Investigations into the Variability and Control of Dioxins Formation and Emissions from Coastal Power Boilers

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EXECUTIVE SUMMARY

Stack dioxin emissions from coastal power boilers burning salt-laden hog fuel have decreased by over 68% since 1995, from 10.5 grams of ITEQ per year in 1995 to 3.3 – 3.4 grams of ITEQ in both 2001 and 2002. These reductions have been realized through a series of capital expenditures and boiler shutdowns and through ongoing efforts to improve power boiler combustion efficiency and decrease particulate emissions. The data collected from over 100 tests on the coastal power boilers indicates that improved combustion efficiency reduces dioxins formation and that reduced particulate emissions generally result in lower stack dioxin emissions. Nevertheless, stack dioxin emissions test results for the coastal power boilers are still highly variable. The results from single tests on any of the coastal power boilers vary by a factor between 5 and 45 and four of the 8 mills have measured emissions in the last three years that exceed the Canada Wide Standard for existing facilities (0.5 ng TEQ/m^3 @11% O_2). Despite the general improvement in dioxin emissions, and the fact that the average stack emissions over the last three years for seven of the eight affected coastal mills are now below the CWS limit for existing facilities, the large variations of individual test results present difficulties for many of the mills in ensuring compliance with the current CWS limit.

Detailed analysis of the results of over 100 stack dioxin emission tests on 8 different power boilers indicates that most of the variation in emissions can be attributed to variations in combustion efficiency, particulate removal efficiency in the ESP or scrubber, hog fuel salt content, and operating temperatures in the air heater or ESP. Very high emissions were primarily due to poor combustion conditions that lead to the formation of high levels of precursors as well as polyaromatic hydrocarbons or PAHs. A three term kinetic model, empirically fit to the stack emission data, accurately correlates the data from the different stack tests and predicts the impacts of changing these four important operating variables. The importance of these operating variables was also confirmed in pilot plant tests at UBC.

The design and arrangement of downstream heat exchangers, particularly the air heater and economizer, can affect the temperature and residence time distribution for dioxins formation by both precursor and *de novo* reactions and the adsorption and desorption of dioxins and furans on fly ash. The temperature of the flue gas entering the air heater and the temperature in the electro-static precipitator were found to dramatically affect dioxin formation in coastal power boilers and to explain much of the differences in emission levels observed between different power boilers. 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 capital investments and new boiler design.

An on-line instrument to continuously measure PAH emissions was tested on one boiler. While it provided very useful data and insights that might be used to optimize combustion conditions and minimize dioxin emissions, it is currently not suitable for continuous monitoring on a hog fuel boiler.

While several dioxin emission control technologies (sulfur addition, ammonia injection, ESP cooling by water spraying or by the introduction of dilution air) were tested in full scale trials, additional studies would be required to improve the efficiency and reliability of these processes or to solve operating problems (boiler plugging, corrosion, etc.) created by their implementation.

The co-firing of high calorific value, solid fuels, such as coal or tire derived fuel (TDF), with salt-laden hog fuel was found to increase combustion efficiency, facilitate the burning of more hog fuel and decrease dioxin emissions, particularly when firing poor quality hog fuel. Co-firing of such a solid fuel in hog fuel power boilers is much more beneficial than the firing of gas and oil as auxiliary fuels as it puts the heat onto the grate and increases combustion efficiency. Sulphur introduced into the boiler particularly with TDF also helps attenuate dioxins formation and emissions although it can adversely affect boiler plugging and increase boiler corrosion problems.

INTRODUCTION

Dioxins are the collective name for 210 different polychlorinated dibenzo-para-dioxins (PCDDs) and polychlorinated dibenzo-furans (PCDFs). While some of these compounds are extremely toxic, others are practically harmless. In total, only 17 of these chemical compounds (7 dioxins and 10 furans) are identified to be toxic to some degree. Of these, 2,3,7,8 - TCDD (tetra-chlorinated dibenzo-dioxin) is the most toxic. The toxicities of the different dioxins and furans are thus quantified using toxicity equivalent factors (TEFs) which give the particular compound's toxicity in 2,3,7,8 - TCDD equivalents. The TEF weighted quantities of dioxins and furans in a sample are referred to as Toxicity Equivalents (TEQ). I-TEFs (as defined by NATO) have been used internationally for many years. The World Health Organization (WHO) has recently put forward a new set of TEFs, which are slightly different from the I-TEFs. Although Canada will adopt the WHO-TEFs in the future, to facilitate comparison with the literature data, all of the TEQ data presented in this report are based on I-TEFs.

Any process that involves chlorine or chloride can be a potential source of dioxins and furans. Dioxin emissions from combustion sources, including medical and municipal solid waste incinerators, have been most extensively investigated. Those studies have shown that even trace quantities of organic or inorganic chloride are adequate to create the very low levels of dioxin emissions (10^{-9} – 10^{-12} g/metre^3) typically seen from combustion processes. Even steel production processes have been found to be dioxin emission sources in spite of the very low levels of chloride entering the production processes.

Chlorine bleaching is also known to form dioxins in effluent discharges [1] from pulp and paper mills. Most mills in North America have, however, now converted to elemental chlorine free (ECF) bleaching in order to meet strict regulatory limits for dioxin and furan emissions in effluents. Emissions from all of the pulp and paper mills in Canada are estimated to total less than 2 g TEQ/year as the concentrations of dioxins and furans in pulp mill effluent are now below the legal limit of quantification (LOQ).

While developing solutions to controlling dioxins emissions from pulp bleaching, researchers at Paprican found that power boilers burning salt-laden bark, or hogged fuel, could also be a significant source of dioxins and furans [2]. In collaboration with staff at the affected Canadian coastal mills, effective strategies, for example polymer-induced settling of ash in clarifiers [3], were developed to minimize the contribution of these combustion-derived dioxins to the final effluent discharge loadings. Further research efforts were then directed at effectively controlling stack-related dioxins emissions, with a focus on approaches that minimize formation at source. Between 1993 and 1998, stack dioxin emissions, under a variety of power boiler operating conditions, were evaluated at four western coastal mills [4-6]. At the four sites, stack dioxins emissions were found to range from 0.064 to 2.8 ng TEQ/m^3, while net dioxins production ranged from 23 to 330 mg TEQ/t of hog fuel [7]. Stack TEQ emission levels did not always correlate with the overall dioxin formation rate in the power boilers. Furthermore, a reduction in stack particulate levels did not always indicate a corresponding reduction in stack dioxins emissions [7]. While some dioxins appeared to have been generated within the particulate collection devices, the excellent TEQ removal efficiency of these units confirmed their essential role in controlling stack dioxins emissions.

Landfilling of the collected ash was not expected to pose a problem to the environment since the associated TEQ loadings (1 - 10 ppb TEQ) were always well below the "toxic substance" level of 100 ppb for solid waste disposal [8]. These dioxins are tightly bound on the ash and, hence, not easily removed by water leaching [9, 10, 11]. A review of dioxin analyses on leachate and water samples taken around the landfill sites of the coastal mills [12], which also included a very comprehensive review of the literature on dioxins, confirmed that only very low levels of dioxins were typically present. 30 of the 47 samples were either completely non-detectable (ND) or contained less than 5 pg TEQ/L (with ND = 1/2DL). A recent Swedish study [11] indicates that the low levels of dioxins seen in leachates from landfills processing ash from municipal waste incineration are primarily due to small particles in the leachate. The Swedish study [11] also found that the dioxin concentrations seen in these landfill leachates are at the same level as the dioxins content in rainwater.

