

EFFECTS OF COMBUSTION AND OPERATING CONDITIONS ON DIOXIN EMISSIONS FROM POWER BOILERS BURNING SALT-LADEN WOOD WASTE

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ABSTRACT

This paper discusses selected results that shed light on the effects of combustion conditions on dioxin/furan emissions from pulp and paper power boilers burning salt-laden wood waste.

We found no correlation between dioxin/furan emissions and carbon monoxide emissions in tests on power boilers at eight different mills. A good correlation was, however, observed between dioxin/furan emissions and stack PAH concentrations in the absence of TDF addition. This suggests that poor combustion conditions responsible for the formation of products of incomplete combustion (PICs), such as PAHs and dioxin/furan precursors, also increase dioxin/furan emissions. In addition, dioxin/furan and PAH emissions were found to generally increase with lower oxygen concentrations at the boiler exit, which generally produce poor combustion performance. On the other hand, ash carbon content increased with higher boiler load and/or low oxygen concentrations at the boiler exit, probably because of lower available residence times and insufficient excess air, which result in incomplete carbon burnout. Our findings are consistent with the current understanding that high ash carbon content generally favours heterogeneous reactions leading to either *de novo* synthesis of dioxins/furans or their direct formation from precursors. Using grate/lower furnace temperatures as a general measure of combustion performance in grate-fired boilers, we also found that a linear increase in the grate/lower furnace temperature produces an exponential decrease in dioxin/furan emissions. Although the extent of this effect appears to be mill-specific, particularly at low temperatures, the results indicate that increasing the combustion temperature may improve combustion performance. It must be noted, however, that there are many variables, such as the stack temperature, contributing to power boiler dioxin emissions. Therefore, higher combustion temperatures, by themselves, will not necessarily result in low dioxin emissions.

KEYWORDS

Dioxins, furans, combustion, wood waste, hog fuel, polycyclic aromatic hydrocarbons, carbon monoxide, combustion performance.

INTRODUCTION

Background

When wood is transported and stored in booms in the marine waters along the west coast of Canada, the bark absorbs significant amounts of sodium chloride. After debarking, the sawmill refuse is hogged, i.e. passed through a disintegrator, or hog, and reduced into a relatively narrow range of sizes. When burning such salt-laden wood waste, power boilers can emit dioxins and furans under certain combustion conditions [1-3]. These emissions are now the subject of regulatory limits to be met by 2006, including the recently adopted Canada-wide standards, i.e. 0.5 ng TEQ/m³ @ 11% O₂ for existing boilers and 0.1 ng TEQ/m³ @ 11% O₂ for new boilers [4]. For the last two years, coastal boiler operators in British Columbia have been collaborating on a research and testing program with the Pulp and Paper Research Institute of Canada and the University of British Columbia to better understand the formation of dioxins and furans in their facilities, and to identify and evaluate possible measures or approaches that will reduce, minimize or avoid dioxin/furan emissions [4]. Detailed results from this program are discussed separately [5-10].

While the presence of significant concentrations of chloride in wood wastes, such as hog fuel, is one of the causes of dioxin/furan emissions, poor combustion conditions are also an important factor [11] because they produce direct polychlorinated dibenzo *p*-dioxin/furan (PCDD/Fs) precursors, such as chlorinated phenols (CPs), chlorinated benzenes (CBs), and other products of incomplete combustion (PICs), such as fly-ash carbon and polycyclic aromatic hydrocarbons (PAHs). Since it is usually formed under fuel-rich, i.e. starved-air, conditions, carbon monoxide (CO) has been previously investigated as a potential surrogate variable for predicting dioxin/furan emissions [12]. However, even under good combustion conditions for which only a small change in the CO concentration [12] is observed, dioxin/furan emissions can still vary by several orders of magnitude. Therefore, the relationship between combustion conditions and the concentration of CO, PICs and dioxin/furan emissions is not well established [13]. Indeed, the effects of downstream conditions on dioxin/furan emissions can mask the effect of upstream combustion conditions found in the furnace, as previously shown by Everaert and Baeyens [14].

A bark-fired boiler can normally operate without auxiliary fuel if the fuel provided contains less than 50% moisture. Since hog fuel at coastal BC mills generally contains more than 50% moisture, varying amounts of natural gas, oil, and solid fuels such as coal or tires have often been used to insure adequate combustion and meet steam generation requirements.

The processes experienced by wood wastes during their combustion are: evaporation of water, pyrolysis and char formation, and char/volatiles oxidation [15]. Pyrolysis is initiated in the lower furnace by starved-air combustion (negative excess oxygen) with underfire air. This step produces carbon monoxide (CO), thermal degradation products and char in the form of fly-ash carbon. When assisted by an auxiliary fuel, pyrolysis should occur at a higher temperature and be more complete. Conversely, a lower combustion temperature increases the formation of dioxin/furan precursors, such as chlorobenzenes (CBs), chlorophenols (CPs) and polychlorinated biphenyls (PCBs), as pointed out by McKay [16]: the poorer the combustion performance, the longer the residence time needed to achieve destruction of dioxins/furans and/or their precursors. McKay has discussed the general conditions required for complete burnout of fly-ash carbon in municipal solid-waste incinerators (MSWIs). However, conditions in MSWIs are not necessarily applicable to hog-fired power boilers. Discussing combustion conditions for hog-fired power boilers, Luthe and Prahacs [17] indicate that significant destruction of dioxins/furans and/or their precursors occurs when furnace temperatures exceed either 950 °C for 3 seconds or 1050 °C for 1.5 seconds. However, they cautioned that these conditions are sometimes difficult to achieve in large-scale incinerators without the use of auxiliary fuels [17].

In the middle and upper furnace, overfire air is normally provided in excess of the stoichiometric oxygen requirements (positive excess air) so as to enhance mixing and combustion, and to complete carbon oxidation before the flue gas exits the boiler. Insufficient overfire air, and/or short residence times due to poor boiler design and high-load operation, would invariably leave significant quantities of CO unoxidized and can produce large amounts of PICs, such as PAHs and dioxin/furan precursors [18]. McKay [16] reviewed the combustion conditions needed to minimize dioxin/furan emissions, and reported that the amount of excess air must be sufficiently high to minimize fuel-rich pockets, but sufficiently low to avoid quenching of combustion reactions, with an optimum level of four to six percent excess oxygen. In summary, the conditions for achieving good combustion are 1) maximization of the so-called '3Ts', i.e. temperature, time, and turbulence (achieved through judicious air distribution), and 2) optimization of the excess-air profile in the furnace [15-16].

Short flue-gas residence times and inefficient air supply in the upper furnace thus create a continuing source of pyrolysis products at the boiler outlet [17], thereby favoring direct dioxin/furan formation from precursors, such as chlorinated alkenes. The additional presence of unburnt carbon in the post-combustion zone of the boiler [17] sets the stage for the so-called *de novo* low-temperature formation of dioxins and furans on fly ash particles [19]. This *de novo* formation occurs mainly during slow post-combustion cooling, over a temperature range from 500 to 200 °C.

Removing sodium chloride (salt) from the hog fuel has been shown to be impractical for many coastal mills, and not necessarily an effective means of mitigating dioxin/furan emissions [20]. For example, Luthe *et al.* reported higher dioxin/furan emissions from a low-salt hog fuel than from a high-salt hog fuel [11]. Consequently, a number of other mitigating strategies have been proposed. One of these involves reducing the chlorine-to-sulphur ratio of the fuel by providing an auxiliary fuel rich in sulphur, such as coal [21] or tire-derived fuel (TDF). Duo *et al.* [7] have also reported that, given adequate combustion conditions, significant reductions in dioxin emissions can generally be achieved by co-firing hog fuel with a TDF containing 1.6 % sulphur, even though the fly-ash carbon content increases with the higher boiler loads seen during the TDF addition tests.

Luthe *et al.* reported that the beneficial effects associated with low chlorine-to-sulphur ratio are not necessarily observed in stack tests if combustion conditions are poor [11]. In boilers with highly variable or unstable combustion conditions, the effect of mitigating strategies will not be as clear as it would be in boilers with good combustion conditions since the extent of dioxin/furan emissions depends on the amount of PICs present in the flue gas and on the concentration of fine, carbon-rich fly-ash particulates passing through the *de novo* formation zone.

Carbon monoxide

Since carbon monoxide is formed mainly in the lower furnace in a fuel-rich atmosphere and then partially consumed by reaction with the overfire air in the upper boiler, it is usually present in low concentrations in the stack gas of well-run boilers. Conversely, high concentrations of CO are generally indicative of poor combustion conditions. For example, Everaert and Baeyens [14, 22] have reported a fair correlation of CO with dioxin/furan emissions. However, CO is not sensitive enough to distinguish between good and excellent combustion in terms of dioxin/furan emissions: Kilgroe *et al.* [12] report that, at low CO concentrations, the correlation between CO and PCDD/Fs completely breaks down. The reason is that global CO concentrations do not measure localized combustion inefficiencies that may produce dioxin and furans. This is confirmed by our observations [5] that some boilers with very low CO emissions may have both stack emissions and dioxin formation rates that are much higher than those measured in other boilers operating with substantially higher CO emissions. Weber *et al.* [13] report that using 4-hour averages slightly improves the relationship. Unfortunately, such a correlation would be of limited utility for on-line monitoring.

Polycyclic aromatic hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons (PAHs) are a complex mixture of non-chlorinated organic compounds having two or more fused aromatic rings, and are usually formed under fuel-rich and poor-mixing conditions [18] as products of incomplete combustion. PAHs are released into the atmosphere as condensed species adsorbed on the carbon of fine fly ash particles [23]. Since these fine particles can penetrate into the respiratory system, PAHs constitute a significant health hazard [23] and, as discussed below, are also possibly involved as precursors in the *de novo* formation of dioxins/furans.

Poor combustion conditions produce high emissions of PAHs as well as CO. A large fraction of the formed PAHs are associated with fine particulate matter, which is largely removed in the various particulate collection devices (e.g. electrostatic precipitator) before stack sampling. It has been proposed that PAHs may also participate directly in the reactions leading to dioxin/furan formation [24-25]. Thus, it is reasonable to assume that the extent of stack dioxin/furan emissions would depend on conditions favouring incomplete combustion, leading to the presence of unburnt carbon in fly ash. The latter favours *de novo* synthesis from PICs adsorbed on carbon, such as PAHs and dioxin/furan precursors. Indeed, Lee *et al.* [26] have demonstrated a correlation between total PAH concentrations and the amount of organic carbon in fly ash.

