Dioxin and Furan Emission Factors for Combustion Operations in Pulp Mills

Prepared for Environment Canada

by
Vic Uloth and Ron van Heek,
PAPRICAN, Prince George, BC
November 5, 2002.

PULP AND PAPER RESEARCH INSTITUTE OF CANADA • 3800 WESBROOK MALL, VANCOUVER, BC, CANADA V6S 2L9

Dioxin and Furan Emission Factors for Combustion Operations in Pulp Mills

by
Vic Uloth and Ron van Heek
Paprican, Prince George, BC

Executive Summary

Based on a review of the literature and emission data compiled by both NCASI and Paprican, the following emission factors are recommended to estimate dioxin and furan emissions from pulp mill combustion processes:

- For power boilers burning clean wood-waste (with or without wastewater effluent treatment plant sludges) – 40 ng TEQ/BDt of hog fuel burned.

- For power boilers burning a combination of clean wood-waste (with or without wastewater effluent treatment plant sludges) and de-inking process sludges – 750 ng TEQ/BDt of hog fuel burned.

- For kraft chemical recovery boilers burning black liquor – 15 ng TEQ/tonne of dry fired black liquor solids.

- For lime kilns fired with either natural gas and/or heavy fuel oil – 9 ng TEQ/tonne of product lime.

- For kraft mill smelt dissolving tanks – 0.55 ng TEQ/tonne of dry fired black liquor solids.

- For sulphite process recovery boilers – 0.5 ng TEQ/tonne of fired red liquor solids.

The concentrations of dioxins and furans on ashes from power boilers burning clean wood-waste (with or without wastewater treatment plant sludges), estimated from the medians for 76 ash samples from 54 different facilities, as compiled by both NCASI and Paprican, are:

- 0.02 pg TEQ/g for grate or bottom ash

- 0.10 pg TEQ /g for multicyclone ash

- 0.46 pg TEQ/g for ESP, scrubber or combined flyash

The amount of each type of ash can be estimated, in the absence of measured data, using data compiled by Paprican for coastal power boilers burning salt-laden hog fuel:

- 15 – 20 kg of grate ash/BD tonne of hog fuel burnt

- 12 – 16 kg of multicyclone ash/BD tonne of hog fuel burnt

- 18 – 41 kg of ESP or scrubber ash/BD tonne of hog fuel burnt

1. Introduction:

Dioxin and furan releases have now been added to the list of substances that have to be reported to the National Pollutant Release Inventory (NPRI). Dioxins and furans (D/F) are expensive to test and heavy reliance is placed on the use of emission factors such as those in USEPA AP-42. Various sectors in the forest products industry have reported difficulties in acquiring accurate emission factors. This problem has been compounded as no authority has compiled a dioxin-furan emission factor book. Heavy reliance is being placed on publications, such as the USEPA AP-42 book, but many of the factors are out of date and do not reflect recent test results.

PAPRICAN has, therefore, undertaken a contract with Environment Canada to prepare a set of emission factors, and supporting material to justify them, for use in inventory compilation by NPRI reporters in the pulp and paper (P&P) and forest products sectors. It is hoped that the resulting guidelines, once distributed to the industry, will improve the mandatory reporting of D/F to the NPRI program.

The development of scientifically-defensible emission factors will entail the following tasks:

- A review of existing scientific literature on D/F formation in and emissions from various P&P combustion processes.

- A review of all valid available D/F stack testing results performed on P&P sources in Canada and other countries.

Based on this review, scientifically-based emission factors will then be proposed for the following pulp and paper mill operations:

- Power boilers burning clean wood-waste (with or without wastewater effluent treatment plant sludges).

- Power boilers burning a combination of clean wood-waste (with or without wastewater effluent treatment plant sludges) and de-inking process sludges.

- Recovery boilers burning black liquor.

- Lime kilns fired with natural gas and/or heavy fuel oil.

- Smelt dissolving tanks.

- Sulphite process recovery boilers.