EMISSION INVENTORY AND CANADA WIDE STANDARDS

In 1997 and 2000, Environment Canada compiled inventories of dioxin emissions from anthropogenic activities. Many of the emission estimates for different sources were based on emission factors taken from USEPA reports or from the open scientific literature. Several of the 1997 emission estimates, in particular, were subsequently revised (generally downward) as a result of further tests. In addition, several significant emission sources, such as barrel burning, were originally missing from the inventory. Nevertheless, the 1997 inventory indicated emissions to air from all Canadian sources totalled about 198 g TEQ/year. Dioxin emissions from conical waste combustors in Newfoundland were estimated to total 74.5 g TEQ/y, 37.6 % of the total. Emissions from coastal power boilers burning salt-laden hog fuel totalled 10.5 g TEQ/y in 1995 and 7.9 grams TEQ/y in 1997 (4 % of the total emissions from anthropogenic sources). The 6 largest sources of dioxins emissions were conical municipal waste combustion in Newfoundland, waste incineration (municipal solid waste incinerators, medical waste incinerators, sewage sludge incinerators, and hazardous waste incinerators), coastal pulp mill boilers burning salt laden wood, residential wood combustion, iron sintering, and electrical arc furnace steel making. The first three were estimated to emit 50 – 60 % of the total. The 6 largest dioxin emission sources were estimated to account for over 80 % of the national emissions and were, therefore, prioritized for early action and targeted for Canada Wide Standards.

The Canada Wide Standards (CWS) program was enacted in 1998 by the Canadian Council of Ministers of the Environment to facilitate federal/provincial/territorial co-ordination in setting priorities and in developing and effectively implementing standards to deal with several priority pollutants (particulate matter, ozone, mercury, benzene, and dioxins). While the standards were only very broadly defined, the development process was to take into consideration environmental benefits, available technologies, opportunities for pollution prevention and collateral benefits from reductions in other pollutants. The standards developed were to be technologically and economically achievable and to deliver measurable environmental benefits. The CWS development process was also to include stakeholder engagement and an evaluation of the socio-economic impacts of the proposed standards before jurisdictional implementation. While several series of workshops have been held to incorporate stakeholder input in the development of standards for different emission sources, to date, few socio-economic evaluations of any of the proposed CWS proposals have yet been either initiated or completed.

A Canada Wide Standard for controlling dioxin emissions from pulp and paper boilers burning salt laden wood was developed and submitted to the CCME in June 2000. It was accepted and endorsed by the CCME in November 2000. The Canada Wide Standard for dioxin and furan emissions from power boilers burning salt-laden hog fuel has set a stack emission limit of 0.1 and 0.5 ng TEQ/m^3 @11% O_2 for new and existing facilities, respectively. Existing facilities burning salt laden wood waste have until 2006 to comply with the 0.5 ng TEQ/m^3 @11% O_2 CWS emission standard. However, neither the pulp and paper industry nor the government was sure if and how these standards could be met and how much it would cost to comply. These concerns arose because:

- Only limited stack tests had been conducted on all of the affected boilers.
- The large variations in measured stack emissions and limited number of results prevented the development of any reasonable correlations between emission levels and boiler design and/or operating parameters.
- It was difficult to compare the test results with literature data because almost all the relevant literature data were obtained on municipal solid waste incinerators.
- Existing theories on dioxin formation mechanisms were all based on incineration processes or lab studies with incinerator ashes. It was not known whether dioxins and furans were formed in hog fuel boilers by the same reaction mechanisms as those seen in solid waste incinerators and it was, therefore, difficult to formulate a universally-effective control strategy.

In consideration of these concerns, the CWS for pulp and paper boilers burning salt laden wood included provisions to review the proposed standards in 2003 using further test data and controlled studies of boiler operations. The affected mills agreed to test each of their power boilers burning salt laden hog fuel twice a year for the years prior to 2003 and annually for the years from 2003 on. The affected mills also agreed to fund an extensive research project led by Paprican and including pilot plant studies at the University of British Columbia (UBC). The planned research and testing program with Paprican and UBC was designed to better quantify the emission levels, to determine the main formation mechanisms of dioxins/furans in the different boilers, and to identify and evaluate possible measures or approaches that will reduce, minimize or prevent emissions. The specific objectives of the research project were to:

- Determine the reasons for the variability in dioxins formation and emission rates for the different boilers.
- Monitor fuel quality and combustion conditions during stack dioxins emission tests at each coastal boiler to elucidate the key operating and combustion conditions that affect dioxins formation and emission rates.
- Determine the key operating and combustion conditions that will allow the affected mills to consistently reduce dioxins formation and lower dioxins emissions.
- Identify measurement techniques that can help ensure good combustion conditions and minimal dioxins emissions.
- Evaluate materials of construction in coastal fluid bed boilers to ensure reliable operation and cost-effective designs for future installations.
- Provide guidance for capital expenditures designed to minimize dioxins formation during the combustion of salt-laden hog fuel.

FACILITIES AND TESTS

The power boilers at the coastal mills, Mills A to H, which participated in the present study, are very different in terms of type, capacity, and design specifications.

- Boiler A is a Stoker boiler with traveling grates. The maximum continuous rate (MCR) for steam generation is 182 t/h (400 klb/h) at a steam pressure of 4327 kPag (625 psig) and temperature of 400° C (750 ° F) at the main steam outlet.

- Boiler B is a Stoker boiler with traveling grates The MCR for steam generation is 245 t/h (540 klb/h) on oil only and 205 t/h (450 klb/h) on hog only at an operating steam pressure of 4327 kPag (625 psig) and with a steam temperature of 400° C (750 ° F) at the main steam outlet.
- Boiler C has vibrating grates. The MCR for steam generation is by design 239 t/h (527 klb/h) on hog fuel only, 180 t/h (396 klb/h) on gas only, and 259 t/h (570 klb/h) on hog plus natural gas, at a maximum pressure of 8962 kPag (1300 psig) and steam temperature of 480° C (896 ° F) at the main steam outlet.
- Boiler D has a fixed grate which is raked manually. The MCR for steam generation is by design 114 t/h (250 klb/h) on hog fuel, 159 t/h (350 klb/h) on hog and oil, and 205 t/h (450 klb/h) on oil only. The operating steam pressure is 4327 kPag (625 psig) with a steam temperature of 400° C (750 ° F) at the superheater outlet. The maximum design steam pressure is 4997 kPag (725 psig).
- Boiler E is a bubbling fluidized bed (BFB). The MCR for steam generation is 272 t/h (600 klb/h). The operating steam pressure is 6516 kPag (942 psig) with a steam temperature of 480° C (896° F) at the main outlet. The maximum allowable working pressure is 8612 kPag (1245 psig).
- Boiler F is a converted BFB boiler. The MCR for steam generation is 156 t/h (343 klb/h) on hog fuel only and 205 t/h (450 klb/h) on oil only. The operating steam pressure is 4325 kPag (625 psig) with a product steam temperature of 400° C (752° F) at the superheater outlet.
- Boiler G is a fixed grate boiler which is raked manually. The MCR for steam generation is 80 t/h (176 klb/h) on oil, 75 t/h (165 klb/h) on gas and 20-80 t/h on hog depending on the hog quality. Steam pressure is 4152 kPag (600 psig) with a product steam temperature of 400° C (750 ° F) at the superheater outlet.
- Boiler H is a fixed grate boiler with an automatic raking system. The MCR for steam generation is 54 t/h (120 klb/h) on hog only and 75 t/h (165 klb/h) on oil only. The operating steam pressure is 4325 kPag (625 psig) with a product steam temperature of 400° C (750° F) at the superheater outlet.