Predicting dioxin/furan emissions using PICs or PAHs

Given the difficulties and high costs of measuring stack dioxin/furan emissions, a number of researchers have attempted to develop simple, easy-to-measure, reliable indicators of dioxin/furan emissions. For example, Lemieux *et al.* [27] found a fair correlation between a surrogate species, vinyl chloride, and PCDD/Fs emissions. However, the range of operating conditions they investigated was quite limited, and no attempt was made to link dioxin/furan emissions to operational variables. Benfenati *et al.* [24] have reported a very strong correlation between micro pollutants, such as PAHs, and dioxin/furan emissions from a fluidized-bed pilot plant boiler. Wilhelm *et al.* [25] studied the role of PAHs and related precursor compounds in the formation of dioxins and furans. They found that high-molecular-weight PAHs, i.e. xanthene, fluoranthene and fluorene, as well as diphenyl and biphenyl compounds, were more likely to participate in PCDD/Fs formation, and that, except for xanthene, furans were formed in greater amounts than dioxins. On the other hand, low-molecular-weight PAHs, such as acenaphthylene, acenaphthene, phenanthrene and anthracene, did not yield dioxins in significant amounts. Luthe *et al.* [23] were the first to characterize in detail the PAH emission profile from several hog-fuel power boilers operated by Canadian pulp and paper producers. A careful analysis of their data (see appendix of [23]) shows that, for most power boilers burning hog fuel, the majority of high-molecular-weight PAHs, i.e. those with four rings or more, are represented by fluoranthene and pyrene. Similarly, Hoerning *et al.* [28] have also shown that the two most abundant high-molecular-weight PAHs resulting from wood combustion are fluoranthene and pyrene. This suggests very strongly that the high-molecular-weight four-ring fraction of stack PAH emissions, would be an excellent indicator for predicting dioxin/furan emissions on-line and for monitoring combustion conditions in boilers burning salt-laden wood waste.

On-line PAH measurements

Obernberger *et al.* [29] pointed out that wood and bark combustion generate very fine aerosol particles with an average diameter ranging from 0.1 to 0.5 micrometers. Depending on combustion conditions, these fine particles may contain considerable amounts of PICs, including PAHs, adsorbed on unburnt carbon, as well as sulphates and chloride [29]. Unlike micron-sized particulate matter, ultra fine particles cannot be captured by the electrostatic precipitator and are emitted into the atmosphere with the combustion gases. A technique that can measure particle-bound PAHs on-line in combustion aerosols has subsequently been developed and tested in the field [30].

Purpose of this work

In this report, we present and discuss selected results that shed light on the effects of combustion conditions on dioxin/furan emissions from industrial power boilers burning salt-laden wood waste. The relationship between readily available surrogate variables, i.e. CO and PAHs, and dioxins/furans emissions is first reviewed. Results from a trial conducted with an on-line PAH sensor are then presented. Subsequently, the effect of boiler load and boiler-exit oxygen on PAH and dioxin/furan emissions is discussed. The relationship between poor combustion performance and high dioxin/furan emissions is also demonstrated.

EXPERIMENTAL

Flue gas sampling

Flue gas was sampled at the stack, typically for 180 minutes, for carbon monoxide (CO), chlorinated dibenzo-p-dioxins/dibenzofurans (abbreviated dioxins/furans), polycyclic aromatic hydrocarbons (PAHs) and particulates. The sampling and analytical methods conformed to the procedures outlined in Environment Canada's reference method for source sampling of semi-volatile compounds, commonly known as Modified Method 5 [31]. The procedures used for the analysis of dioxins/furans and PAHs conform to the requirements of the United States Environmental Protection Agency [32]. A. Lanfranco and Associates Inc., Langley, B.C. performed the flue gas sampling, and AXYS Analytical, Sydney B.C., performed the analysis of the sampling extracts. Results for stack PAHs are reported here as the total of all 16 species reported under the Canadian NPRI program [5, Table A-2]. Results for dioxins/furans are reported in NATO Toxicity Equivalents (TEQs).

Grate/lower furnace temperature, fuel moisture and boiler-exit oxygen

Temperatures in the lower furnace were determined with an infrared pyrometer by using the available observation ports and doors in the lower furnace of each boiler. Details on the different boilers and measurements are provided in reference [5]. Other combustion variables, such as boiler steam load, hog fuel feed rate and/or steam production from hog fuel, and boiler-exit oxygen, were either recorded or logged manually from the mill's DCS output at half-hour or hourly intervals during a stack test. Hog-fuel moisture was determined with the oven-dried method using composite samples of hog fuel taken during each stack test. More details about the measurements are presented elsewhere [5].

On-line measurement of PAHs

The stack monitoring version of the photoelectric aerosol sensor (PAS) manufactured by EcoChem Analytics (Murrieta, CA) was used for the on-line PAH trials. One unit was installed in the unheated ESP rapper room of the hog-fuel power boiler at Mill B. The stack monitoring system includes a PAS 2000 PAH analyser, a separate dilution system controlled by a mass flow meter and a heated stack probe. Jahnke [33] exhaustively discussed the use, design and challenges of dilution systems.

Because of the high moisture content (20-30 %) of the stack gases, the nominal dilution factor was set to 100:1 so as to avoid bringing the sample mixture below its dew point during periods of cooler weather. The recommended calibration factor ($\approx 1.25 \mu\text{g}/\text{m}^3$ per pA) was used. Signal averaging was performed over two-minute intervals, and the value displayed by the analyser was recorded by the mill's DCS at one-minute intervals.

RESULTS AND DISCUSSION

Effect of surrogate variables on dioxin/furan emissions

Carbon Monoxide

The lack of a significant correlation between carbon monoxide and dioxin emissions is clearly shown in Figure 1 for the eight boilers participating in the stack sampling program. The fitted curve is for Mill A. In general, correlations for intramill data are very poor, as illustrated by the fitted curve for the power boiler at Mill A. For example, even though the dioxin/furan emissions for the power boiler at Mill D are consistently very low, its carbon monoxide emissions are quite variable, i.e. from 50 to 570 ppm. The two highest CO values shown for Mill D in Figure 1 are attributable to low oxygen levels in the boiler, i.e. 1.4 and 1.9 %, which would be expected to preclude oxidation of CO to CO₂. On the other hand, Mill F has very variable dioxin/furan emissions which do not seem to be related to combustion conditions, with carbon monoxide varying between 100 and 800 ppm and dioxin/furan emissions from 0.02 to 0.55 ng TEQ/m³ @ 11% O₂. Again, however, no correlation between CO and dioxin/furan emissions is evident. Mill C shows the same trend as Mill F but with lower CO values, which indicates that the *de novo* mechanism for dioxin/furan formation may be dominant for these two mills because of a higher stack temperature [8], rather than being dependent on combustion conditions through the precursor mechanism. Nevertheless, the results from all participating mills suggest very strongly that carbon monoxide would not be a reliable surrogate variable for monitoring combustion conditions leading to significant dioxin/furan emissions.

Polycyclic Aromatic Hydrocarbons (PAHs)

An illustration of the relationship between stack PAH emissions and stack dioxin/furan emissions is shown in Figure 2 for the power boilers at Mills A, B, D, E, and G. The fitted curve is for Mill A. Even though the data show a fair amount of scatter at low PAH concentrations, dioxin/furan emissions generally increase with PAH emissions, in contrast to their relationship with CO. Some general correlation is apparent at higher PAH concentrations for the boilers at Mills A, B and G, i.e. the higher the PAH emissions, the higher the dioxin/furan emissions. The slope of the correlation appears to be mill-specific for low dioxin/furan emissions. For example, this slope is lower for Mills D and E at low dioxin/furan values than that for Mills A, B and G. The two highest dioxin/furan emission concentrations observed for Mill G follow a very steep slope probably caused by very poor combustion conditions. The consequence of the latter would be to produce a higher rate of dioxin/furan formation from precursors, and/or a lower rate of destruction of dioxins/furans and/or their precursors. These high values could also be caused by less efficient particulate removal in the electrostatic precipitator. Overall, the results indicate that PAHs would be a good indicator for monitoring combustion conditions favourable to elevated dioxin/furan emissions.

Effect of combustion and operating conditions on dioxin/furan emissions

Results of the on-line PAH sensor trial at Mill B

Several operating problems such as condensation in the sample line were initially encountered with the instrument because of numerous leaks produced by poor equipment design and poor workmanship during fabrication.

After rectifying these problems, we initiated trials of the on-line PAH monitor at Mill B in early October 2002. Figure 3 shows data for PAHs, particulates, steam production from hog fuel, and boiler-exit oxygen during a typical two-day period. The concentration of particulates was measured with an opacity monitor located at the stack. With the boiler operating normally, the level of particle-bound PAHs generally follows steam production from hog fuel or the hog-fuel load. Sharp drops in hog fuel steam load are usually accompanied by an equally sharp increase in boiler-exit oxygen, possibly because of manual control of the air levels. During normal operations, this produces a small, but significant, dilutive effect on PAH levels, which tends to be inversely correlated to boiler-exit oxygen levels, i.e. the lower the boiler-exit oxygen, the higher the PAHs.

However, during boiler upsets, the level of particle-bound PAHs also tends to increase sharply with the level of particulates being emitted, as evidenced by the three-minute long spike recorded on the evening of December 10th, around the cursor line in Figure 3. A close-up of a similar incident recorded early on the morning of November 27th is shown in Figure 4. The incident occurred as a result of a sudden interruption of the hog fuel feed into the furnace, which resulted in poor combustion conditions due to insufficient pyrolysis. Significant particulate carryover occurs during the start-up phase following resumption of the fuel feed because of excess underfire air going through a relatively thin layer of hog fuel. Notice also the sharp increase in the oxygen level and the relatively long time it took for that level to go back to the value recorded prior to the incident, thereby reflecting a significant loss of thermal efficiency.

To verify if the results obtained by the PAH monitor were comparable to those obtained during recent stack tests, we calculated three-hour average PAH emissions during six consecutive periods and compared the results to those obtained from some recent three-hour stack tests on the same boiler. As illustrated in Table I, the values obtained with the PAH monitor were well within the range of those obtained during the stack tests. Two additional stack tests were scheduled so as to further validate the monitor's calibration.

However, the dilution pump of the PAH monitor failed after only five months of continual operation, just prior to the scheduled stack tests. The dilution pump was quickly replaced, and the monitor will be re-installed shortly before the next stack tests. While on-line monitoring of PAH emissions would be very useful in helping a mill develop guidelines that will reduce dioxin emissions, it is very clear that the tested instrument is currently not reliable enough to be used for routine combustion performance optimization. It is still very much a research tool that requires intensive maintenance and attention.

To explore in more detail the relationship between PAH emissions and boiler-exit oxygen, we plotted three-hour average PAH emissions versus three-hour average boiler-exit oxygen concentrations over a three-week period. The results, shown in Figure 5, reveal that the data are clustered into three groups.