2. Literature Review:

2.1 Power Boilers Burning Clean Wood-Waste (With or Without Wastewater Effluent Treatment Plant Sludges):

2.1.1 Rational for Reviewing the Current Emission Factor:

In developing their recommended emission factor for "industrial wood combustion", 0.82 ng TEQ/kg of wood burned [EPA/600/P-98/002Aa, April 1998], the U. S. Environmental Protection Agency relied heavily on a series of four tests conducted on five industrial wood waste boilers by the California Air Resources Board [CARB, 1990a – d]. Two of the tested boilers were characterized as "quad-cell wood-fired boilers"[CARB, 1990 a and d]. Both of these boilers burned only clean wood waste and sawdust and both had lower emissions (0.50 and 0.64 ng TEQ/kg of wood burned) than the average for the CARB tests, which was accepted by EPA as a reasonable emission factor [EPA/600/P-98/002Aa, April 1998]. Quad cells or fuel cells are now only rarely used in Canadian pulp mills for wood waste combustion as they are relatively inefficient in comparison to either a spreader-stoker grate fired boiler or a fluid bed boiler. Studies at one pulp mill on the British Columbia coast showed that dioxins production and emissions for two fuel cells firing salt laden hog fuel were approximately 8 times those for the larger spreader-stoker fired boiler at the same site.

In addition, the other three boilers tested in the CARB studies fired mixed wastes. The two spreader stoker boilers tested at an electrical utility (emission factor = 0.82 ng TEQ/kg of wood burned) fired a 70:30 mixture of wood waste and "urban wood waste" [CARB, 1990b]. The fluid bed boiler tested in the CARB studies (emission factor = 1.32 ng TEQ/kg of wood burned) also fired wood wastes (the nature and source of which was not clarified, at least in the EPA summary [EPA, 1998]) and "agricultural wastes allowed by existing permits" [EPA, 1998, CARB, 1990c]. The results of these tests should be viewed with suspicion as several researchers have shown that the combustion of "urban wood wastes" and wood-based product residues, such as plywood, hardboard or treated wood, produces much higher dioxin emissions than the combustion of clean "natural" wood or bark (see Table 2.1.1 later in this report). Nakao et al. [2002] have shown that the amount of dioxins formed in open-air incineration of wood scrap are 10 to 230 times greater than those formed in burning natural wood in a forest fire. Schatowitz et al. [1994] also showed that the combustion of waste wood chips from building demolition produced dioxin emissions that were 82 to 216 times those produced by burning natural wood chips or even uncoated chipboard chips in a wood furnace. Kolenda et al. [1994] showed that the combustion of plywood (hardened with $(NH_4)_2SO_4$, with or without a PVC coating) or plywood and untreated wood mixtures in seven large (>1 MW) wood burning facilities produced dioxin emissions 5 to 70 times those from combustion of untreated pine wood alone. Oehme and Muller [1995] also showed that burning waste wood treated with pentachlorophenol produced dioxin concentrations on the baghouse filter ash that were 10 to 100 times those observed when burning "natural" wood waste alone.

As the CARB studies on which EPA based their emission factor estimate were conducted on old inefficient fuel cells or on boilers burning mixed wastes including demolition wastes, treated wood, or wet agricultural wastes, it is likely that this emission factor would significantly overestimate the emissions from a relatively modern spreader-stoker fired boiler or fluid bed boiler firing only clean wood waste, such as hog fuel.

2.1.2 Emissions from Residential Wood Combustion:

Section 4.2 of EPA/600/P-98/002Aa [April 1998] provides an excellent summary of dioxin test results for both residential and industrial wood combustion up until 1996. A wide range of emissions and emission factors were noted in both sectors. For residential wood stoves, burning clean wood only, dioxin emissions ranged from 0.064 ng TEQ/dscm to 0.18 ng TEQ/dscm (dscm = dry standard cubic meters of gas; standard indicates that gas volumes and flows have been normalized to “standard conditions” of temperature (273 K) and pressure (101.325 kPA or 1 atmosphere)). The corresponding emission factors ranged from 0.77 ng TEQ/kg of dry wood to 1.9 ng TEQ/kg of dry wood. EPA subsequently recommended a rather conservative emission factor of 2 ng TEQ/kg of dry wood for residential wood combustion, based on the observation that a good percentage of the wood burned in homes is burned in fireplaces, rather than in more efficient wood stoves. More recent testing by Environment Canada [Report ERMD 2000-01, 2000] indicates that this emission factor is about 4 times too high for residential wood stoves and release estimates for this sector were subsequently substantially reduced using an emission factor of 0.5 ng TEQ/kg of wood.