The vast majority of the stack sampling tests were carried out by A. Lanfranco & Associates. Dioxin/furan and PAH emissions in the stack gases were determined using modified EPA method 5 (MM5). While Environment Canada has set the Limit of Quantification for stack dioxin emission tests at 0.030 ng (10^{-9}) ITEQ/dry standard cubic metre (dscm), an extensive study by the American Society of Mechanical Engineers using side by side, simultaneous stack traverses indicates that 99 out of 100 single dioxin emission measurements should fall within 0.069 ng ITEQ/dscm of the true concentration when the emission concentration is in the range from 0.02 to 0.9 ng ITEQ/dscm ["Reference Method Accuracy and Precision (ReMAP): Phase 1 – Precision of Manual Stack Emission Measurements" prepared by S. Lanier and C. Hendrix for the American Society of Mechanical Engineers, February 2001]. This indicates that any single test on a boiler complying with a CWS of 0.1 ng ITEQ/dscm could fall between 0.031 and 0.169 ng ITEQ/dscm. The poor precision and reproducibility of the stack dioxin emission test makes data interpretation at low concentrations very difficult and risky.

For research and information purposes, stack PM emissions were estimated during dioxin/furan sampling based on filter weight gains only, while EPA method 5 was used for compliance tests for PM emissions. PM emission tests were generally conducted immediately prior to or after the stack dioxin emission tests. Stack O_2 and CO_2 were tested by the stack samplers using the Fyrite method, while CO was measured with a portable CO meter. SO_2 emissions were tested by absorbing the flue gas samples in a 3% peroxide solution, which oxidizes SO_2 to SO_4^{2-}, followed by the barium-thorin titration analysis. HCl samples were collected by water absorption and sent to a commercial analytical lab for analysis with standard methods like ion chromatography. Axys Analytical and Philip Analytical Services were the designated analytical labs for PCDD/Fs and PAHs for both stack and ash samples. Both used high resolution GCMS for analysis of PCDD/Fs and low resolution GCMS for analysis of PAHs. Technicians at Axys noted that there could be significant uncertainties in the analyzed ash PAH concentrations due to wide variations in the recovery efficiencies.

Ash samples were taken for analysis during most of the power boiler stack dioxin emission tests. To better correlate the combustion and emission performance test data, testing and sampling activities were carefully coordinated with operation and measurement plans. During each test, while the stack flue gas was being sampled, hog and ash samples were also taken. Hog samples are used to determine the hog salt and moisture content. In addition to dioxins/furans, almost all of the stack tests also measured flue gas particulate, CO, CO_2, O_2, and moisture content. Most of the stack tests also included SO_2, HCl, and polyaromatic hydrocarbon or PAH emissions, while ash samples were analyzed for unburnt carbon, dioxin/furans, and PAHs. Meanwhile, grate/bed and free board combustion conditions were observed through observation ports or doors in the walls of each furnace, the temperature profile in the furnace were measured with a laser pyrometer, and downstream flue gas temperatures were measured using thermocouples.

Typically, three hog fuel and three fly ash or electrostatic precipitator catch samples were taken as grab samples during each stack test. The individual samples were mixed together after each test to make a composite sample for the test. The analytical results reported in this document are all based on composite samples. The hog moisture content was tested usually by the mill technical lab, while the salt content was tested by commercial analytical labs. The project steering committee decided to use hot leaching as the standardized extraction method for determining the hog fuel's salt content.

Key operating data were also collected and recorded during each stack test.

RESULTS AND DISCUSSION

Stack Emissions

A total of 103 stack dioxin tests were carried out on the eight coastal power boilers from 2000 through 2002. The number of stack dioxin emission tests was substantially greater than the minimum of 64 required under the CWS agreement, providing a very significant data base for analysis. As shown in Figure 1, stack dioxin concentrations varied significantly between individual tests on a given boiler and between boilers at different pulp mills. While some of the variability was due to tests where boiler combustion conditions, or operating conditions in the final particulate collection devise, were deliberately altered in order to provide data for correlation validation, some boilers showed consistently higher average emission levels than others. It is also evident from Figure 1 that the number of stack tests exceeding the 0.5 ng TEQ/m^3 @11% O_2 CWS emission standard declined slightly from 5 or 6 per year in 1995 – 2000 to only 1 in 2002. It must be noted, however, that there were still 2 or 3 stack tests in 2002 that produced emissions estimates very close to the 0.5 ng TEQ/m^3 @11% O_2 CWS emission standard. For most of the coastal boilers, the average emission levels tested in 2002 were lower than those tested in the previous two years [13]. The overall average dioxin emissions from all of the power boilers at the coastal BC mills were 0.239, 0.280, and 0.130 ng TEQ/m^3 at 11% O_2, respectively, for the years of 2000, 2001 and 2002. In comparison, the average for all of the dioxin emission tests on these boilers between 1992 and 1999 was 0.493 ng TEQ/m^3 at 11% O_2.

In 2001, stack dioxin emissions were also measured for a power boiler at an interior BC mill in order to better compare the emission levels for coastal and interior power boilers. In two tests on an interior BC power boiler, stack dioxin emissions of 0.0004 to 0.0007 ng TEQ/m^3 @11% O_2 were measured despite relatively high stack particulate emissions (130 – 195 mg/ m^3 @12% CO_2). Subsequent analysis of stack emission data from 37 tests on 16 power boilers at mills in Canada and the United States indicated that dioxin emission levels for power boilers at interior pulp mills burning salt-free wood waste, with or without wastewater treatment plant sludge, were 2-3 orders of magnitude lower than the typical levels observed from power boilers at coastal mills [14]. The low dioxin emission levels at interior mills (0.0004 – 0.086 ng I-TEQ/dscm @8%O_2 in the tests at Canadian mills) was due primarily to the absence of chloride in the hog fuel and to lower hog moisture content, which helped ensure better combustion conditions.

Figure 2 shows the total dioxin emissions, in grams of ITEQ per year, from 1995 through 2002 for all 8 coastal boilers. The total dioxin emissions depend not only on stack dioxin concentrations but also on hog steam loading and the number of days that a specific boiler was operated. Total dioxin emissions were estimated based on the averages of the stack tests for each boiler during each year and the amount of hog fuel burned each year. While there is a high degree of uncertainty in these emission estimates (to the point that the emissions estimates for the years 2000, 2001 and 2002 are statistically indistinguishable), it is evident that total dioxin emissions from coastal power boilers have declined significantly since 1995. Dioxin emissions from the burning of salt-laden hog fuel are estimated to have declined by over 68 %, from 10.5 grams TEQ in 1995 to 3.3-3.4 grams in both 2001 and 2002. It is also worth noting that the level of uncertainty in the emission estimates has not decreased in the last three years, again reflecting the extreme variability in dioxin emission test results for several of the 8 boilers.