The first group shows a negative correlation between PAH emissions and boiler-exit oxygen. PAH emissions for this group range from 15 to 35 ng/m³ and the oxygen level from 5 to 7 percent. Particulate concentrations range from 20 to 30 mg/m³. This negative correlation is typically seen when the boiler is running smoothly at high hog-fuel loads (greater than 75 % of MCR) and with low particulate emissions. The observed trend indicates that the boiler may operate with low PAH and particulate-matter emissions when hog-fuel firing rates (and lower furnace temperatures) are high, if oxygen concentrations are kept within an optimum range, i.e. greater than about five percent.

The second group of data is representative of a low hog fuel load (less than 75 % of MCR). In response to lower demand for steam, operators usually decrease the hog fuel load. Since the air supply is often controlled manually, however, they would temporarily increase the auxiliary-fuel feed rate and the oxygen level to prevent a sudden increase in CO, combustibles and particulate emissions. These actions stabilize particulate and PAH emissions at a minimal level. Hence, there is a second group of data, for which PAH

emissions average from 15 to 20 ng/m³, and do not vary significantly over the 7 to 9 percent oxygen range. Particulate concentrations are around 10 to 15 mg/m³.

The third group is typical of upset conditions and high particulate carryover, such as that exemplified in Figure 4 above, whereby PAH emissions average about 30 ng/m³, and the oxygen level ranges from 6.5 to 8 percent. During upset conditions, particulate concentrations can vary from 50 to 100 mg/m³, with occasional spikes to 200 mg/m³.

In summary, results obtained during the trial show that, under normal operating conditions, PAH emissions are proportional to the hog-fuel load and inversely proportional to the boiler-exit oxygen concentration. Indeed, high PAH emissions indicate that, at higher hog fuel loads, insufficient carbon burnout and increased PAH formation is occurring in the overfire region of the boiler because of low oxygen levels. This, in turn, may increase the production of dioxin/furan from either precursors or fly-ash carbon. We will examine the validity of this relationship with data from other participating mills in the next section.

Boiler load versus fly-ash carbon content

The effect of increasing boiler load (as % of MCR) on the carbon content of fly ash is shown for four of the power boilers in Figure 6. The fly-ash particulates in each boiler presumably have a shorter residence time at higher boiler loads, and one would expect less carbon burnout. Increasing the boiler load would, therefore, be expected to increase the carbon content of the fly-ash particulates. Fly ash from the power boiler at Mill F, a bubbling fluidised bed (BFB) boiler with very good combustion conditions, shows the lowest carbon content, whereas that from Mill C, which has a grate-fired boiler and poorer combustion conditions, exhibits the greatest carbon content and appears to fluctuate between two carbon content ranges, i.e. 20-35 % and 50-75 %. The higher carbon content for fly-ash from the Mill C boiler appears to have been caused by a 20-percent drop in overfire air flow. The earlier data (1993) for Mill B is very similar to that of Mill C with the lower carbon content. Since no auxiliary fuel was used at Mill B during the 1993 tests, combustion performance was probably then poorer than during more recent tests. Also, the presence of a hog dryer during the 1993 tests may have resulted in high carbon carryover, thereby producing the higher ash carbon content seen for those tests.

Fly-ash carbon content versus boiler-exit oxygen

In addition to shortening residence times, increasing boiler load also increases oxygen consumption in the furnace. One might thus expect a significant increase in ash carbon content as the boiler load increases. This expected relationship is verified in Figure 7 for the power boiler at Mill B. An exception to this trend, indicated with a different symbol in Figure 7, occurred during one stack test, when the flow of natural gas was apparently increased during the last hour of the test, thereby decreasing the amount of carbon produced during the test and producing a slightly lower result.

PAH emissions versus boiler-exit oxygen

The effect of boiler-exit oxygen on PAH emissions is shown in Figure 8 for the power boiler at Mill B. Each point represents a separate three-hour stack test. For a low auxiliary fuel level, i.e. less than approximately 20 % steam production from natural gas, this graph shows that large amounts of PAHs are produced when the oxygen level drops below 5 percent. Fuel-rich regions that favour the formation of PAHs are thus created in the hog-fuel bed, especially when the boiler load is increased. An even larger, non-linear, i.e. power-law, increase in PAHs occurs below 4 percent oxygen, which suggests very sooty conditions in the boiler. We also see the same exception to the trend that was seen in Figure 7: the increase in the flow of natural gas during one stack test at Mill B improved combustion conditions, thereby producing a slightly lower result.

Dioxin/furan emissions versus boiler-exit oxygen and fly-ash carbon content

The relationship between dioxin/furan emissions and boiler-exit oxygen for the power boiler at Mill B appears to be linear: Figure 9 shows dioxin/furan emissions increasing fourfold, as the oxygen level drops from 7.5 to 3 percent. This is a relatively small increase compared to the hundredfold increase observed in PAH emissions over the same oxygen concentration range. Since this fourfold increase in dioxin/furan emissions roughly corresponds with the four fold increase in ash carbon content observed in Figure 7, this suggests that, for Mill B at least, dioxin/furan formation mainly depends on the amount of carbon and/or dioxin/furan precursors available for heterogeneous reactions leading to either *de novo* synthesis or direct formation from precursors. The amount of carbon is strongly dependent on higher boiler loads (Figures 6, 7 and 8). Therefore, at higher boiler loads, there is less time available for complete carbon burnout, and/or destruction of PICs, such as dioxin/furan precursors and PAHs, and one sees higher dioxin/furan emissions. If the extent of dioxin/furan emissions at Mill B were only dependent on the amount of particle-bound PAHs, however, the same power-law trend with respect to boiler load, which was observed in Figure 8 for PAH emissions, would also be evident in Figure 9.

In a similar fashion, the data from power boiler tests at Mill F, when no TDF was being co-fired with hog, show an increase in dioxin/furan emissions as a result of an increase in PAH emissions, which may usually be produced by a decrease in available boiler oxygen. This is illustrated in Table II. The data for June 6th, 2002 shows that, when poor combustion conditions fostered by a low boiler-exit oxygen concentration, i.e. 2.4 %, are encountered with no TDF input, an increase in the concentration of dioxin/furan emissions corresponds to a similar increase in PAH emissions. Thus, as with Mill B, it appears that, in the absence of TDF co-firing, dioxin/furan emissions are very strongly dependent on PAH emissions.

On the other hand, the additional sulfur from TDF co-firing helps suppress the formation of dioxins/furans by reducing Cl_2 to HCl [8], even when poor combustion conditions favour the formation of PAHs and dioxin/furan precursors. Because of a low chloride-to-sulfur ratio during TDF co-firing, dioxin precursors are then less likely to form dioxins and furans, as shown by Duo *et al.* [7], despite poor combustion conditions. Referring to Table II, this behaviour is demonstrated by the February 6th, 2002 TDF test, during which unusually high PAH levels were produced in the middle of the test by a sudden drop in the boiler-exit oxygen concentration from 4.4 to 1.7 percent. As expected by the low chloride-to-sulfur ratio, the increase in PAH emissions did not result in a corresponding increase in dioxin/furan concentration. Much better combustion conditions prevailed on February 7th, 2002 with very stable oxygen concentrations and lower CO and PAH levels, thereby producing even lower dioxin/furan emissions than on the previous day.

A somewhat different situation prevails for the power boiler at Mill D (Table III). While there is also a very strong correlation between low boiler-exit oxygen levels and high PAH emissions for this boiler, no correlation is apparent between dioxin/furan emissions and either low boiler-exit oxygen levels or PAH emissions. As this is a relatively large boiler (205 tonnes/hr based on oil; 114 tonnes/hr based on hog) that is consistently operated at low oil-based boiler loads, i.e. usually less than 65 percent of oil-based MCR, residence times are probably sufficient to destroy most of the dioxins/furans and/or their precursors even with a relatively poor combustion performance. In addition, this boiler has a very efficient ESP and low particulate emissions, i.e. less than 30 mg/m^3 . This means that dioxin/furan emissions would depend mainly on combustion conditions found in the lower furnace, rather than other variables, such as boiler load or boiler-exit oxygen. Indeed, the temperature data in Table III suggests that such a relationship is present for four of these tests, as an increase in the lower furnace temperature produced better combustion conditions leading to a decrease in dioxin/furan emissions. The October 30th, 2001 test does not seem to fit this pattern, and will be discussed further below.

Dioxin/furan emissions versus combustion performance

The effect of combustion performance on dioxin/furan emissions is shown in more detail in Figure 10 for the power boilers at Mills D and G, with the grate/lower furnace temperature being used as a general indication of combustion performance. The most interesting feature of this graph is that the semi-logarithmic slopes for both fitted lines are nearly identical. This may reflect similar activation energies for the destruction of dioxins/furans and/or their precursors. Both fitted lines suggest that such destruction increases exponentially with temperature, as indicated by McKay [16]. Conversely, dioxin/furan emissions appear to increase *exponentially* as the grate/lower furnace temperature decreases and combustion performance deteriorates.

Referring to Mill D and to Table III, during the September 28th, 1994 test, the #9 boiler was running at a hog steam rate of 82 tonnes/hour (40 % of oil-based MCR; Table I in [2]) and a gas steaming rate of 50 tonnes/hour, producing a total steam flow of 132 tonnes/hour (64 % of oil-based MCR). The average grate temperature during that test was quite low, i.e. 810 °C, thereby indicating that combustion performance was poor. Unlike all the other tests, the second 1994 test (Table III, 29-Sep-94) was performed by co-firing the #9 power boiler (with very little gas) at a hog steam rate of 91.9 tonnes/hour (45 % of oil-based MCR) with two other small “VUX boilers”, #1 (15.3 tonnes/hour) and #2 (16.4 tonnes/hour), for a total steam flow of 124 tonnes/hour. The average grate temperature during that test was 825 °C, which would indicate a slight improvement in combustion conditions. Consequently, the #9 boiler was operating with a lower total steam flow on September 29, 1994 than during the previous day’s test (Table III, 28-Sept-94), but *at a higher hog steam rate*. As the three boilers have a common precipitator and stack, much higher stack PAH emissions were observed during the September 29, 1994 test when co-firing the two much smaller boilers than with the #9 boiler operating alone, despite the higher boiler-exit oxygen levels, i.e. 5.1 %, measured for the #9 boiler during that test. This indicates that very poor combustion conditions were present in the two smaller boilers. Surprisingly, the increase in PAH emissions did not produce a corresponding increase in dioxin/furan emissions. In fact, the 30% drop observed on September 29th, 1994 for dioxin/furan emissions from the three boilers can probably be attributed to the slight improvement in combustion performance for the #9 boiler as evidenced by the small increase in the #9 boiler grate temperature, produced by the higher hog steam rate, and not to the lower total steam load on the #9 boiler. This indicates that the contribution to the stack dioxin/furan emissions from the #1 and #2 power boilers is very small, probably because of their relatively small size and small boiler load (33% of MCR) during the September 29th, 1994 test. This observation is corroborated by Luthe *et al.* [2]: a mass balance of the multicyclone ashes from the two small boilers showed that their total TEQ contribution was less than 13 % of that typically collected by the multicyclone system of the much larger #9 boiler.

