PCDD/F emissions were low when the average air-heater inlet temperature was below 370° C. Above 370°C, PCDD/F emissions increased substantially. This critical temperature seems to agree with much of the literature data. For example, a review by Addink and Olie [16] indicated that the maximum rate for de novo formation occurred at 300-330° C with residual carbon on fly ash and 350-375° C with activated carbon and fly ash. It is less likely that the bulk of the air heater can maintain its temperature in the above optimum ranges if the inlet temperature is below 370° C than if above 370° C. Based on these findings, guidance may be established that in order to minimize PCDD/F formation and emissions, a

power boiler burning salt-laden hog fuel should be designed such that the flue gas entering the air heater would be no hotter than 370° C. However, the temperatures currently seen in these sections of the boiler are largely determined by the original boiler design specifications and layout. While the boiler layout cannot be readily changed for an existing boiler, the correlations developed in this work can be used to guide future boiler modifications and new boiler design.

A similar correlation exists between the average stack PCDD/F emissions and the average temperature of the flue gas to the stack or scrubber, as shown in Figure 9, except for one point representing some bad combustion conditions in Boiler G. The average PCDD/F emissions were low when this temperature was below 190° C. When the stack or scrubber inlet temperatures exceeded 190°C, PCDD/F emissions increased substantially. This temperature is somewhat lower than the “lowest” temperature reported in the literature [16] for de novo formation of PCDD/Fs (200° C). Given that the temperature in the stack is slightly lower than that in the ESP, however, the present results should not be considered to disagree with the literature.

Figure 10 shows that the average concentration of PCDD/Fs in the fly ash also increased as the average temperature of the flue gas to the stack or scrubber increased. However, there was little correlation between the average levels of fly ash PCDD/Fs and the average air-heater inlet temperature. These results suggest that the ESP would be a major process unit for PCDD/F formation only when it is hot. It is, therefore, essential to design and operate a power boiler burning salt-laden hog fuel to keep the ESP temperature below 190° C in order to limit PCDD/F formation and emissions. A model simulation of this effect is presented in a separate paper of the same series [17]. Again, the current ESP temperatures are primarily determined by the original boiler designs and cannot be readily altered for existing boilers.

Given a specific boiler design, operating the boiler under optimized conditions may reduce PCDD/F formation and emissions. Boiler operation is a complex process, consisting of many subsystems including the steam, fuel, air, heat exchanger, and flue gas cleaning systems [6]. Detailed analysis of these subsystems is beyond the scope of this paper. As all the mills measure the steam generation rate and hog steam load, the effect of the average steam load on PCDD/F formation and emissions is considered here as an example. Figure 11 shows that the optimum hog steam load in terms of stack dioxin emissions was approximately between 65% and 90% of the hog MCR. High dioxin emissions are expected if the boiler is operated beyond this range, particularly if the hog steam load is too low. Although there seems to be an optimum hog steam load with respect to fly ash dioxin concentrations, as shown in Figure 12, the optimum range appears to be 5-10% lower, approximately between 60% and 80% of the hog MCR. This difference suggests that

- The combustion performance affects stack dioxin emissions more than ash dioxin formation
- Higher ash carryover and a higher ESP temperature caused by higher steam loads lead to higher levels of ash dioxin formation but their effect on stack dioxin emissions is less critical.
- De novo reactions in the ESP lead to increased ash dioxin concentrations but do not contribute much to stack emissions, unless the ESP temperatures are high (>190°C).

These suggestions agree with the results shown in [12].

SUMMARY

Analysis of our experimental results obtained on 8 hog fuel power boilers at BC coastal pulp mills indicated that some boilers had consistently higher PCDD/F emissions than the others. In order to examine the effect of facility design on dioxin formation and emissions, the intramill tests conducted over the past 3 years were regrouped for presentation purposes and the individual results within the group were averaged to give each group a “representative” emission level. Mills D, E, and H have only one group each. However, Mills A, B, C, F, and G are each presented in two or three groups to reflect the substantial equipment modifications or variations in operating conditions during the different stack tests.

The general emission performance of a specific boiler was evaluated in terms of average emission levels and performance consistency, or variability, based on the predominating dioxin formation mechanism. Correlations were developed using group average parameters. The following conclusions were drawn:

PCDD/Fs were formed mainly by precursor reactions in Boiler A and the key to additional emission reduction on this boiler is to further improve combustion performance. Coal (or TDF) is preferred as an auxiliary fuel rather than oil or natural gas because coal co-firing increases combustion temperatures on the grate, improving combustion in the lower furnaces.

PCDD/Fs were formed by both de novo synthesis and, to a lesser extent, precursor reactions in Boiler B. The key to maintaining good combustion performance is to operate this boiler at moderate hog steam loads (e.g. <85% of the MCR). Firing auxiliary fuel in this boiler helped hog combustion and the two preferred load burners are the left-rear and right-front ones. The economizer would be preferably located before the air heater. Such an arrangement would limit de novo formation of PCDD/Fs and also reduce the possibility of fires in the air heater and MC ash chutes. However, a relocation of the economizer and air heater would be costly.