The reduction in dioxins emissions since 1995 can be attributed in part to increased understanding of the dioxin formation mechanisms and the conditions that result in high stack emissions. Emissions have been reduced largely through improvements in combustion and reductions in the emissions of fine particulates. The data collected from over 100 tests on the coastal power boilers indicates that improved combustion efficiency reduces dioxins formation and that reduced particulate emissions generally result in lower stack dioxin emissions. As summarized in Table I, the affected mills have:

- Built new bubbling fluidized bed (BFB) boilers or converted older boilers to a BFB design
- Shut down old, inefficient small boilers
- Upgraded existing electrostatic precipitators (ESP) and wet scrubbers, and
- Installed a new wet ESP

The mills have also:

- Traded hog between mills so that the poorest quality hog, with either high salt or moisture content, is directed to the boilers that can most effectively burn it without increasing emissions, and
- Improved boiler operations and combustion efficiency by:
    - Improving the mixing of hog fuel and sludge;
    - Better balancing the combustion air supply and optimizing excess oxygen levels in the boilers;
    - Monitoring and avoiding high emissions of CO and PAHs;
    - Improving combustion on the grate, or in the fluidized bed, through the addition of alternative, high calorific value, solid fuels, such as coal and TDF; and

- Reducing temperatures in the electro-static precipitators by reducing the operating steam pressure/temperature, spraying water at the inlet to the ESP, or introducing ambient air for flue gas dilution. These temperature reduction methods were only implemented on a trial basis. More studies are needed to fully determine the impacts of these measures on boiler operations and potential operating problems, such as back end and ESP corrosion.

Despite the general improvement in dioxin emissions and the fact that the average stack emissions over the last three years (see Table II) are now generally below the CWS limit of 0.5 ng TEQ/m^3 at 11% O_2 for existing facilities, the large variations of individual test results, illustrated in both Figure 1 and Table II, present difficulties for many of the mills in ensuring compliance with the current CWS limit. As illustrated in Table II, dioxin emissions in tests on any of the coastal power boilers routinely vary by a factor between 5 and 45. Four of the 8 mills have measured emissions in the last three years that exceed the CWS, with failure rates as high as 40%.

Table I: A summary of the capital modifications undertaken at the various coastal mills to reduce power boiler stack dioxin emissions between 1995 and 2003.

Mill	Technology implemented	% Reduction in Dioxin Emissions	Estimated Reduction in dioxin emissions, g TEQ/y	Cost, millions of dollars
B	ESP upgraded and new hog presses installed	90	2.4	$15.8
D	Shut down old, inefficient boilers and improved ESP performance	83	0.3	$1.0 - 2.7
E	Replaced 3 old boilers with new BFB	96.5	1.7	$120
F	Converted old Stoker Boiler to BFB	-	(increased by 0.25)	$ 20
J	Mill closed	100	0.4	--
A	New, wet ESP installed	73	2.6	$12

Table II: Summary of dioxin emissions tests for each coastal power boiler in tests from 2000 through 2002.

Power Boiler at Mill	No. of tests	Average Emissions ng TEQ/m^3 at 11% O_2	Highest Emission Level, ng TEQ/m^3	Lowest Emission Level, ng TEQ/m^3	Ratio of High to Low	No. of tests above 0.4 ng TEQ/m^3	No. of tests above 0.5 ng TEQ/m^3
A	16	0.274	2.57	0.01	252	2	2
B	12	0.108	0.29	0.015	19.3	0	0
C	12	0.394	0.868	0.16	5.4	5	3
D	12	0.037	0.138	0.01	13.8	0	0
E	18	0.055	0.176	0.016	11.0	0	0
F	17	0.212	0.55	0.012	45.8	2	1
G	10	0.542	1.72	0.056	30.7	4	4
H	6	0.046	0.144	0.016	9.0	0	0

Formation Mechanisms and Operating Variable Impacts

Studies on municipal solid waste incinerators [15] indicate that dioxins may be formed at high temperatures and/or at low temperatures (600-200º C) through two primary formation mechanisms:

- Formation at high temperatures of chemically similar (chlorinated) precursors, such as chlorobenzenes (CBs), chlorophenols (CPs), or polychlorinated biphenyls (PCBs)
- Formation at high temperatures of products of incomplete combustion (PIC), such as PAHs and unburned carbon
- Condensation, adsorption and desorption reactions involving these gas-phase precursors and fly ash (precursor formation)
- Solid-phase reactions on the surface of fly ash involving metal chlorides and PAHs or unburned carbon (*de novo* formation).

All of the data collected on dioxins formation in coastal power boilers burning salt-laden hog fuel indicates that the test results obtained on waste incinerators can also be applied to hog fuel boilers. Extensive analysis of the power boiler test results indicates that the observed large variations in stack dioxin emissions often reflect changes in the primary dioxin formation mechanism (see the last paragraph in the "Predicting Stack Emissions" section below). In particular, very high emissions were primarily due to poor combustion conditions that lead to the formation of high levels of precursors as well as polyaromatic hydrocarbons or PAHs.

Analysis of the dioxin emission data for the coastal power boilers further indicates that, in addition to hog fuel quality, the boiler design and air system can also affect combustion performance, leading to different quantities and species of products of incomplete combustion (PICs), such as chlorinated precursors, and/or to differing concentrations of unburnt carbon in the boiler fly ash. The design and arrangement of downstream heat exchangers, particularly the air heater and economizer, can affect the temperature and residence time distribution for dioxins formation by both precursor and *de novo* reactions and the adsorption and desorption of dioxins and furans on fly ash. The temperature of the flue gas entering the air heater and the temperature in the electro-static precipitator were found to dramatically affect dioxin formation in coastal power boilers and to explain much of the differences in emission levels observed between different power boilers. The design and performance of the particulate removal device can also affect stack particulate emissions and consequently dioxin emissions.

While operating guidelines and proposals for equipment modifications were developed to reduce dioxin and furan formation and emissions in several of the power boilers, no single solution was identified. The proposed operating guidelines for several of the power boilers would help ensure good combustion, while most of the suggested equipment modifications were targeted to reduce flue gas temperatures into the air heater and ESP. The temperatures currently seen in these sections of the boiler are largely determined by the original boiler design specifications and layout. Changing the gas flow route is physically difficult, if not impossible, in many of the boilers and is likely to be very expensive. Impacts on the combustion air temperature and combustion efficiency resulting from these changes also need to be fully examined by design engineers on a boiler by boiler basis. While the boiler layout cannot be readily (or perhaps economically) changed for an existing boiler, the correlations developed in this work can be used to guide future boiler modifications and capital investments and new boiler design.

Correlations to Predict Stack Dioxin Emissions

Numerous studies [16 – 18 for example] have recently shown that both organic chlorine (e.g. PVC) and inorganic chlorides (e.g. NaCl) can be significant chlorine sources for PCDD/F formation during combustion processes. However, when the current study was initiated, it was not precisely known how NaCl participates in dioxin formation reactions and under what conditions NaCl behaves like, or unlike, PVC. We, therefore, carried out a thermodynamic analysis of high temperature salt chemistry and examined its influence on dioxin and furan formation in power boilers burning salt-laden wood waste by determining the relationships between Cl_2, HCl, NaCl (g) and NaCl (c). Our thermodynamic analyses [19] indicate the presence of sulfur at low concentrations enhances PCDD/F formation by increasing HCl concentrations. At high concentrations, sulfur inhibits de novo formation of PCDD/Fs through Cl_2 reduction by excess SO_2.