Subsequently, the two small boilers were converted to gas-firing boilers, thereby enabling the #9 boiler to be run at significantly higher steam rates. As seen in Table III, this produced a marked improvement in combustion performance as demonstrated by the higher grate temperatures and lower dioxin/furan emissions, as well as a significant decrease in boiler-exit oxygen due to higher oxygen consumption.

An unusual combination of a higher-than-normal boiler load, very low boiler-exit oxygen levels and very low auxiliary fuel usage produced higher PAH emissions than usual for both the October 2001 tests at Mill D. Higher boiler loads produce more carryover, especially when one has a thinner bed on the grate. Interestingly, only one of these tests showed relatively high dioxin/furan emissions (Table III, Oct-30-01). These emissions did not fit the expected exponential dependency pattern observed with grate temperature (Mill D, Figure 10). The normal practice for the tests at Mill D is to clean the grate immediately prior to a stack test, which was the case for the October 30th, 2001 test. This would have produced a thinner bed with more carbon carryover, thereby leading to increased dioxin/furan emissions. On October 31st, 2001, however, the grate was cleaned twelve hours prior to the test, which probably provided for a thicker bed and less carryover in the lower furnace than for the October 30th, 2001 test. The July 30th, 2002 test also had high PAH emissions produced in spite of slightly higher boiler-exit oxygen levels, which should have

also resulted in dioxin/furan emissions similar to those recorded during the October 30th, 2001 test. However, since grate/lower furnace temperatures during the July 30th, 2002 test were 115 °C higher than during the October 30th, 2001 test, better combustion conditions in the lower furnace probably resulted in significantly more destruction of dioxins/furans and/or their precursors, thus overcoming the effects of oxygen-deficient conditions in the boiler.

A notable feature in Figure 10 is the relatively high dioxin/furan emissions found for the power boiler at Mill G, compared to those recorded for the boiler at Mill D. The correlation of the fitted line for stack tests on this boiler is excellent, which strongly indicates that combustion performance (as characterised by the grate temperature) affects dioxin/furan emissions. Since the boiler at Mill G is relatively small (86 tonnes/hr of steam production based on firing oil) and has no overfire air, there is less opportunity for significant carbon burnout and/or destruction of dioxins/furans and/or their precursors, especially when combustion conditions are poor. Thus, much higher grate temperatures than the ones found at Mill D are needed so as to effect destruction of dioxins/furans and their precursors. The observation ports in the boiler at Mill D are also much higher in the boiler (15-20 feet above the grate) than those in the boiler at Mill G, thereby producing lower temperature readings.

Lower grate temperatures, characteristic of poor combustion, appear to favour the formation of dioxins over furans: as shown in Figure 11 for the boiler at Mill G, the emission congener profile is dominated by dioxins at lower grate/lower furnace temperatures, and by furans at higher temperatures. This is supported by results reported by Altwicker [34], who showed that the rate of dioxin congener formation from chlorophenols is higher at lower temperatures than that of furans. On the other hand, at higher combustion temperatures, chlorophenols predominantly form furans. As the toxicity equivalent factors (TEFs) for the tetra- and penta-substituted dioxin congeners are ten times higher than those of their corresponding furan congeners, this has a significant impact in terms of reportable stack TEQ emissions.

Since there is no overfire air, boiler operators at Mill G can only manipulate primary airflow to change grate temperatures. With the primary airflow set higher than the optimal value, i.e. that required to give 4 to 6 % oxygen at the boiler exit [16], the combustion efficiency and the grate temperature decreased, thereby increasing both PAH and dioxin/furan emissions (Table IV, Nov-22-01). Conversely, increasing the grate temperature by decreasing primary airflow resulted in less cooling and enhanced pyrolysis and combustion in the lower furnace, as illustrated in the May 24th, 2002 test (Table IV, May-24-02). Since there is no secondary air to compensate, this action also has the effect of reducing boiler-exit oxygen, to a value slightly below 6 percent, which lies within the optimal range of four to six percent recommended by McKay [16]. These combustion conditions greatly improved combustion performance, as evidenced by drastically reduced PAH and dioxin/furan emissions.

Figure 12 shows a semi-logarithmic graph of the effect of combustion conditions as measured again by the grate/lower furnace temperature on dioxin/furan emissions for the power boilers at three other mills, Mills A, B and H. The fitted lines are those obtained with the data from Mills D and G in Figure 10. The extent of the effect of combustion conditions on stack dioxin emissions appears to be mill-specific, particularly at low temperatures. The cluster around 1 ng TEQ/m³ represents tests at Mills A and B in 1992-93. Although improvements were made to both operations since 1992, the effect of boiler load is still clearly apparent for the power boiler at Mill B, either because the air distribution is still not optimal (the grate/lower furnace temperatures are still not high enough) or because hog and air distribution on or through the grate are highly variable at high boiler loads. As demonstrated in the previous section, reducing boiler load resulted in lower emissions because of lower carryover, but also reduced grate/lower furnace temperatures, steam production and boiler thermal efficiency. Decreasing the flow of underfire air, particularly when the boiler loading is reduced, would improve pyrolysis conditions, as evidenced at Mill G. On the other hand, increasing overfire air so that boiler-exit oxygen is between four and six percent would accelerate carbon burnout and enable the boiler to be run at higher loads.

Emissions from the power boiler at Mill A during the 2002 coal-fired trials were lower than those measured under normal operating conditions. However, during one of the 2001 trials (July 24th), the boiler experienced extremely poor combustion conditions, under low-load conditions, to the point that the hog-fuel pile was smoldering. This resulted in very high, atypical PAH and dioxin/furan emissions for this boiler, because the actual combustion temperature inside the hog pile, where most of the combustion was centred, was probably much lower than the measured grate temperature.

Notice that, at high boiler loads, the grate/lower/furnace temperatures for the power boilers at Mills A, B and H are correspondingly higher than at low boiler loads, and their emissions tend to follow the fitted curve for Mill G (Figure 12). This is better seen with a linear graph (Figure 13) of the effect of combustion performance, as measured by the grate/lower furnace temperature, on dioxin/furan emissions for the power boilers at Mills A, B, D, G and H. Although the extent of this effect appears to be mill-specific, particularly at low temperatures, it is clear that dropping the combustion temperature generally worsens combustion performance and increases the variability of emissions. Recently, Yasuhara *et al.* [35] have shown that a significant increase in emissions occurs at similarly low grate temperatures when burning chlorine-laden wood in a pilot-scale incinerator. Conversely, increasing the combustion temperature may improve combustion performance.

Some of the lowest dioxin/furan emissions are observed for the fixed-grate boiler at Mill H, which seems to have the best combustion performance. With the exception of one test, these emissions lie slightly below the fitted curve shown in Figure 12 for the power boiler at Mill G.

The data presented above show that for grated-fired boilers, improved combustion performance significantly decreases dioxin/furan emissions. Although the extent of this effect appears to be mill-specific, particularly at low temperatures, the results indicate that increasing the combustion temperature may improve combustion performance. It must be noted, however, that there are many variables, such as the stack temperature [8], contributing to power boiler dioxin emissions. Therefore, higher combustion temperatures, by themselves, will not necessarily result in low dioxin emissions. Boiler-exit oxygen is also an important variable, particularly when combustion conditions are not optimal; higher oxygen concentrations (four to six percent at the boiler exit) facilitate carbon burnout, whereas lower oxygen concentrations favour the formation of PICs, such as PAHs and dioxin/furan precursors.

CONCLUSIONS

- 1) We did not find any correlation between dioxin/furan emissions and carbon monoxide emissions in tests on boilers at eight different mills.
- 2) A good correlation was, however, observed between dioxin/furan emissions and stack PAH concentrations in the absence of TDF addition. This suggests that poor combustion conditions responsible for the formation of products of incomplete combustion (PICs), such as PAHs and dioxin/furan precursors, also increase dioxin/furan emissions. In addition, dioxin/furan and PAH emissions were found to generally increase with lower oxygen concentrations at the boiler exit, which generally produce poor combustion performance. On the other hand, ash carbon content increased with higher boiler load and/or low oxygen concentrations at the boiler exit, probably because of lower available residence times and insufficient excess air, which result in incomplete carbon burnout. Our findings are consistent with the current understanding that high ash carbon content generally favours heterogeneous reactions leading to either *de novo* synthesis of dioxins/furans or their direct formation from precursors.

- 3) Using grate/lower furnace temperatures as a general measure of combustion performance in grate-fired boilers, we also found that a linear increase in the grate/lower furnace temperature produces an exponential decrease in dioxin/furan emissions. Although the extent of this effect appears to be mill-specific, particularly at low temperatures, the results indicate that increasing the combustion temperature may improve combustion performance. It must be noted, however, that there are many variables, such as the stack temperature, contributing to power boiler dioxin emissions. Therefore, higher combustion temperatures, by themselves, will not necessarily result in low dioxin emissions.

ACKNOWLEDGMENTS

We wish to thank the people of the environmental and power/recovery departments at participating mills for their help during the trials and for assistance in varying combustion parameters so that their effect on dioxin/furan emissions might be better elucidated. Special thanks also go to the people of the electrical/instrumentation department at Mill B for their help in installing and troubleshooting the on-line PAH monitor. Financial support from Howe Sound Pulp and Paper, NorskeCanada, Pope & Talbot, Western Pulp Partnership, and Natural Resources Canada is gratefully acknowledged. Finally, we thank Al Lanfranco and his test crew for generating consistently high-quality and reliable data. We would also like to acknowledge numerous discussions with Vic Uloth and Doug Singbeil, and we also thank them for thoroughly reviewing the manuscript.