PCDD/Fs were formed by a combination of precursor reactions and de novo synthesis in Boiler C. The combustion performance was not good with the boiler being operated at very low hog steam loads. It is possible that the boiler might not be providing sufficient gas and solid reaction times at high combustion throughputs necessary for the designed hog steam capacity and, particularly, for the designed high steam temperatures and pressures. Firing natural gas in the upper furnace did not help hog combustion, nor reduce dioxin emissions. The downstream flue gas temperatures were adversely high for this boiler, which could cause significant formation of dioxins/furans by de novo reactions. Although a detailed cost assessment is not available, measures required to lower the air heater and ESP temperatures are expected to be expensive.

Neither precursor reactions nor de novo synthesis were significant in Boilers D and E. The hearth burner, which is located close to the grate in Boiler D, helped improve combustion performance. Excellent combustion performance can be maintained in Boiler E, a large, tall bubbling fluidized bed boiler. The economizer, being located before the air heater for both boilers, limited de novo formation of PCDD/Fs.

PCDD/Fs were formed by a combination of precursor reactions and de novo synthesis in Boiler F. This boiler is the thinnest relative to its hog MCR and therefore has the highest flue gas velocities. The combustion efficiency was generally high, as expected for a fluidized bed boiler, although the ash unburned carbon content increased at high steam loads. In order to maintain the best combustion performance, the secondary air flow should be increased and the tertiary air flow should be reduced or closed. De novo formation of PCDD/Fs was possible because of the high temperature in the air heater. To minimize de novo formation, the air heater should be placed after the economizer. However, a relocation of the economizer and air heater would be costly and physically difficult for this mill. The addition of TDF, a sulfur containing fuel, can inhibit de novo formation even with the existing economizer location.

PCDD/Fs were formed mainly by precursor reactions in Boiler G. This boiler has a large cross-section to hog MCR ratio but it is too short relative to its hog MCR. Lower dioxin emissions can be expected with improved combustion conditions, which would lead to reduced levels of PICs. Improvements in the combustion efficiency may be possible by installing a hearth burner, modifications to the over fire air system, and operation of the boiler around the optimum steam load.

Neither precursor reactions nor de novo synthesis were significant in Boiler H. High quality hog fuel produced in the hog dryer ensured good combustion performance. De novo formation of PCDD/Fs should also be limited due to the presence of a substantial amount of sulfur in the sludge and fuel oil and rapid cooling of the flue gas across the hog drier.

Higher flue gas temperatures in the post-GB (generating bank) processes promote dioxin formation by both de novo and precursor reactions. Based on average values for the eight hog boilers, stack dioxin emissions increased with air heater inlet temperatures above 370° C. Stack dioxin emissions, as well as ash dioxin contents, increased also with average temperature to scrubber/stack above 190° C. The optimum range of hog steam load was roughly between 65% and 80% of the hog MCR in terms of both stack dioxin emissions and fly ash concentrations. The actual optimum range is very much boiler specific.

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NOMENCLATURE

- BDt = Bone dry tonnes
BFB = Bubbling fluidized bed
ESP = Electrostatic precipitator
GB = Generating bank
Hog fuel = Bark and wood waste
LOI = Loss on ignition
MC = Multicyclones
MCR = Maximum Continuous Rating for steam generation
ng = nanogram (10^{-9} g)
PAHs = Polycyclic (polynuclear) aromatic hydrocarbons (only the 16 species required to be reported in the National Pollutant Release Inventory (NPRI) program in Canada are included for this study)
PCDDs = Polychlorinated dibenzo-p-dioxins
PCDFs = Polychlorinated dibenzo-furans
PIC = Products of incomplete combustion
PM = Particulate matter
t/h = metric tonnes per hour
T = Temperature
TEF = Toxicity equivalent factor of dioxins/furans
TEQ = Toxicity Equivalent to 2,3,7,8-tetra-chlorinated dibenzo-p-dioxin
= $\sum\{(TEF)_i \cdot C_i\}$, where $(TEF)_i$ is the NATO TEF of congener i, C_i is its concentration.

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Table 1. Summary of Boiler Design and Operating Parameters and Test Results