In an effort to better predict stack dioxin emissions and the influence of operating parameters on those emissions, a semi-empirical kinetic model was proposed [19] to describe PCDD/F formation in power boilers burning salt-laden wood waste. A simplified version is used as a stack emission model,

$$[\mathrm{TEQ}]_{\mathrm{stack}} = \mathrm{A} + \mathrm{B}\cdot \exp(-\mathrm{C}/\mathrm{T}_{\mathrm{ESP}}) + \mathrm{D}\cdot [\mathrm{PAH}]_{\mathrm{stack}} \cdot [\mathrm{NaCl}]^2{}_{\mathrm{hog}} \qquad (1)$$

where A, B, C and D are four model parameters estimated with the experimental data. The first term on the right hand side (A) reflects the particulate phase dioxin emissions and is determined by the ESP particulate control efficiency. The second term represents the gas phase emissions and is a function of the ESP outlet temperature, T_{ESP}. In examining dioxin emission data for 12 different municipal solid waste incinerators, Flemish researchers [20] recently concluded that the ESP operating temperature was the single most important operating variable influencing dioxin emissions. The third term is related to *de novo* synthesis and indicates that the amount of dioxins formed by either the *de novo* or precursor mechanism increases as the concentration of precursors (characterized by the high molecular weight PAH compounds in the flue gas) or the hog fuel salt content increases. Only the high molecular weight (HMW) PAH compounds with a molecular structure of four or more rings are capable of forming dioxins and furans. As pyrene and fluoranthene are dominant HMW PAH species in wood waste combustion flue gases, only the concentrations of these two PAH compounds are used in the equation. The equation predicts that stack dioxin emissions will increase linearly with decreasing electrostatic precipitator (ESP) efficiency or increasing concentrations of precursor PAH compounds, exponentially with increasing ESP temperature, and to the second order with hog salt content. The stack emission model was verified with both intra-mill and inter-mill test data. The verification with the test data from the 6 mills with dry ESPs is shown in Figure 3. The proposed correlation fits the measured mill data very well indicating that much of the variability in stack test results can be explained by variations in the hog salt content, concentrations of precursor PAH compounds (an indirect measure of combustion efficiency) and ESP operating temperature.

The ESP operating temperature was observed to vary from test to test in a given boiler as a result of variations in the operating steam pressure or temperature, the boiler load, and the heat transfer efficiency in the various heat exchanger banks. Figure 4 shows a schematic drawing of a typical fluid bed power boiler illustrating the locations of the various heat exchanging tube banks. The layout and size of these tube banks varies from boiler to boiler. Bypassing heat exchangers due to plugging or tube leaks was observed to have a dramatic influence on the stack temperature and dioxin emissions. Further investigations indicated that stack dioxin emissions increase exponentially with the air heater inlet temperature, as illustrated in Figure 5. The retention time for the flue gas in the air heater is usually much longer than that 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 [21]. It is, therefore, not surprising to see dioxin formation and stack emissions increase as the flue gas temperature into the air heater is increased. The temperatures currently seen in the air heater are largely determined by the original boiler design specifications and layout. Changing the gas flow route is physically difficult, if not impossible, in many of the boilers and is likely to be very expensive. Mills can minimize dioxin emissions by ensuring that all heat exchange banks and tubes upstream of and in the air heater are clean and that plugged or leaking tubes in those banks are replaced or repaired at each shutdown. In the longer term, the mills can consider capital expenditures, such as installing or relocating an economizer, to lower gas temperatures into the air heater. The impacts on the combustion air temperature and combustion efficiency resulting from these changes will, however, need to be fully examined by design engineers on a boiler by boiler basis. While the boiler layout cannot be readily (or perhaps economically) changed for an existing boiler, the correlations developed in this work can be used to guide future boiler modifications and capital investments and new boiler design.

Additional correlations were also developed [22] which showed how combustion efficiency, as characterized by the grate or lower furnace temperature, impacted dioxin and furan emissions and the dioxin congener profile. As expected, poorer combustion resulted in much higher levels of precursor PAH emissions and higher dioxin and furan emissions. Although the extent of this effect appeared to be mill specific (depending a lot on the location of the observation doors and windows in the lower furnace), the results indicate that the destruction rate for dioxin and furan precursors increase with higher grate or lower furnace temperatures and that the addition of high calorific value, solid fuels like coal or tire derived fuel (TDF) can be beneficial in reducing dioxin emissions. As illustrated in Figure 6, using data from Mill G, lower combustion temperatures, characteristic of poor combustion, appear to favour the formation of dioxins over furans. The dioxin/furan stack emission profile is dominated by dioxins when grate temperatures are low and combustion is poor; the congener profile is dominated by furans when combustion is good and grate or lower furnace temperatures are high. This conclusion is also supported by the results of Altwicker [23] who showed that dioxin formation from chlorophenols is higher at lower temperatures and that chlorophenols predominantly form furans at higher combustion temperatures. As the TEFs for the tetra and penta dioxin congeners are ten times higher than those for the corresponding furan congeners, this has a significant impact in terms of reportable stack TEQ emissions.

Monitoring PAH Emissions

Carbon monoxide (CO) emissions are readily and continuously measured at the stack of many incinerators and boilers. Carbon monoxide emissions are widely used as an indicator of combustion efficiency. While no strong correlation was evident between CO emissions and dioxins formation, or emissions, in any of the coastal power boilers [22], stack polyaromatic hydrocarbon or PAH emissions were found to correlate well with the measured stack dioxin emissions, according to Equation (1). Stack testing for PAH is, however, almost as costly as testing for dioxins as stack PAH emissions are usually determined using the same modified method 5 test used for measuring dioxin emissions. In addition, a long turn around time is required for laboratory analysis of the PAH sample extract. We did, however, identify an on-line PAH emission monitor, which had been used by Environment Canada and the United States Environment Protection Agency in several short term emission tests. An instrument was subsequently purchased and tested at Mill B to see if it might be routinely used to monitor combustion efficiency and control dioxins formation and emissions. Problems with condensation in the sample lines were initially encountered with the instrument due to poor equipment design and poor workmanship during fabrication. After these problems were rectified, the instrument was used to develop several useful operating guidelines for the power boiler at Mill B [22]. The instrument continued, however, to be plagued by a series of operating problems including failure of the dilution air pump. It required a lot of attention and maintenance to ensure reliable operation. While on-line monitoring of PAH emissions would be very useful in helping a mill develop guidelines that will reduce dioxin emissions, the tested instrument is currently not reliable enough to be used for routine combustion efficiency optimization. It is still very much a research tool that requires intensive maintenance and attention. The purchased instrument may, however, be moved from Mill B after some planned calibration tests and set up on other power boilers to help develop operating guidelines which can reduce stack PAH and dioxin emissions.

Emission Control Technologies

Through the course of this research program and our earlier studies, the BC coastal mills have run many trials in an attempt to develop effective dioxin emission control strategies and technologies. These trials, which have been carried out on several of the power boilers and have, in many cases, necessitated significant capital expenditures and/or operating costs increases, included:

- Sulfur addition by introducing concentrated non-condensable gases or CNCGs. This method was found to significantly reduce dioxin formation and emissions [24]. However, co-firing CNCGs caused superheater and generating bank plugging and could increase boiler corrosion rates under certain boiler-specific conditions [25]. It cannot be applied to boilers with higher steam temperature and pressure (> 6200 kPAg or 900 psig) or to even low pressure boilers on a continuous basis without further systematic tests.
- Addition of low sulfur coal to hog/sludge fuel [26]. Coal was found to improve combustion performance, helping the mill burn more hog and reduce dioxin formation and emissions, particularly when burning low quality hog fuel.
- Addition of tire derived fuel (TDF) [27, 28]. Similar to coal, the use of higher calorific value TDF in a fluidized bed has proven to be an effective method to control dioxin formation and emissions. In particular, sulphur introduced into the boiler helps attenuate dioxins formation and emissions [7, 24, 27, 28].
- Ammonia addition. Significant dioxin reduction (up to 90%) was observed in pilot plant, fluidized bed combustion trials with salt-laden wood waste at Canmet. Full scale trials at one coastal mill were, however, less successful producing only a 20-40% reduction in dioxin emissions. Ammonia or urea injection is an expensive technology. Its performance in terms of reducing both dioxins and boiler NO_X emissions needs to be improved.
- ESP cooling by water spraying or air entrainment. Tests were conducted on two power boilers during the course of the current study. This technique seemed very effective in some of the trials but not successful in other trials. It is still under investigation.
- Boiler upgrade. A few mills, particularly those with high emission variability, are examining ways to modify the boiler systems to improve hog combustion efficiency and to reduce dioxin formation and emissions through carefully planned capital expenditures.