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FIGURE LEGENDS

- Figure 1: Relationship between carbon monoxide and dioxin/furan emissions for the power boilers at all participating mills (Mills A-H). No correlation is found between dioxins/furans emissions and carbon monoxide. The fitted curve is for Mill A.
- Figure 2: Relationship between stack PAH emissions and dioxin/furan emissions for the power boilers at Mills A, B, D E, and G. Although there is a significant amount of scatter at low levels of PAHs, dioxin/furan emissions generally increase with PAH emissions. The fitted curve is for Mill A. The two highest dioxin/furan values observed for Mill G follow a very steep slope caused by poor combustion performance, which favours a higher rate of dioxin/furan formation from precursors.
- Figure 3: Selected results from the on-line PAH monitor trial at Mill B: hog-fuel steam load, PAH, particulate and boiler-exit oxygen concentrations for a two-day period in early December 2002. Hog-fuel load, PAH and particulate concentrations are inversely correlated to boiler-exit oxygen.
- Figure 4: Close-up of hog-fuel steam load and PAH, particulate and boiler-exit oxygen concentrations during a boiler upset on November 27th, 2002. The incident occurred as a result of a sudden interruption of the hog-fuel feed into the furnace. Significant particulate carryover occurs during the start-up phase following resumption of the fuel feed because of excess underfire air going through a relatively thin layer of hog fuel.
- Figure 5: Effect of boiler-exit oxygen on PAH emissions during varying operating conditions over a three-week period (3-hour moving averages) for the power boiler at Mill B. The first group shows a negative correlation between PAH emissions and boiler-exit oxygen. The second group of data is representative of a low hog fuel load. The third group is typical of upset conditions and high particulate carryover such as the incident exemplified in Figure 4.
- Figure 6: Effect of boiler load (as a percent of oil-based MCR) on fly-ash carbon content for the power boilers at various mills. Boiler loads for Mill F are as percent of hog-based MCR. The fly-ash particulates in each boiler should have a shorter residence time at higher boiler loads, and one would expect less carbon burnout. Increasing the boiler load, therefore, increases the carbon content of the fly-ash particulates.
- Figure 7: Effect of boiler-exit oxygen on fly-ash carbon content for the power boiler at Mill B. Under normal operating conditions, increasing boiler load also increases oxygen consumption in the furnace. One might, therefore, expect a significant increase in ash carbon content as the boiler load increases.
- Figure 8: Stack PAH emissions versus boiler-exit oxygen for the power boiler at Mill B. Large amounts of PAHs are produced when the oxygen level drops below 5 percent at the boiler exit. An even larger, non-linear, i.e. power-law, increase in PAHs occurs below 4 percent oxygen, which suggests very sooty conditions in the boiler.
- Figure 9: Stack dioxin/furan emissions versus boiler-exit oxygen for the power boiler at Mill B. Dioxin/furan emissions increase five fold, as the oxygen level drops from 7.5 to 3 percent. Note that the correlation in Figure 9 could be improved if only data from the high hog load

tests are included. Thus, we obtain $y = -0.0384x + 0.349$ and a R^2 of 0.7566. In this case, dioxin/furan formation mainly depends on the amount of carbon available for *de novo* heterogeneous reactions.

- Figure 10: Semi-logarithmic graph of stack dioxin/furan emissions versus grate/lower furnace temperature (a general measure of combustion performance) for the power boilers at Mills D and G. The September 29th, 1994 test at Mill D (indicated by the pale diamond) was performed by co-firing two smaller hog-fired power boilers, #1 and #2, in addition to the main #9 boiler. All other tests at Mill D were performed with only the #9 boiler operating. The semi-logarithmic slopes for both fitted lines are nearly identical. This may reflect similar activation energies for the destruction of dioxins/furans and/or their precursors. Both fitted lines suggest that such destruction increases exponentially with temperature.
- Figure 11: Effect of combustion performance on the dioxin/furan congener profile of stack emissions for the power boiler at Mill G. As the grate/lower furnace temperature (a general measure of combustion performance) increases, the profile becomes increasingly dominated by furans.
- Figure 12: Semi-logarithmic graph of stack dioxin/furan emissions versus grate/lower furnace temperature (a general measure of combustion performance) for the power boilers at Mills A, B, and H. The fitted lines are those obtained in Figure 10 with the data for the power boilers at Mills D and G. The results displayed inside the oval were obtained at Mill A and B in 1992-93. The emissions for the power boilers at Mills A, B and H at high boiler loads with correspondingly high grate/lower furnace temperatures tend to follow the fitted curve obtained in Figure 10 for the power boiler at Mill G.
- Figure 13: Stack dioxin/furan emissions versus grate/lower furnace temperature (a general measure of combustion performance) for the power boilers at Mills A, B, D, G and H. The fitted lines are those obtained in Figure 10 with the data for the power boilers at Mills D and G. Improving combustion performance generally decreases dioxin/furan emissions.

TABLE I:
Comparison of three-hour averages and stack tests for PAHs for the power boiler at Mill B.

<i>Three-hour average results</i>		<i>2001-2002 stack tests</i>	
<i>Time</i>	<i>µg/m³</i>	<i>Date</i>	<i>µg/m³ (@ 11% O₂)</i>
<i>Oct-10-02 18:00-21:00</i>	<i>0.068</i>	<i>Oct-10-01</i>	<i>0.067</i>
<i>Oct-10-02 21:00-24:00</i>	<i>0.064</i>	<i>Oct-11-01</i>	<i>0.050</i>
<i>Oct-11-02 00:00-03:00</i>	<i>0.075</i>	<i>May-08-02</i>	<i>0.110</i>
<i>Oct-11-02 03:00-06:00</i>	<i>0.043</i>	<i>May-09-02</i>	<i>0.050</i>
<i>Oct-11-02 06:00-09:00</i>	<i>0.069</i>	<i>May-28-02</i>	<i>0.102</i>
<i>Oct-11-02 09:00-12:00</i>	<i>0.041</i>	<i>Aug-20-02</i>	<i>0.075</i>

TABLE II:
Comparison of with and without the co-firing of tire-derived fuel (TDF): Operating conditions and emission results for the power boiler at Mill F [7]

<i>Parameter</i>	<i>Unit</i>	<i>Feb-6-02</i>	<i>Feb-7-02</i>	<i>Jun-6-02</i>
<i>Steam generation rate</i>	<i>t/hr</i>	<i>145</i>	<i>153</i>	<i>141</i>
<i>Lower furnace temperature</i>	<i>°C</i>	<i>1016</i>	<i>1032</i>	<i>1033</i>
<i>TDF addition rate</i>	<i>%</i>	<i>5</i>	<i>5</i>	<i>0</i>
<i>Boiler-exit oxygen</i>	<i>%</i>	<i>4.4</i>	<i>4.1</i>	<i>2.4</i>
<i>Flue gas CO</i>	<i>ppm</i>	<i>790</i>	<i>359</i>	<i>347</i>
<i>Cl/S ratio</i>	<i>w/w</i>	<i>0.38</i>	<i>0.70</i>	<i>3.20</i>
<i>PCDD/Fs, TEQ @ 11% O₂</i>	<i>ng/m³</i>	<i>0.020</i>	<i>0.010</i>	<i>0.290</i>
<i>PAHs @ 11 % O₂</i>	<i>µg/m³</i>	<i>9.3</i>	<i>0.510</i>	<i>14.8</i>

TABLE III:
Comparison of selected operating conditions and emission results for the power boiler at Mill D

<i>Parameter</i>	<i>Unit</i>	<i>Sep-28-94</i>	<i>Sep-29-94*</i>	<i>Feb-21-01</i>	<i>Oct-30-01</i>	<i>Oct-31-01</i>	<i>Jul-30-02</i>
<i>Total steam generation rate</i>	<i>as % of MCR</i>	<i>64</i>	<i>45</i>	<i>64</i>	<i>62</i>	<i>62</i>	<i>48</i>
<i>Lower furnace temperature</i>	<i>°C</i>	<i>813</i>	<i>825</i>	<i>919</i>	<i>921</i>	<i>916</i>	<i>1035</i>
<i>Boiler-exit oxygen</i>	<i>%</i>	<i>4.6</i>	<i>5.1</i>	<i>4.3</i>	<i>1.9</i>	<i>1.4</i>	<i>2.9</i>
<i>Flue gas CO</i>	<i>ppm</i>	<i>n/a</i>	<i>n/a</i>	<i>70</i>	<i>159</i>	<i>989</i>	<i>144</i>
<i>PCDD/Fs, TEQ @ 11% O₂</i>	<i>Ng/m³</i>	<i>0.13</i>	<i>0.09</i>	<i>0.010</i>	<i>0.140</i>	<i>0.020</i>	<i>0.008</i>
<i>PAHs @ 11 % O₂</i>	<i>Mg/m³</i>	<i>0.900</i>	<i>13.08</i>	<i>0.060</i>	<i>1.010</i>	<i>2.340</i>	<i>1.570</i>

**: The September 29th, 1994 test at Mill D was performed by co-firing two smaller hog-fired power boilers, #1 and #2, in addition to the main #9 boiler. All other tests at Mill D were performed with only the #9 boiler on-line.*

TABLE IV:
Comparison of selected operating conditions and emission results for the power boiler at Mill G

<i>Parameter</i>	<i>Unit</i>	<i>Nov-22-01</i>	<i>May-24-02</i>
<i>Total steam generation rate</i>	<i>as % of MCR</i>	<i>49.8</i>	<i>62.2</i>
<i>Auxiliary steam generation rate</i>	<i>as % of MCR</i>	<i>21.9</i>	<i>6.0</i>
<i>Lower furnace temperature</i>	<i>°C</i>	<i>868</i>	<i>1118</i>
<i>Boiler-exit oxygen</i>	<i>%</i>	<i>7.85</i>	<i>5.54</i>
<i>Flue gas CO</i>	<i>ppm</i>	<i>140</i>	<i>150</i>
<i>PCDD/Fs, TEQ @ 11% O₂</i>	<i>ng/m³</i>	<i>1.288</i>	<i>0.056</i>
<i>PAHs @ 11 % O₂</i>	<i>µg/m³</i>	<i>4.083</i>	<i>0.147</i>