Boiler ID	Hog MCR	Furnace cross-sectional area ¹	Furnace volume ²	Boiler height ³	Stack test date	Hog steam rate/Hog MCR	Steam quality		GB exit flue gas T	Air-H inlet flue gas T	Air-H outlet flue gas T	Flue gas to scrubber or stack T	Ash rate ⁴	Ash ⁵ carbon content	Stack TEQ@11% O ₂	Fly ash TEQ	Note
	t/h steam	m ²	m ³	m		%	T, °C	P, psig	°C	°C	°C	°C	kg/t	%	ng/m3	ng/g	
A	182	78.0	921.4	20.3	2000-01	76-93	388-396	646-677	371-406	255-290	199-207	199-207			0.047-0.20	5.61-8.29	A1
					Jul24-01	54	382	626	352	260	193	193			2.57	14.8	A2
					2002	74-107	393-410	654-677	404-441	287-309	202-216	202-216			0.01-0.513	0.75-8.48	A3
B	204	74.5	876.6	23.9	2000	33-79	397-398	n/a	320-332	320-332	243-266	137-168	29.1 (59)	19.5 (31)	0.04-0.23	n/a	B1
					2001-02	49-89	396-399	591-620	336-386	336-386	237-264	191-206					0.02-0.19
C	239	91.7	1177.6	23.8	2000-02	32-67	440-451	970-1062	358-405	358-405	199-215	176-243	30.4 (22)	43.6 (14)	0.16-0.56	0.5-4.6	C1
					April-01	50-51	450-451	1135-1139	417	417	250	254					0.40-0.87
D	115	36.8	529.8	23.2	2000-02	68-106	357-382	604-658	350-405	312-345	147-203	119-176			0.01-0.138	2.71-5.82	
E	272	143.1	3005.6	32.5	2000-02	53-73	444-479	861-909	398-444	261-303	163-186	163-186	35.6	2.58	0.014-0.176	0.17-1.79	
F	156	49.7	1103.8	28.7	2000-02	76-107	396-398	557-604	376-407	376-407	284-301	179-206	38.1	9.71 (13)	0.021-0.55	1.19-8.90	F1
					2002	89-104	398-399	588-600	397-407	397-407	286-301	163-166					0.012-0.289
G	60	27.6	223.6	15.1	2000-01	35-85	344-360	530-547	n/a	n/a	174	138-164	24.4 (44)		0.069-1.72	0.89-2.63	G1
					2002	80-91	351-358	548-556	337-340	291-304	174-182	174-178				0.056-0.27	2.55-4.42
H	54	26.5	183.5	12.9	2001-02	70-98	388-392	594-629	326-363	326-363	162-192	140-159			0.012-0.144	0.34-0.78	

1. The cross-section of the bed area is larger (81 m2) than the main body of the furnace for Mill F

2. From Grate/Bed to the Bullnose tip. The lower furnace arc volume is deducted for HSPP & Elk Falls.

3. From Grate/Bed to the boiler Roof at steam drum centerline

4. Only that portion of flyash is included, where samples were usually taken for ash PCDD/Fs tests. The ash rate is given as kg of dry ash per tonne of hog burned.

The value in the brackets is the rate of grate+total flyash for Mill B. The value in the brackets is the rate of grate ash for Mill C

The ash rate for Mill B is based on test in May 2002, while the ash rates for Mills C,D and E are three year average of 2000, 01 and 02.

5. ESP ash (MC ash) for Mill B; Total flyash (ESP ash) for Mill C; Total flyash for Mill E; Total flyash (ViscDyn+MC ash) for Mill F; ESP ash (MC ash) for Mill G.

Note: A1 = pre-coal trial; A2 = bad combustion; A3 = coal trial. B1 = hog dryer on line; B2 = dryer off but presses on. C1 = normal; C2 = higher steam pressure. F1 = normal;

F2 = water spraying. G1 = Incomplete data, unstable operation; G2 = improved operation. See the first 2 paragraphs of Section "Results and" for more details.

Table III. Comparison of Design and Typical Operating Conditions in the Two BFB Boilers

	Air Supply	Section Length	Excess Air	Combustibles	Velocity
	Sm³/min	m	%	in % CO	m/s
Mill E Test ID: 8-Mar-01					
Prime Air	2,740				
		2.8	-18.1	5.4	2.12
Secondary Air	926				
		4.3	9.6	0	2.79
Tertiary Air	74				
		6.5		0	
Burner Air	521				
To & at Bull Nose		7.4	27.4	0	5.26
Mill F Test ID: 31-Jan-01					
Prime Air	1,465				
		5.5	-38.2	13.1	2.53
Secondary Air	508				
		7.8	-16.7	5	4.92
Burner Air	703				
		2.8	12.9	0	5.86
Tertiary Air	586				
To & at Bull Nose		2.6	37.7	0	11.03