Pilot Plant Research at UBC

Combustion experiments using salt-laden hog fuel were conducted in a pilot-scale, 0.3 m diameter, bubbling fluidized bed combustor, equipped with a bag house. 22 fly ash samples collected in the baghouse were analyzed for dioxins and furans. Fly ash analyses were used in this study, instead of stack emission tests, in order to speed up the test program and to keep testing costs reasonable. The total dioxin concentrations were found to vary from 0.12 to 6.1 ng TEQ/g as combustion conditions, the hog fuel salt content, gas cooling rates and the baghouse temperature were varied [29]. Despite very high hog salt contents (up to 2.5% NaCl), however, a great majority of the ash samples contained very low dioxin concentrations (< 1 ng TEQ/g). Over the 0 to 2.5 % hog fuel salt content range investigated, the ash dioxins increased with increasing hog salt content. Large variations in ash dioxin concentrations and TEQs were, however, also observed in tests at the same hog salt concentration due to uncontrolled (and often unmeasured) changes in other process variables. The pilot plant tests indicated that the operating temperature for the particulate collection device was an important process variable for dioxins formation. The ash dioxin concentrations increased with increasing baghouse temperature in tests with similar hog fuel salt content. For given combustion conditions, ash dioxins also increased with increasing flue gas CO concentrations and with increasing ash carbon content. Process upsets caused by fuel feed blockages strongly influenced the concentration and TEQ of ash dioxins. A direct correlation between ash dioxins levels and hog moisture content could not be established based on the two moisture levels investigated (20 and 55 %). However, high hog moisture content was observed to affect combustion conditions, such as the combustion chamber and flue gas temperature profiles, the flue gas CO concentration, and ash carbon content. The observed effects of changing hog fuel moisture content are likely to impact dioxin formation.

Fouling and Corrosion Implications of Proposed Emission Control Technologies
A review of relevant literature [25] was conducted to better understand how the practice of firing salt-laden hog fuel influences materials performance (fouling/corrosion) of the various components within power boilers. The knowledge base derived from the review provided a framework necessary to evaluate the possible fouling/corrosion repercussions of potential dioxin control strategies. Several promising control strategies were evaluated in this context [25]. It was found that gaseous HCl and NaCl fume are the likely end products associated with combusting salt-laden hog fuel. Of the two, NaCl fume likely has a more pronounced influence on both fouling and corrosion. NaCl fume is expected to increase the fouling propensity, especially in the presence of alkali sulphates. The increased propensity is related to the effectiveness of NaCl in lowering the first melting temperature of sulphate-containing deposits. From a corrosion perspective, NaCl-containing deposits can be particularly corrosive to heat transfer boiler tubes made from carbon, low alloy and stainless steel. The dominant corrosion mode is expected to be active oxidation, a mode which occurs below the melting temperature of the deposit. More studies are needed to fully determine the impacts of temperature reduction measures on boiler operations and potential operating problems, such as back end and ESP corrosion.

CONCLUSIONS AND RECOMMENDATIONS

1. Stack dioxin emissions from coastal power boilers burning salt-laden hog fuel have decreased by over 68% since 1995, from 10.5 grams of ITEQ per year in 1995 to 3.3 – 3.4 grams of ITEQ in both 2001 and 2002. These reductions have been realized through a series of capital expenditures and boiler shutdowns and through ongoing efforts to improve power boiler combustion efficiency and decrease particulate emissions. The data collected from over 100 tests on the coastal power boilers indicates that improved combustion efficiency reduces dioxins formation and that reduced particulate emissions generally result in lower stack dioxin emissions.

2. Stack dioxin emissions test results for the coastal power boilers are still highly variable. The results from single tests on any of the coastal power boilers vary by a factor between 5 and 45 and four of the 8 mills have measured emissions in the last three years that exceed the Canada Wide Standard for existing facilities (0.5 ng TEQ/m^3 @11% O_2). The large variations of

individual test results present difficulties for many of the mills in ensuring compliance with the current CWS limit.

3. Detailed analysis of the results of over 100 stack dioxin emission tests on 8 different power boilers indicates that most of the variation in emissions can be attributed to variations in combustion efficiency, particulate removal efficiency in the ESP or scrubber, hog fuel salt content, and the operating temperatures in the air heater and ESP. Very high emissions were primarily due to poor combustion conditions that lead to the formation of high levels of precursors as well as PAHs. A three term kinetic model, empirically fit to the stack emission data, accurately correlates the data from the different stack tests and predicts the impacts of changing these four important operating variables. The importance of these operating variables was also confirmed in pilot plant tests at UBC.

4. Stack dioxin emissions were found to increase exponentially with increases in either the electrostatic precipitator (ESP) operating temperature or the flue gas temperature into the air heater. 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 capital investments and new boiler design.

5. While operating guidelines and proposals for equipment modifications were developed to reduce dioxin and furan formation and emissions in several of the power boilers, no single solution was identified. The proposed operating guidelines for several of the power boilers would help ensure good combustion, while most of the suggested equipment modifications were targeted to reduce flue gas temperatures into the air heater and economizer.

6. An online instrument to continuously measure PAH emissions was tested on one boiler. While it provided very useful data and insights that might be used to optimize combustion conditions and minimize dioxin emissions, it is currently not suitable for continuous monitoring on a hog fuel boiler.

7. While several dioxin emission control technologies (sulfur addition, ammonia injection, ESP cooling by water spraying or the introduction of dilution air) were tested in full scale trials, additional studies would be required to improve the efficiency and reliability of these processes or to solve operating problems (boiler plugging, corrosion, etc.) created by their implementation.

8. The co-firing of high calorific value, solid fuels, such as coal or tire derived fuel (TDF), with salt-laden hog fuel was found to increase combustion efficiency, facilitate the burning of more hog fuel and decrease dioxin emissions, particularly when firing poor quality hog fuel. Co-firing of such a solid fuel in hog boilers is much more beneficial than the firing of oil and gas as auxiliary fuels as it puts the heat onto the grate and increases combustion efficiency. Sulphur introduced into the boiler, particularly with TDF, also helps attenuate dioxins formation and emissions although it can adversely affect boiler plugging and increase boiler corrosion problems.