Figure 1

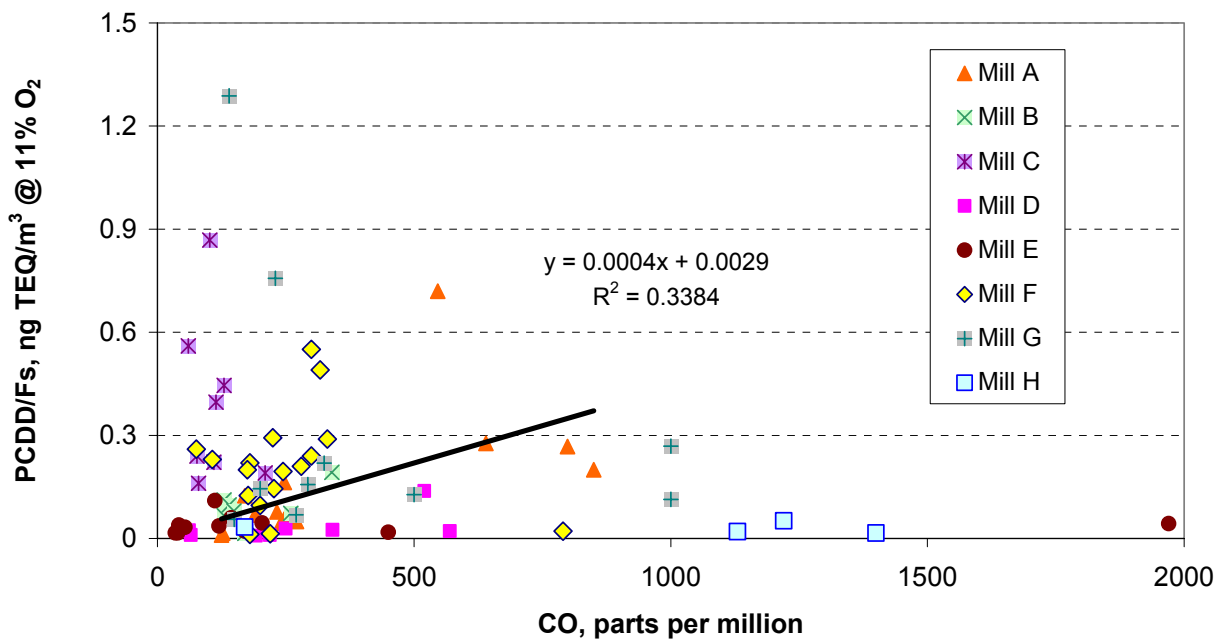


Figure 2

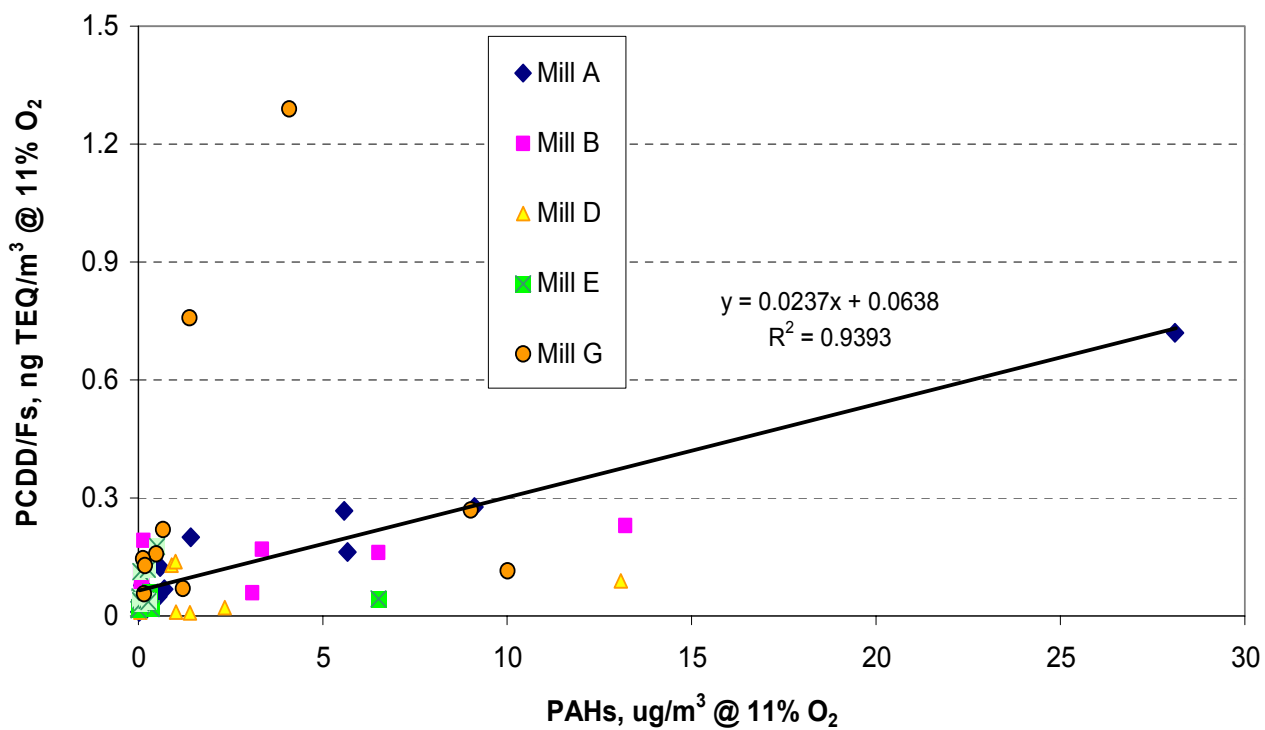


Figure 3

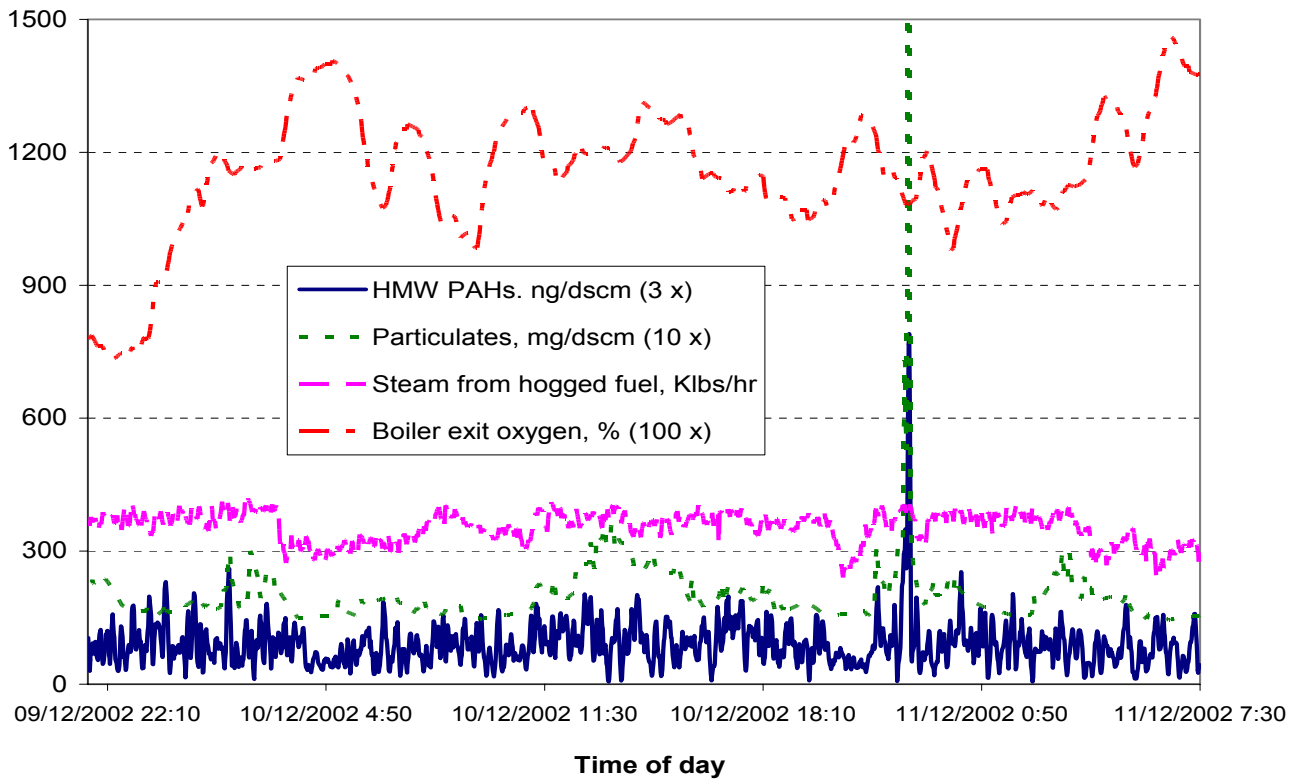


Figure 4

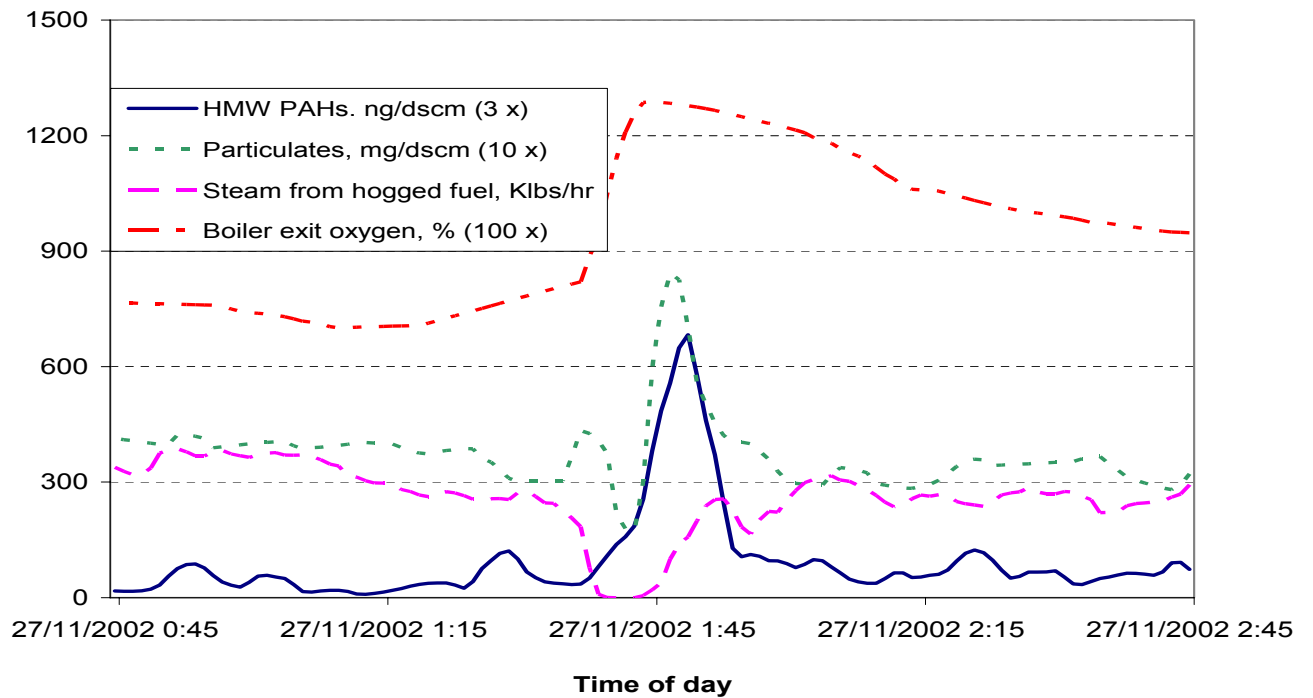