For Mill E

PA = fluidizing air

SA = lower & upper 2nd air + hog chutes + start burner air

TA = tertiary air + load burner air

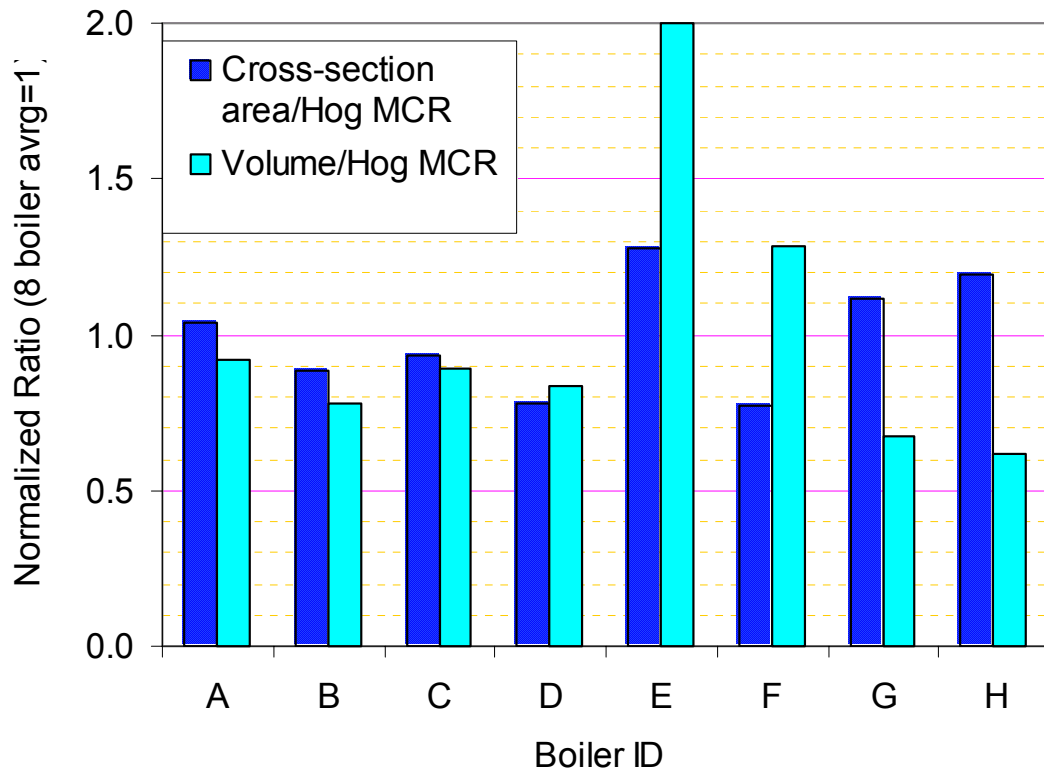


Figure 1. Comparison of boiler cross-section area and volume

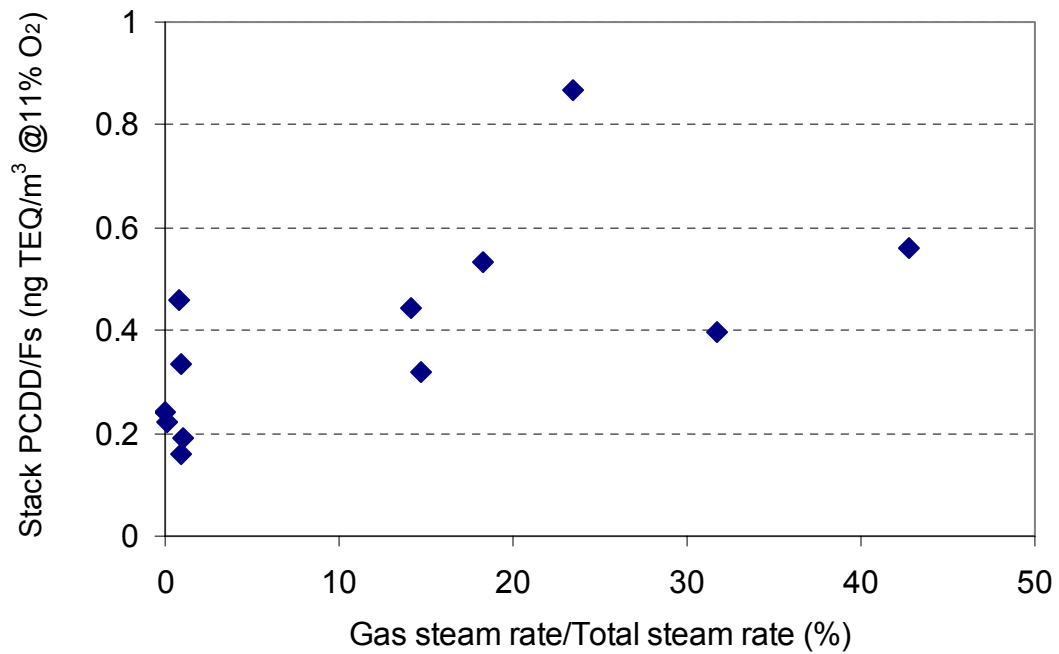