2.1.3 Emissions from Industrial Wood Combustion:

For industrial wood combustion [EPA/600/P-98/002Aa, April 1998], the results of the four CARB studies (summarized earlier) and tests for 5 boilers burning bark and wood residues [NCASI, 1995] were reviewed. As the average emission factor for the boilers in the NCASI study (0.4 ng TEQ/kg of feed) was similar to that in the CARB studies, EPA again decided to use the more conservative emission factor estimate (0.82 ng TEQ/kg of wood). Since some of the units tested by NCASI were at wood products facilities, it is likely that their results may also have been skewed high due to the combustion of treated wood wastes.

The EPA report [1998] noted, based on tests by EPA on a three-cell dutch oven at a lumber products plant where all the wood was stored in salt water, that their proposed emission factor would not be appropriate for facilities burning wood waste containing high levels of chloride (see section 2.1.4). They also noted that tests by Umweltbundesamt [1996] on 30 facilities of varying designs and using different types of wood fuel, indicated elevated dioxin and furan emissions when combustion conditions were poor, as indicated by elevated carbon monoxide emissions, and/or when the fuel contained elevated chlorine or chloride concentrations. Chipboard, preservative-treated wood and PVC-coated wood were found to contain up to 0.2, 1.2 and 0.3 % chloride by weight, respectively, versus the 0.001 to 0.01 % chloride by weight typical in untreated wood and bark [EPA, 1998]. Typical emission levels reported from studies on wood fired boilers are summarized in Table 2.1.1. The elevated concentrations of chloride in several of the waste wood sources at least partially explain the higher levels of dioxin emissions observed when burning demolition wastes or treated wood versus natural or clean wood waste [Nakao et al., 2002, Schatowitz et al., 1994, Kolenda et al., 1994, and Oehme and Muller, 1995].

Table 2.1.1: Dioxin Emissions from Wood Waste Combustion

Literature Reference	Type of Combustor	Nature of Fuel	Dioxin Emissions, pg TEQ/dscm @ 11 % O_2	Emissions Factor, ng TEQ/kg of dry wood
Schatowitz, 1994	Automatic chip furnace Automatic chip furnace Automatic chip furnace Household stove	Wood chips Uncoated chipboard Demolition Waste Household waste	66 - 214 24 - 76 2,700 – 14,200 114,000	0.79 – 2.57 0.29 – 0.91 26 – 173.3 3,230,000
CARB, 1990 a-d	Quad cell Quad cell Spreader stoker Fluid bed boiler	Wood waste Wood waste Wood and urban wood waste Wood and agricultural wastes	116* 246* 246* 229*	0.50 0.64 0.82 1.32
NCASI,1995	Two coal burners and three spreader stokers	Wood wastes at various wood products facilities and pulp mills	0.4 – 281*	0.4
Kolenda, 1994	9.6 MW incinerator 9.6 MW incinerator 9.6 MW incinerator 39 MW grate incinerator	Pine wood Plywood residues Untreated wood and treated product residues Wood and coated plywood residues	3 – 5 2 – 210 25 110 – 150	
Zimmerman, 2001	1 MW pilot combustor	Wood waste - under good firing conditions Wood waste - under oxygen-deficient conditions	12 – 16 51 – 94	
Valttila, 1993	Fluid bed (65 – 84 MW) Stoker grate (47 MW) Circulating fluid bed (59 MW)	Bark and pulp mill sludge	140 – 390 1,090 710	
Maatila, 1992	60 MW district heating boiler	Bark and coal Bark, coal and chlorinated waste plastics	16.4 – 23 38 – 103	
Pandompatam, 1997	Batch type, three cell pilot incinerator	Aspen bark (0.007 % Cl) Aspen bark soaked in salt water (0.76 % Cl)	20 3,200	
EPA, 1998	Dutch oven boiler	Salt laden wood wastes		17.1