Figure 5

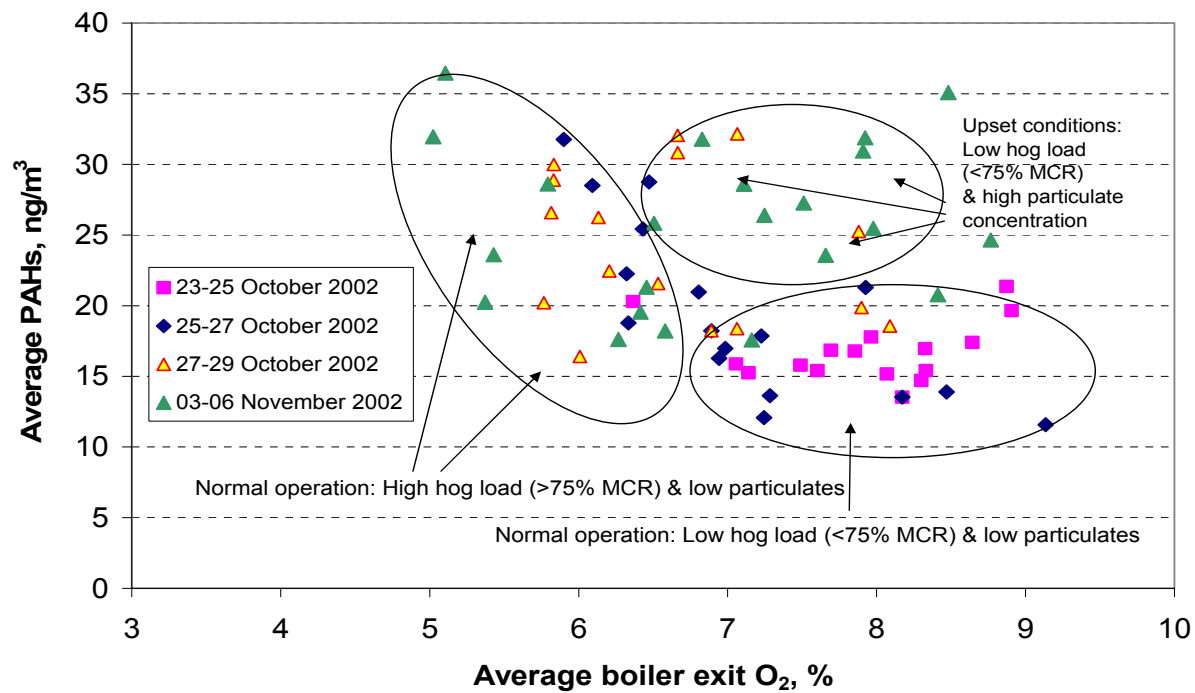


Figure 6

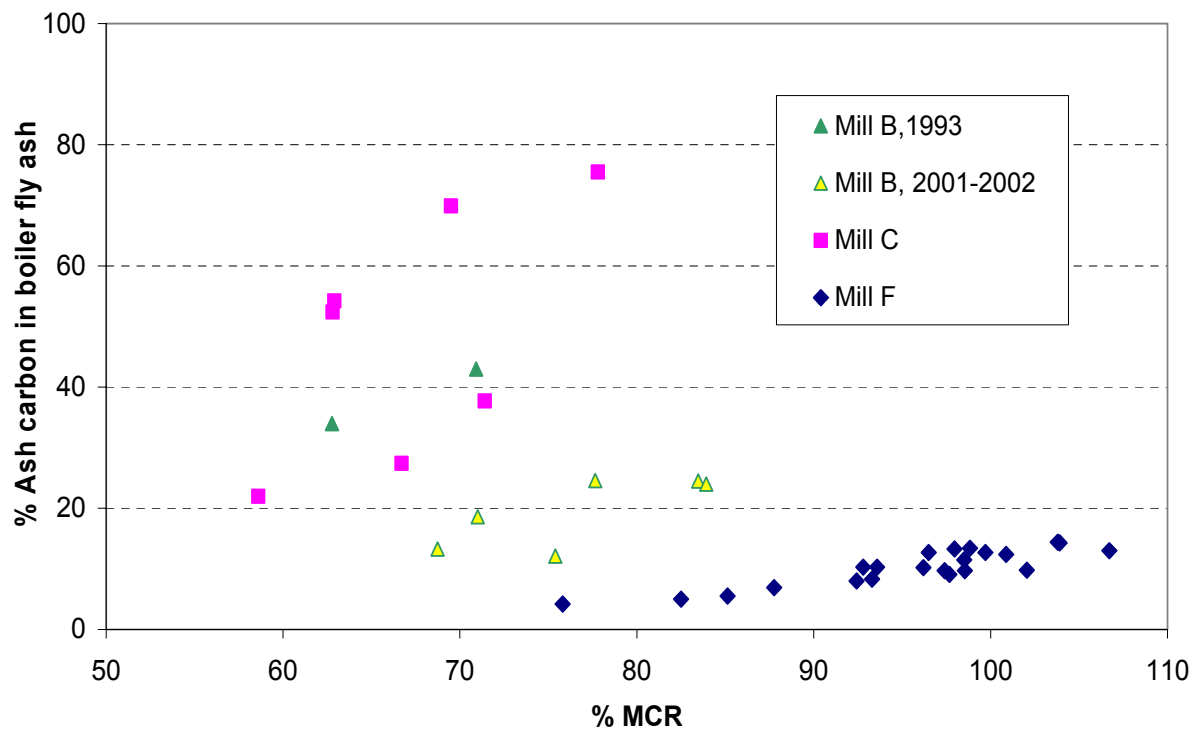


Figure 7

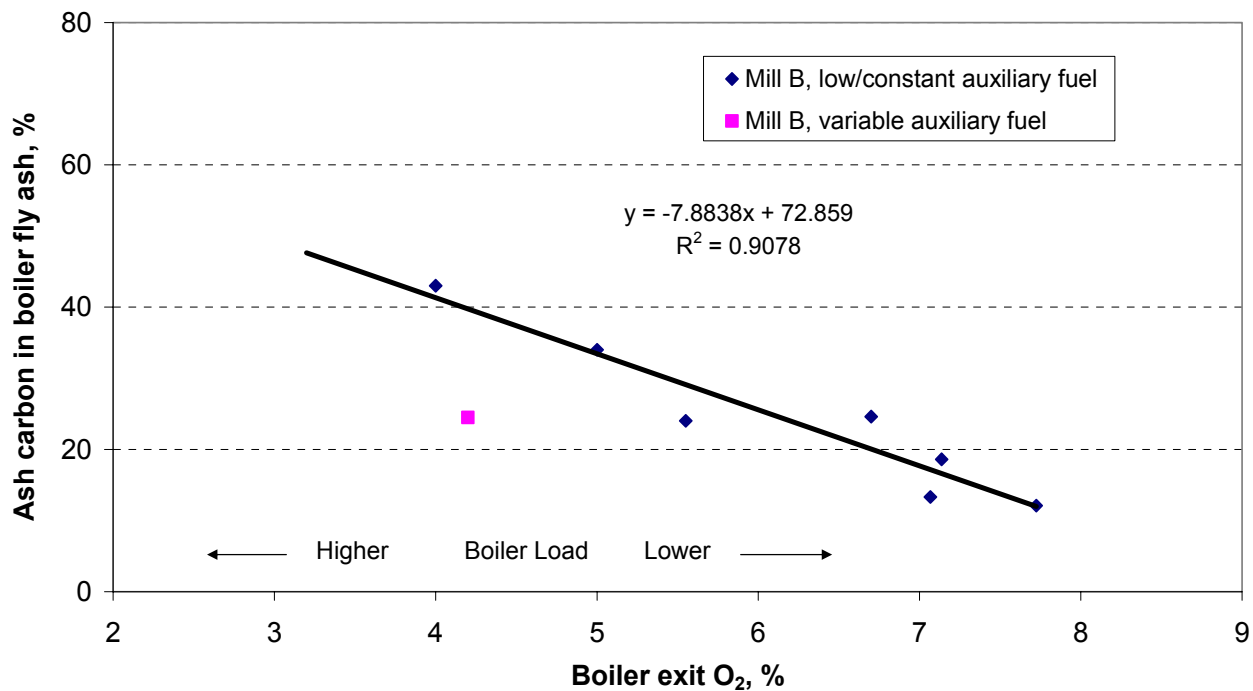


Figure 8

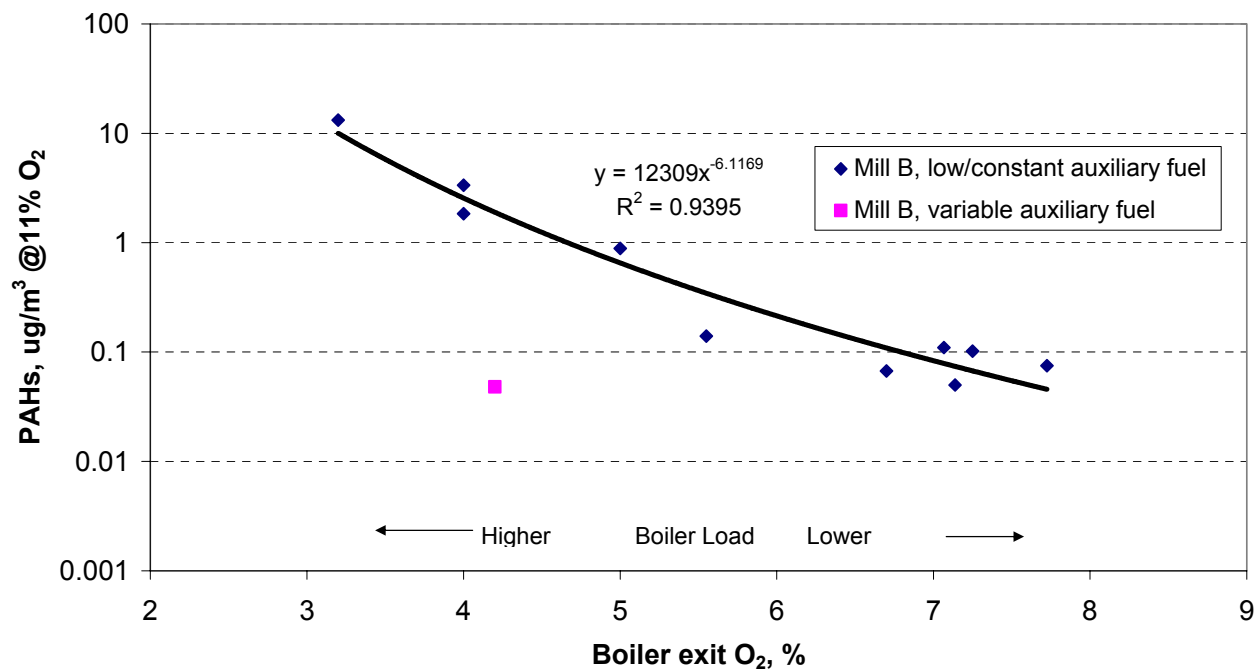


Figure 9