Figure 2. Effect of firing auxiliary fuel on dioxin emissions, Mill C

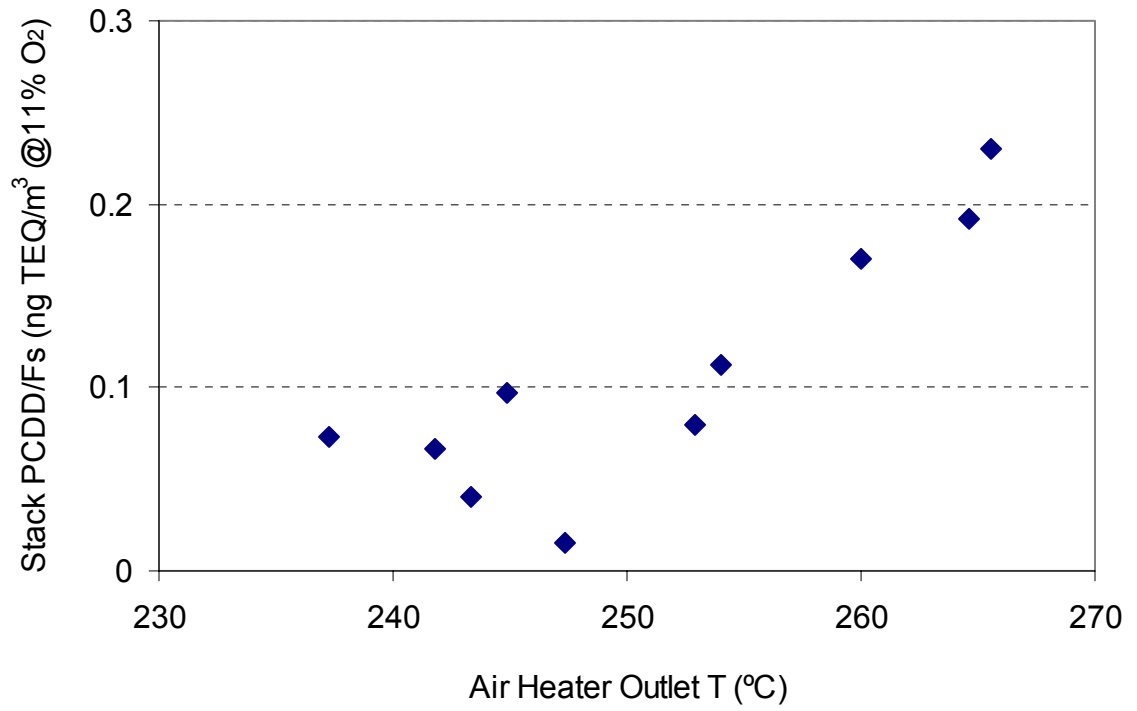


Figure 3. Effect of air heater outlet temperature on stack dioxin emissions, Mill B

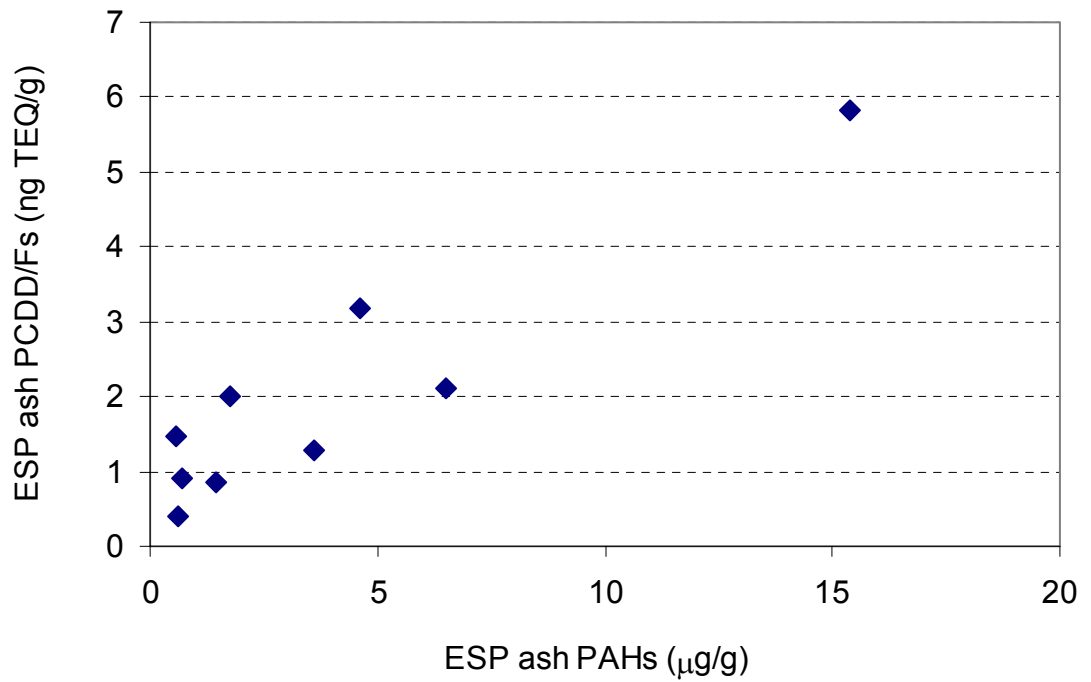


Figure 4. Correlation between ESP ash PCDD/F concentrations and ash PAH concentrations at Mill B