* at 12 % CO_2; see Appendix A

In contrast to many of the above studies, test burns on a power boiler at Northwood Pulp in Prince George, BC using a chlorophenol contaminated hog fuel indicated a high level of dioxin destruction [LC Engineering, April 1989]. The boiler was operated at a steam production rate of approximately 100 tonnes per hour or 60 % of the maximum rated capacity. Eight runs were completed in late September 1987. Two test runs were needed to develop the baseline (no chlorophenol injection), three for the condition where the fuel was spiked to a chlorophenol concentration of 57 ug/g of hog fuel and three for the condition where the chlorophenol concentration was 436 ug/g of hog fuel. All dioxins and furans were destroyed during the baseline and low chlorophenol spike conditions. While trace quantities of dioxins and furans were detected in the stack gases during the high spike condition trials, dioxin destruction efficiencies ranged from 99.9994 to 100 %. The need to assess destruction efficiencies when the boiler was operating closer to maximum rated capacity was, however, noted in the study.

2.1.4 Effect of Chlorides and Chlorine on Dioxin and Furan Emissions:

Pandompatom et al. [1997] at the Alberta Environmental Centre used a batch-type three-chamber incinerator to fire hogged bark with and without salt addition. Clean aspen bark, untreated except for sizing, was used as the control sample. The test sample was similar bark soaked in NaCl brine and then air dried to a moisture level comparable to the control sample. The chloride contents of the two hog samples were 0.007 and 0.76 % by weight on dry hog, respectively. The resulting dioxin and furan emissions were 0.02 and 3.2 ng TEQ/dscm, demonstrating the feasibility of using simulated salt-laden hog to examine the effects of hog chloride content on dioxin and furan emissions. Vesterinen and Flyktman [1996], in co-combustion of refuse derived fuel and wood chips in a 4 MW bubbling fluid bed boiler, found a clear relationship between fuel chlorine content and dioxin and furan concentrations in the flue gas. Halonen et al. [1993 a,b] in pilot scale work also found that the chlorine content of the fuel correlated well with dioxin and furan concentrations at high gas temperatures, ie. at the furnace exit, but the correlation disappeared as the gas temperature decreased. Maatila et al. [1992] similary found that dioxin and furan emissions from a 60 MW district heating boiler increased by a factor of 2 to 5 when chlorinated waste plastics were co-fired with coal and bark. In this study, dioxin and furan concentrations correlated better with the measured HCl levels in the flue gas than with chlorine concentrations in the fuel.

2.1.5 Effect of Co-firing Wastewater Treatment Plant Sludges:

Studies on the No.5 power boiler at Fletcher Challenge Canada's Elk Falls Pulp and Paper mill [Bovar-Concord Environmental, May 1994] showed that the disposal of waste water treatment plant sludges through incineration in the hog fuel power boiler caused no significant increases in most stack emissions at either normal or catch-up disposal rates. This boiler burned salt-laden hog fuel and had much higher dioxin emissions than normally seen for power boilers burning clean wood waste [Luthe et al., 1996]. A decline in stack emissions of dioxins and furans with increasing sludge firing rates was later found to be due to sulphur introduced with the waste water treatment plant sludges and a resulting reduction of the chloride/sulphur ratio in the blended biomass fuel [Luthe et al., 1996, Luthe et al., 1998b]. NCASI [1995] similarly showed lower dioxin and furan emissions for one facility firing clean wood waste and biosludges (0.001 ng TEQ/kg of feed) than the average emissions for the five boilers in the CARB [1990 a – d] study (0.82 ng TEQ/kg of feed).

Valttila [1993], on the other hand, found that when 5 – 14 % biosludge was burned with bark in three different types of pulp mill boilers, dioxin and furan emissions were higher than when bark alone was burned (see Table 2.1.1). He noted that burning up to 20 % sludge in the bubbling fluidized bed boiler did not result in any greater emissions than burning 5 - 14 % sludge, provided proper combustion conditions were maintained in the boiler. Valttila attributed the increases in dioxin and furan emissions for each boiler to the higher concentrations of chlorine or chloride in the sludges relative to bark.