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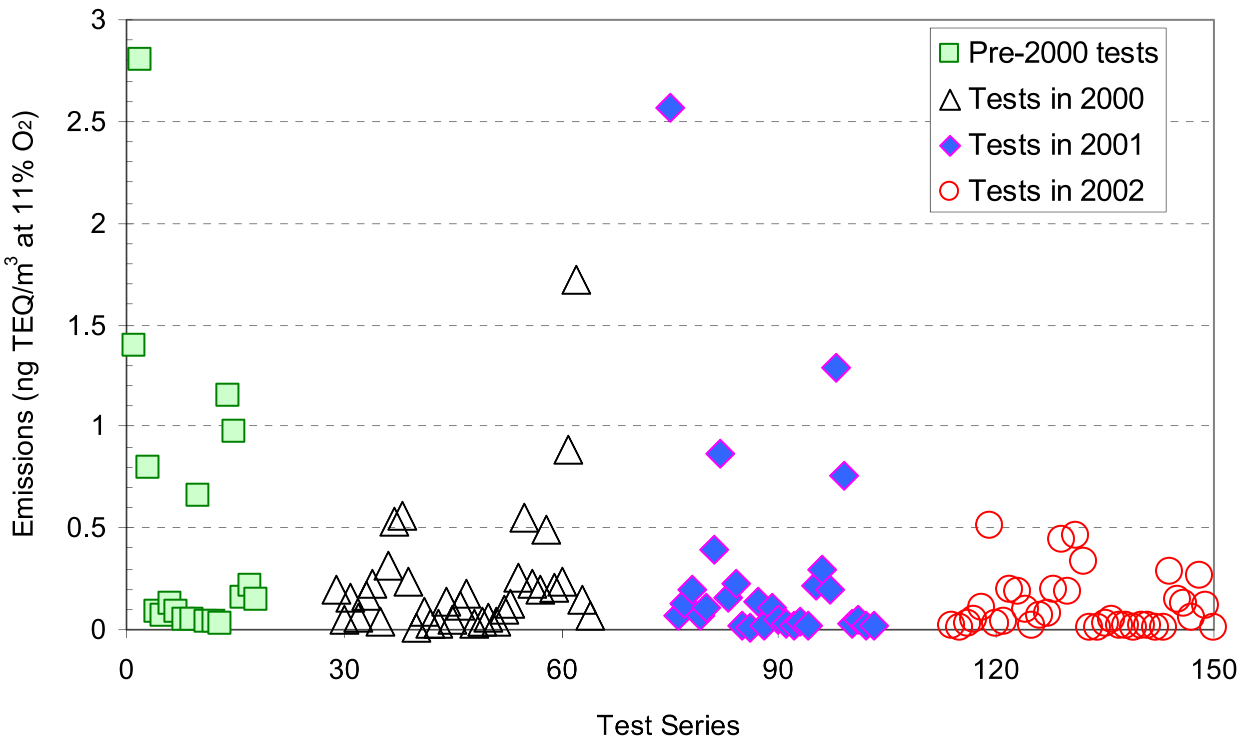

Figure 1. Stack emission test results from 1992 through 2003 for the power boilers at all eight affected BC coastal mills.

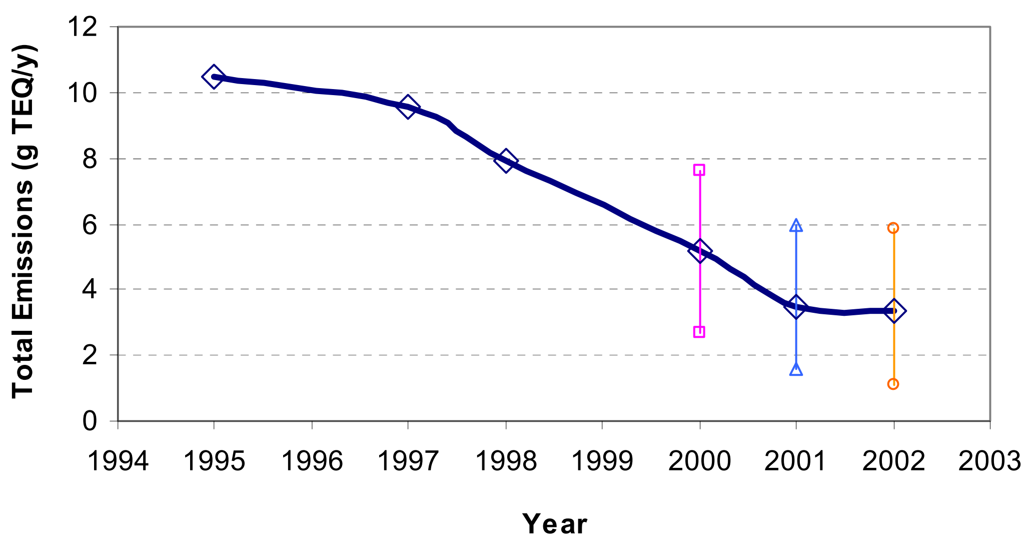

Figure 2. Average annual total dioxin emissions from the eight BC coastal power boilers from 1995 through 2002. The bars for 2000, 2001 and 2002 indicate the uncertainty in each emission estimate.

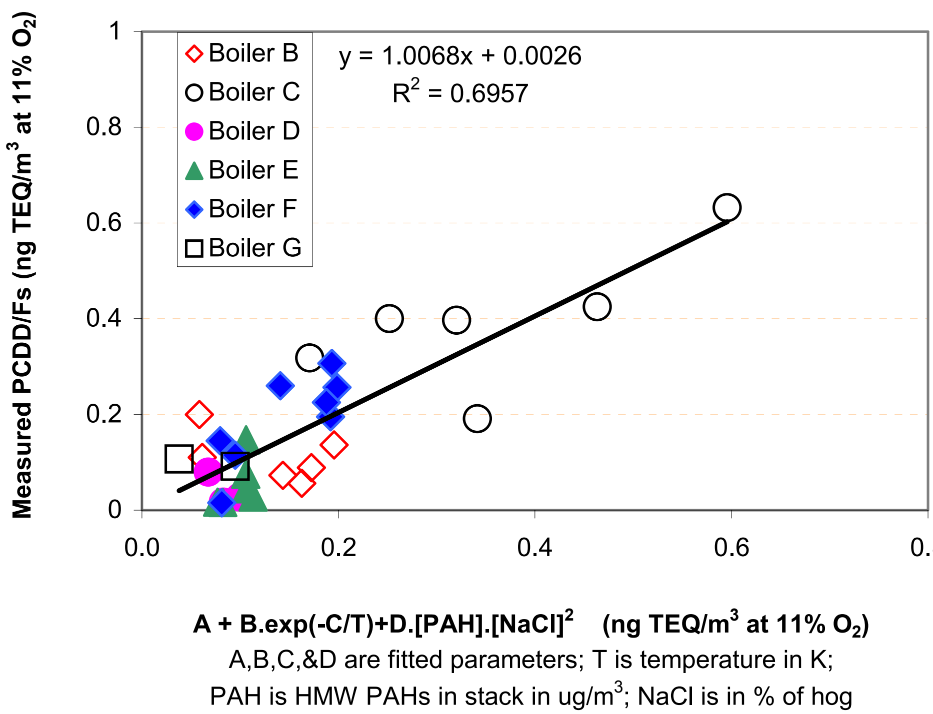

Figure 3. Intermill data correlation based on duplicate and triplicate stack tests**.**