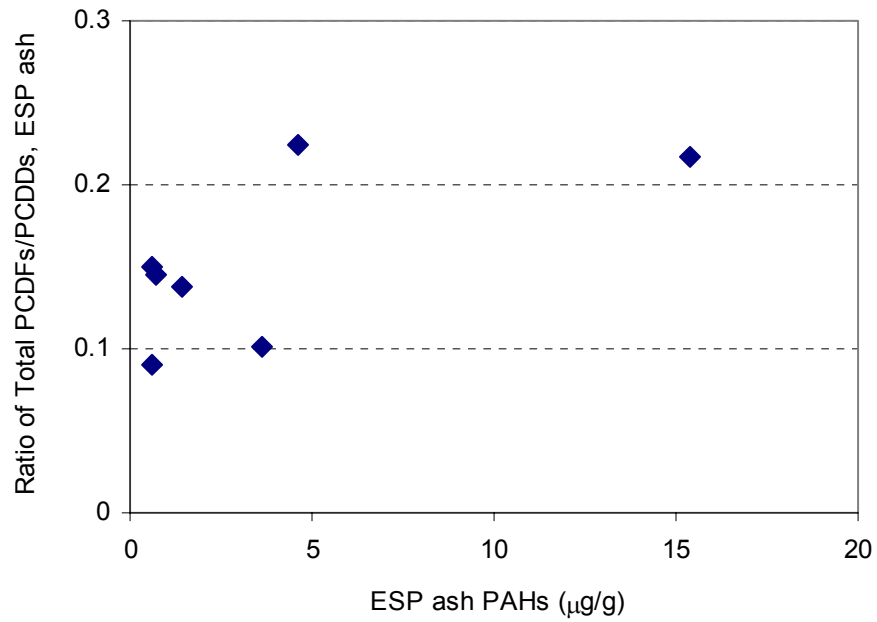


Figure 5. Effect of ESP ash PAH concentrations on the ratio of total PCDFs to PCDDs at Mill B

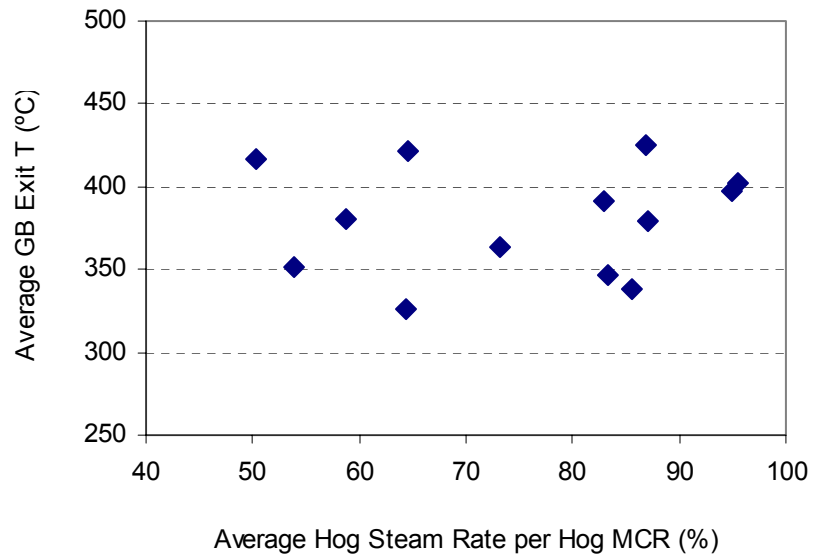


Figure 6. Effect of group average hog steam load on group average GB exit temperature

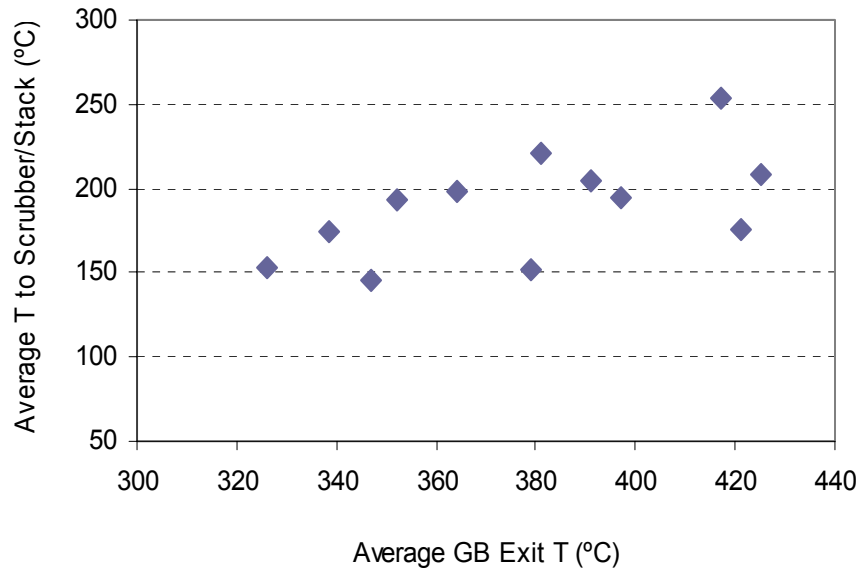


Figure 7. Effect of group average GB exit temperature on group average temperature to scrubber/stack

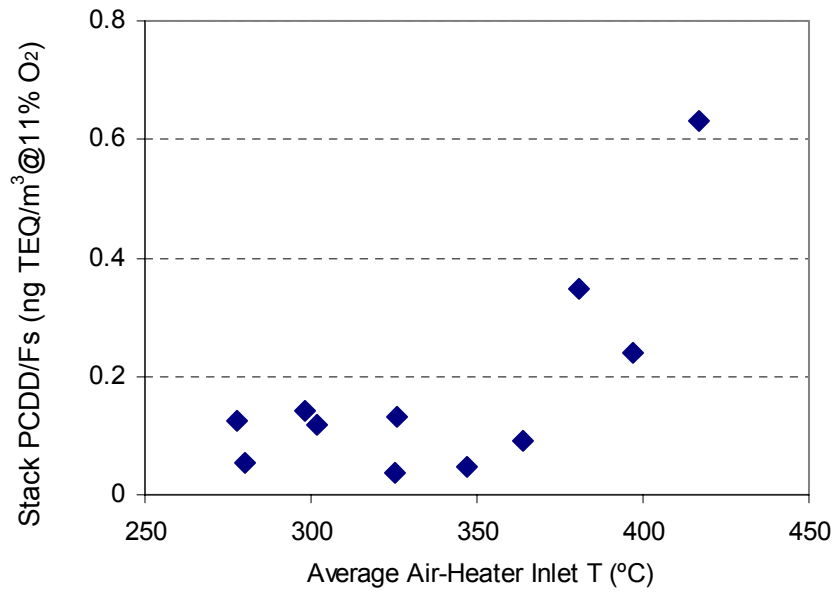


Figure 8. Effect of group average air heater inlet temperature on dioxin emissions