The impact of sludges in general on boiler dioxin and furan emissions is likely to depend on the chloride, sulphur and moisture contents of the sludge relative to that of the wood waste. If the sludge chloride content is significantly higher than that in the wood waste, and the sludge sulphur content is not correspondingly high, it is likely to increase dioxin formation. Similarly, if the sludge is quite wet, it is likely to reduce the boiler combustion efficiency and increase the dioxin and furan formation potential.

2.2 Power Boilers Burning a Combination of Clean Wood-Waste (With or Without Wastewater Effluent Treatment Plant Sludges) and De-inking Process Sludges:

Douglas et al. [1997] reviewed the results of field trials on the burning of paper de-inking sludges (PDS) in a Canadian Biomass Fluid Bed attached to the number 4 stoker grate boiler at Avenor's (now Bowater's) Thunder Bay pulp mill. The ABB patented fluidized bed process incorporated a refractory-lined furnace chamber. For the purpose of heat recovery, flue gases from the combustor were ducted to the number 4 boiler through the boiler ashpit. The authors noted that while mechanical dewatering can reduce the moisture content of PDS to 40 – 60 %, the high inert content of these materials make them difficult to burn on conventional stoker grates. Three sets of emission tests completed on the number 4 power boiler stack, while up to 4 tph of PDS were burned in the attached Biomass Fluid Bed, showed dioxin and furan emissions of 2.2, 70.3 and 2.7 pg TEQ/dscm at 11% O_2. Corresponding PAH emissions (total emissions of 25 PAH compounds analysed) in the three tests were 15.7, 24.1 and 5.0 ug/dscm at 11 % O_2. The high dioxin emissions in the second test were attributed to low fluid bed temperatures and combustor trips an hour before the test started and a half hour before the stack test was completed.

2.3 Recovery Boilers Burning Black Liquor:

McCubbin [1997] prepared a very comprehensive review of the literature and available data on dioxin and furan emissions from kraft mill chemical recovery boilers for the U. S. EPA. It included data compiled by both NCASI and Paprican, as well as several literature references to dioxin tests on full scale recovery boiler stacks or on electrostatic precipitator catch ash samples. Data complied by NCASI for tests on 13 recovery boilers showed average dioxin and furan emissions of 23 pg TEQ/dscm, even when a very high test result (432 pg TEQ/dscm) was included in the data set. NCASI suggested rejecting that particular test because the results failed to pass quality control verification tests in the analytical laboratory. NCASI also suggested disregarding all the tests for the particular mill (mill A in Appendix D) because they were statistical outliers (see the note on page D-1 in Appendix

D). At the other 12 mills, dioxin and furan emissions ranged from zero to 27.2 pg TEQ/dscm. Similarly, tests on two coastal B. C. recovery boilers, firing black liquors with very high chloride content (as high as 5.4 % on dry black liquor solids), showed dioxin and furan emissions between 0.38 and 5.2 pg TEQ/dscm at 11 % O_2 [Luthe et al., 1997a].

Bostrom [1990] reported on dioxin tests on the number 8 recovery boiler at the MoDo paper mill in Husum , Sweden. The concentrate from a bleach plant ultra filtration system, treating first stage caustic extraction stage effluent, was burned with the black liquor in this mill. Two stack test showed maximum dioxin emissions of 9 – 15 pg TEQ/dscm [Bodein, 1997], “lower than the levels measured on the same boiler in 1985 when no bleach plant residues were burned”.
Using all the available data at the time of the study, McCubbin [1997] concluded that changes in the chloride concentration of black liquor that might result from foreseeable changes in mill operations, related to systems closure, will not lead to increases in emissions of PCDD/F from recovery boilers. He also concluded that there was no evidence of a systematic difference in PCDD/F emissions between older direct contact evaporator equipped recovery boilers and newer non-direct contact or “low odour” recovery boilers.