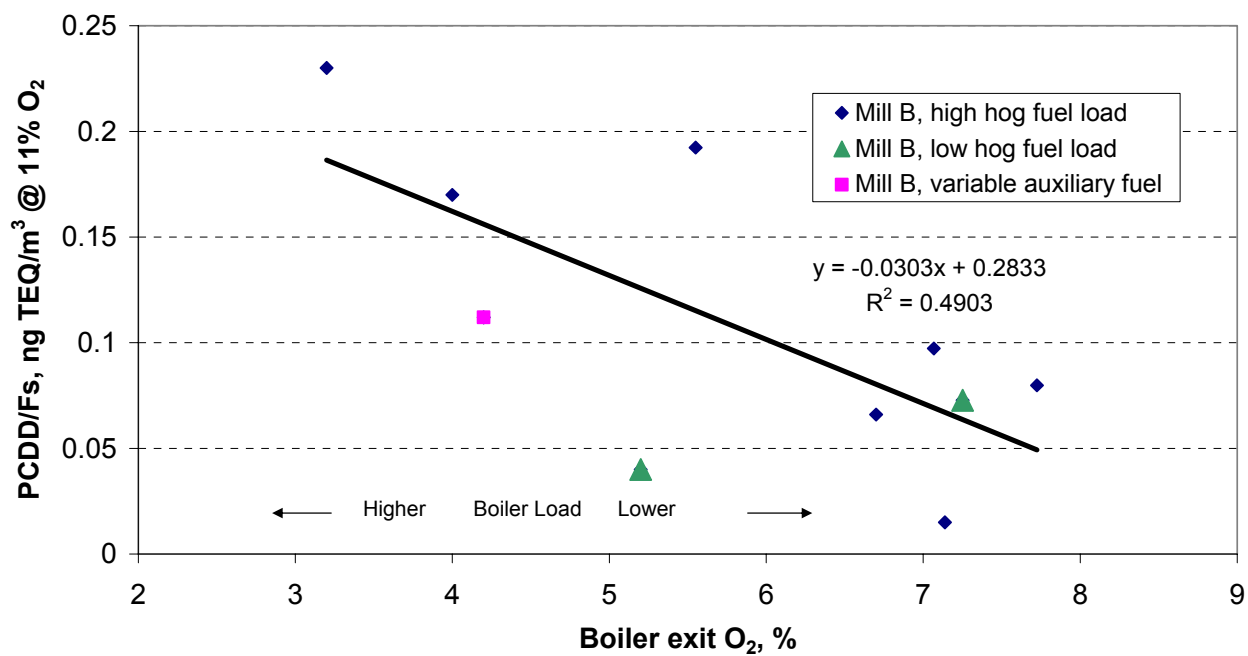


Figure 10

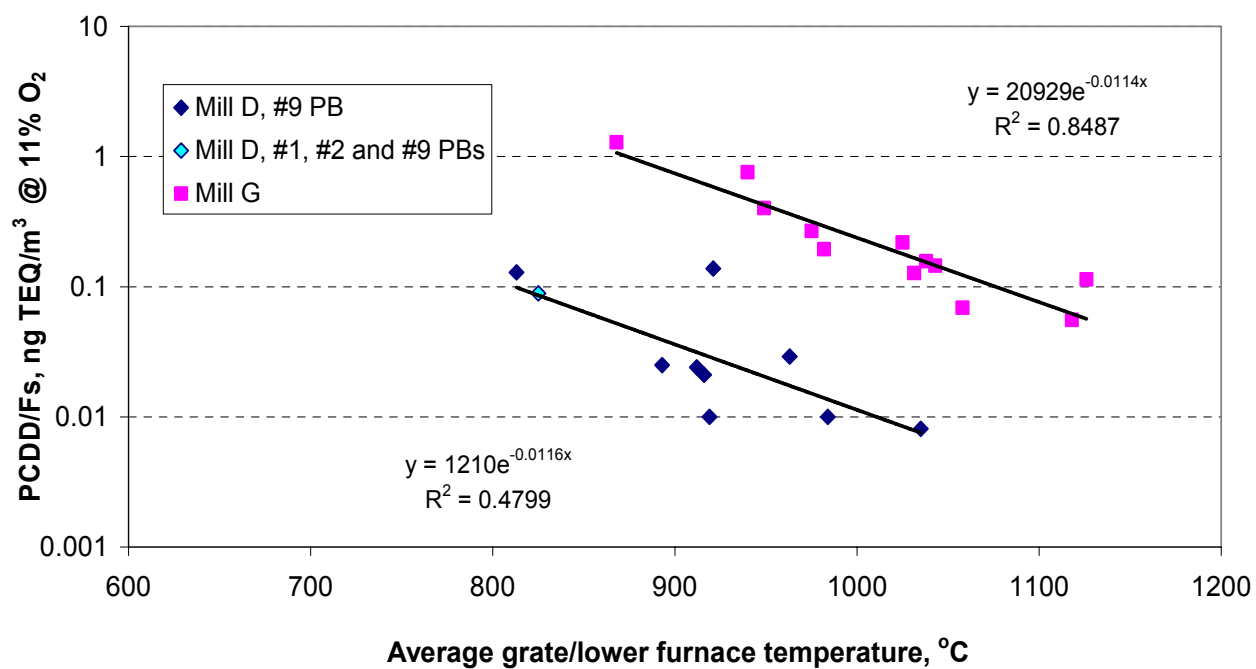


Figure 11

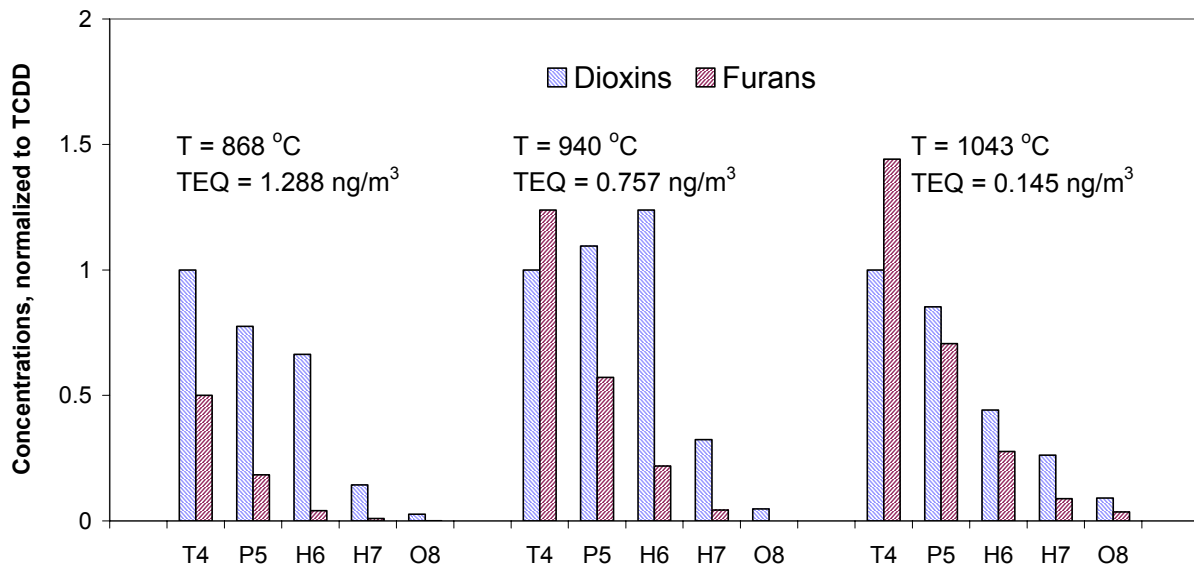


Figure 12

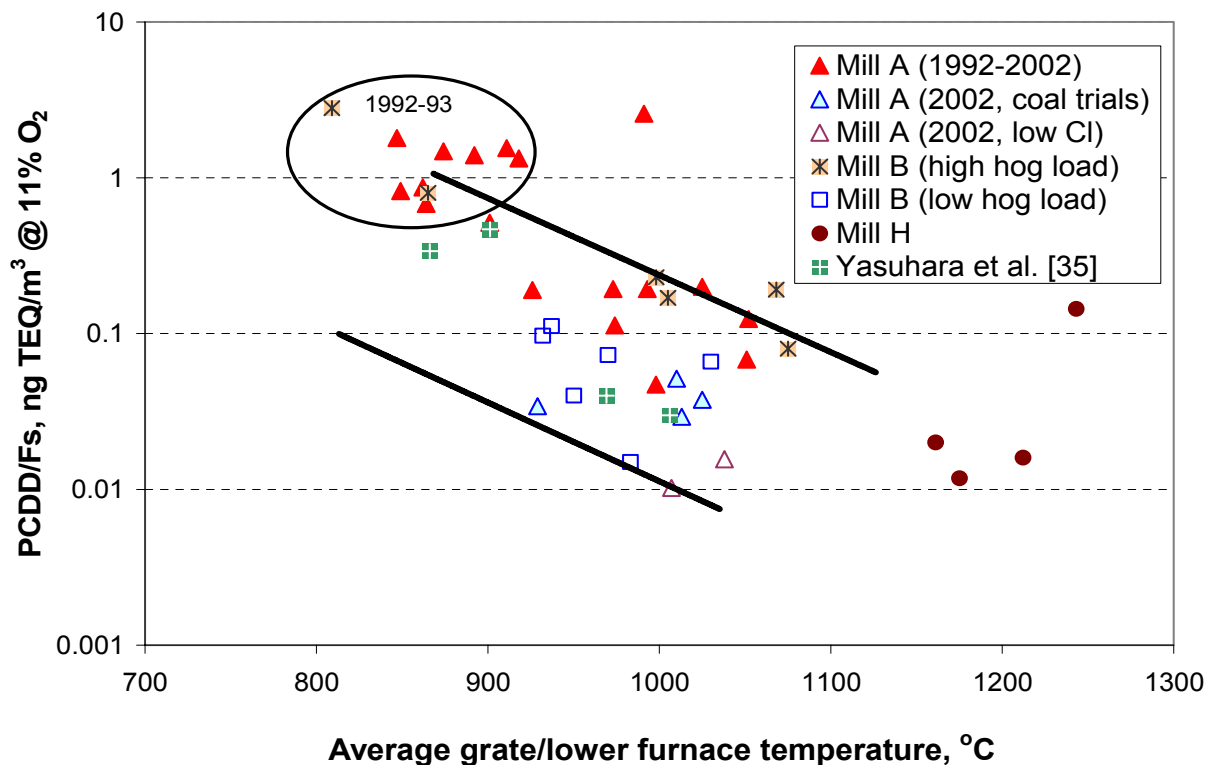


Figure 13