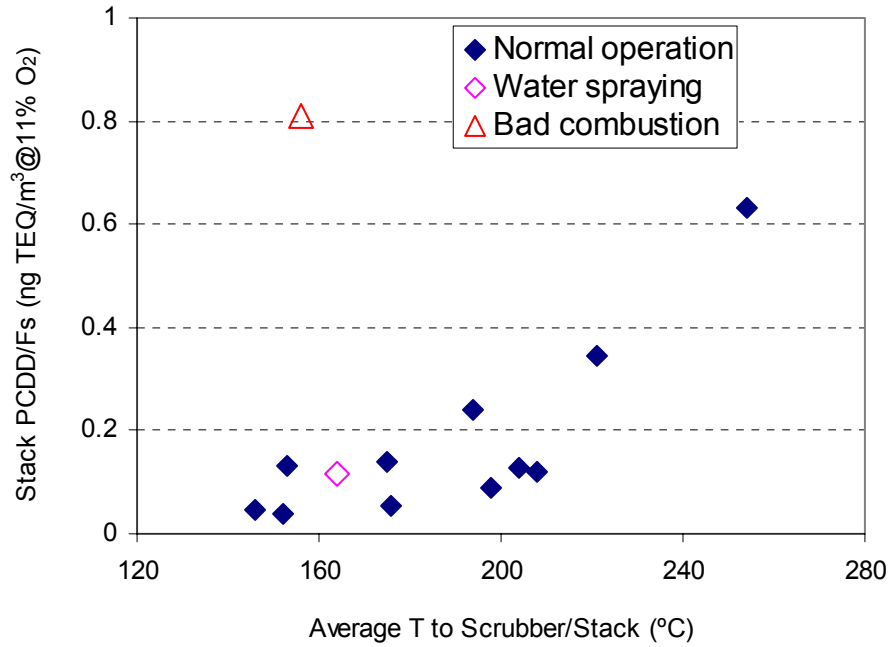


Figure 9. Effect of group average temperature to scrubber/stack on dioxin emissions

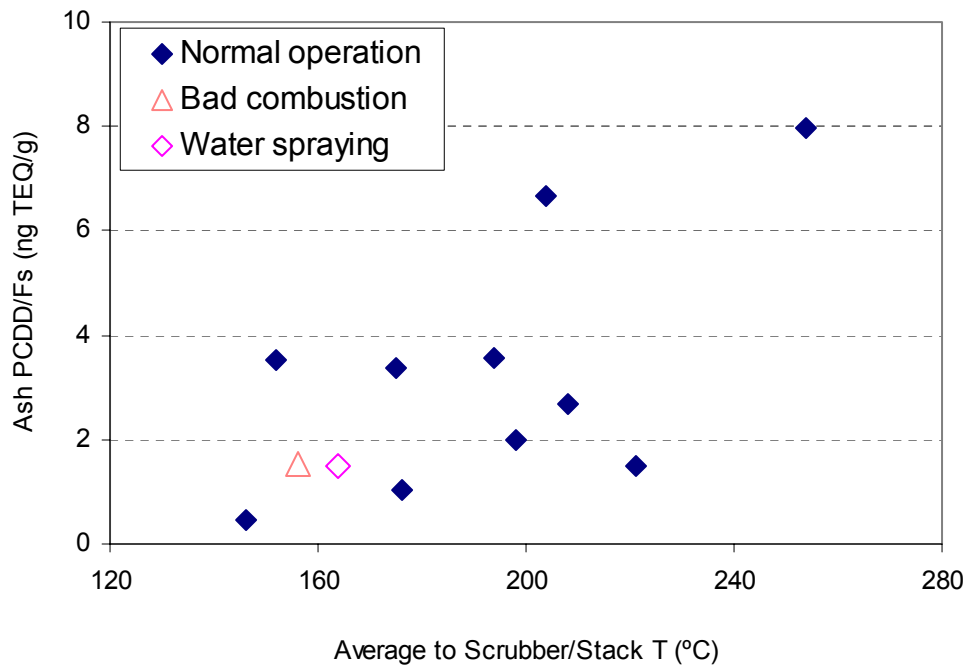


Figure 10. Effect of group average temperature to scrubber/stack on ash dioxin concentrations