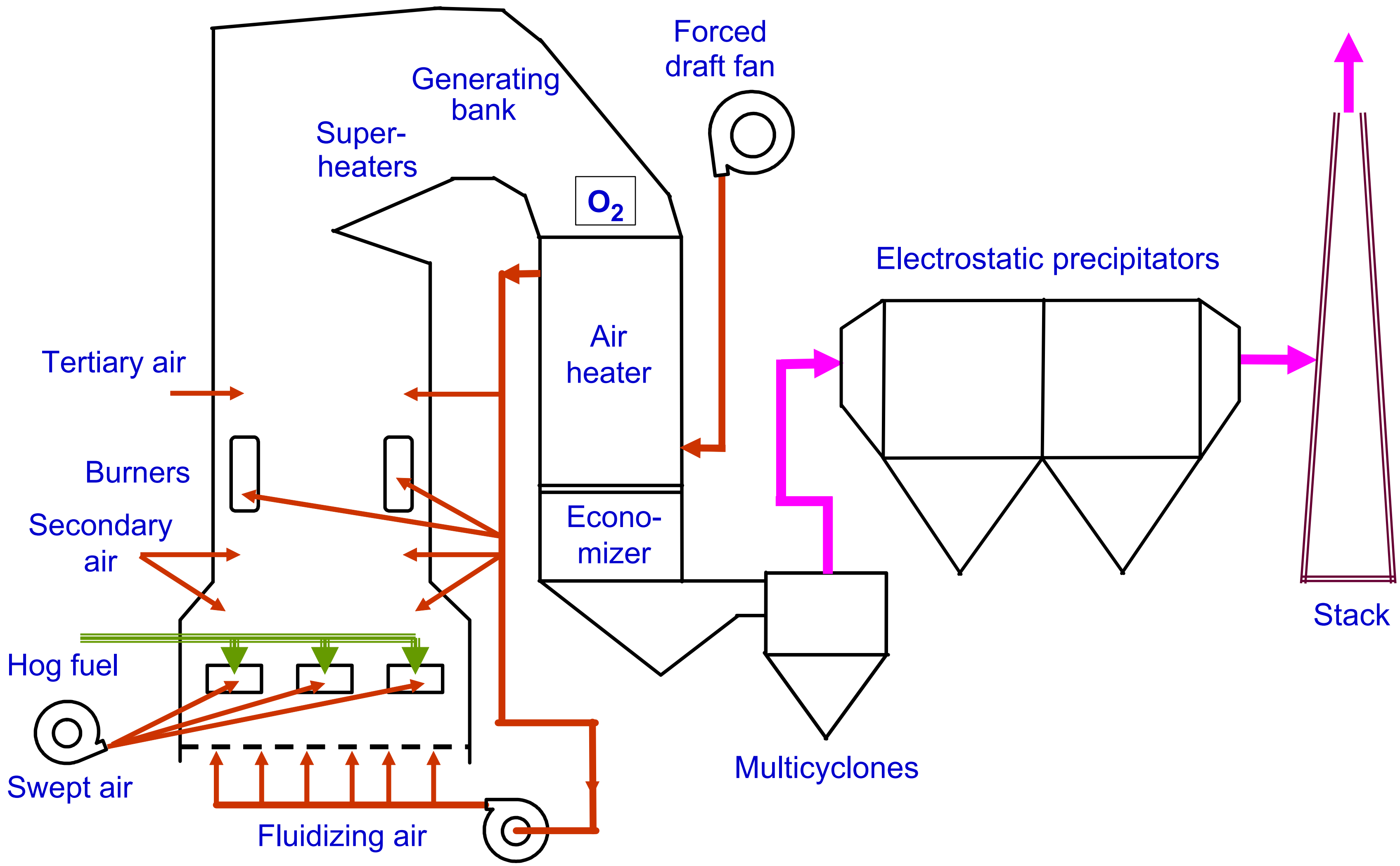

Figure 4. A schematic drawing of a typical fluid bed power boiler showing the location of the various heat exchanging tube banks. The layout and size of these tube banks varies from boiler to boiler.

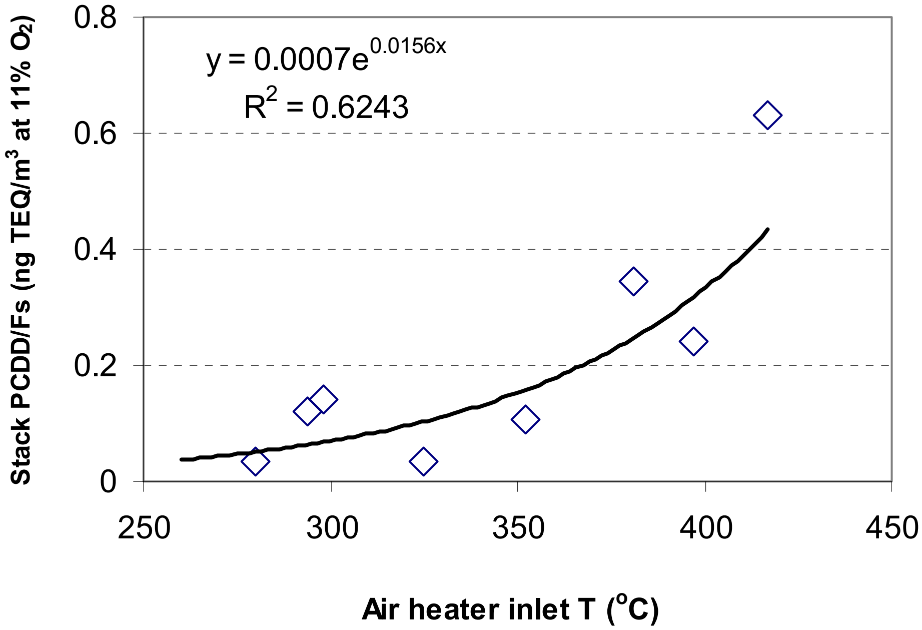

Figure 5. Correlation of stack dioxin emissions with average air heater inlet temperatures.

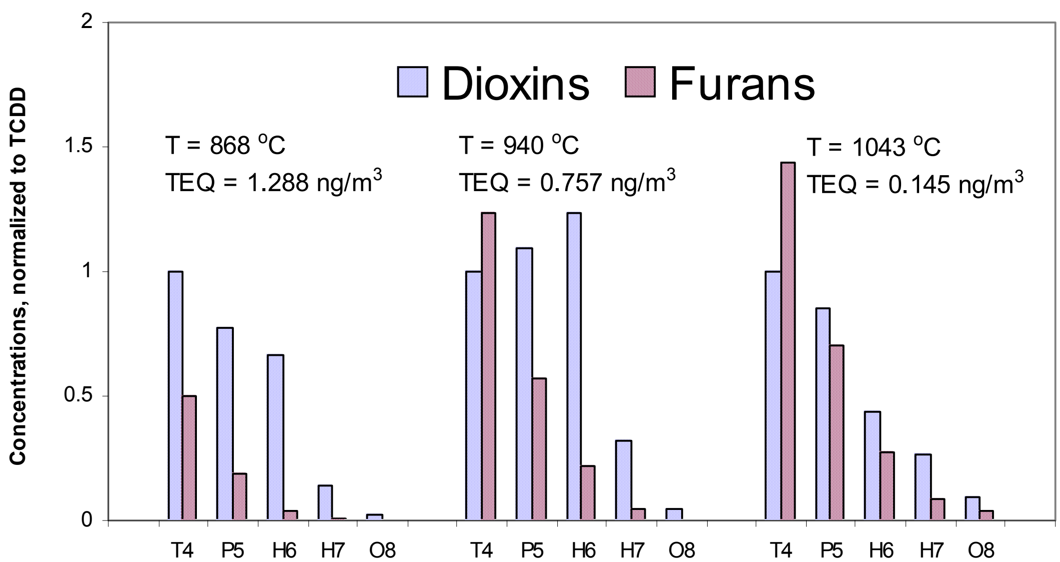

Figure 6: Effect of combustion performance on the dioxin/furan congener profile of stack emissions at Mill G. As the grate/lower furnace temperature (a general measure of combustion performance) increases, the profile becomes increasingly dominated by furans.