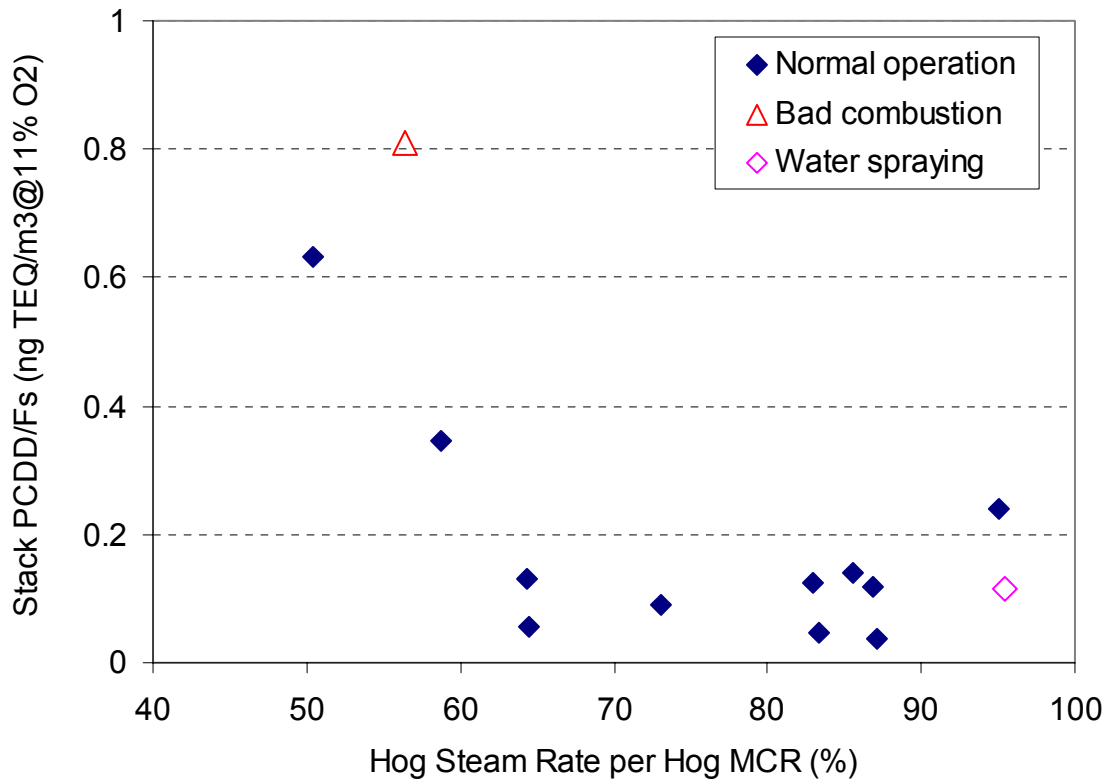


Figure 11. Effect of group average hog steam load on dioxin emissions

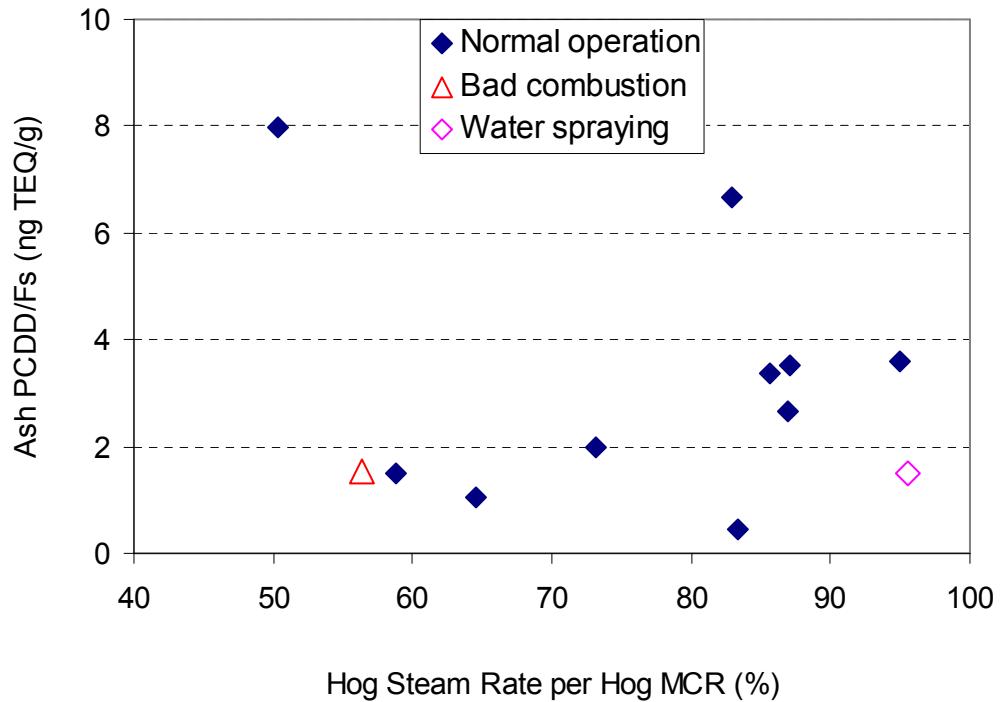


Figure 12. Effect of group average hog steam load on ash dioxin concentrations