2.4 Lime Kilns Fired With Natural Gas and/or Heavy Fuel Oil:

There is no data available in the open literature on dioxin and furan emissions from lime kilns at pulp and paper mills. The data that is available on dioxin and furan emissions from cement kilns must be regarded with suspicion as many of these kilns supplement their fuel with organic industrial wastes and compete with incinerators in the hazardous waste disposal sector. Many of the wastes used in cement kilns may contain either chlorides or metals, such as copper, which catalyses dioxin formation. The lime mud (CaCO3) fed to lime kilns in the pulp and paper industry is, by contrast, substantially free of any organic contaminants, as even small amounts of such contaminants in condensates used for mud washing can reduce mud settling rates and the mud solids concentrations fed to the kiln. Low mud solids result in high kiln energy usage and most mills consequently monitor condensate quality and mud solids content carefully. While some mills have looked at the possibility of using coal or tire derived fuel (TDF) in their lime kilns, all Canadian pulp and paper mill lime kilns currently use only natural gas, heavy fuel oil or tall oil as a fuel source. Some data from tests on 4 lime kilns at U. S. mills will be reviewed in the next section of this report.

2.5 Smelt Dissolving Tanks:

There is no data available in the open literature on dioxin and furan emissions from smelt dissolving tanks. As dioxin emissions from recovery boilers are generally quite low, 0.5 – 10 pg TEQ/dscm [Luthe, 1995; McCubbin, 1997] and smelt from the recovery boiler is rapidly quenched from 700 – 800 C to less than 100 C in the dissolving tank, formation of dioxins via de novo synthesis is expected to be negligible. Some data on the dioxin and furan concentrations on green liquor dregs (the suspended solids removed from the green liquor exiting the dissolving tank) will be reviewed in the next section of this report and used to estimate potential emission factors for this unit operation.

2.6 Sulphite Process Recovery Boilers:

There is no data available in the open literature on dioxin and furan emissions from sulphite recovery boilers. As sulphur dioxide concentrations are exceedingly high in sulphite recovery boilers, and sulphur dioxide has been shown to attenuate dioxins formation in power boilers burning salt-laden hog fuel [Luthe, 1998b], in kraft chemical recovery boilers burning black liquor contaminated with high concentrations of sodium chloride [Luthe, 1995; McCubbin, 1997] and in municipal waste incinerators [Griffin, 1994, Lindbauer, 1992, Frankenhaeuser, 1994], dioxin and furan emissions from sulphite recovery boilers are likely to be very low. Some data from tests on 2 sulphite recovery boilers in the U.S., compiled by NCASI, will be reviewed in the next section of this report.

3. Review of Stack Test Results and Development of Emission Factors:

Both the United States and Canada have regulatory programs with requirements for annual reporting by industrial facilities of the emissions of certain substances to the environment. The U.S. program is commonly known as TRI (Toxic Release Inventory) while the Canadian program is the National Pollutant Release Inventory (NPRI). The two programs have many similar features, due in part to environmental provisions contained in the North American Free Trade Agreement (NAFTA). However, there are some important differences. In the area of dioxin and furan emissions, NPRI releases are to be reported in toxic equivalents using the International Toxicity Equivalency Factors (ITEQ), which range from 0.001 to 1 for the 17 congeners that must be measured under both NPRI and TRI guidelines (see Table 3.1). Environment Canada has specified a level of quantification (LOQ) of 32 pg TEQ/dscm for gaseous streams. When measurements are below this value, a facility has the option of reporting the measured value or that the measured release is less than the LOQ. In addition, if a facility has no information at all, it may indicate this on the reporting form and not provide release or transfer estimates.

In the TRI program, the reporting threshold is 0.1 g/y, based on the total of the 17 analysed congeners, not in TEQs. Because NPRI releases are reported in ITEQ units, and TRI releases are reported as the total of the 17 congeners, reported emissions will be much lower for Canadian mills. Using emission data for 11 kraft recovery boilers, the National Council for Air and Stream Improvement (NCASI) in the U. S. has estimated [Pinkerton, 2001] that the emissions expressed in ITEQ units are less than 3 % of the total for the 17 congeners. Because much of the data on dioxin and furan emissions from pulp and paper sources, that is available, was compiled by NCASI, we have appended the raw data to this report, allowing readers to check the emissions of any given congener or to covert emissions using other toxicity equivalency guidelines, such as those from the World Health Organization (WHO).

The data compiled in the appendices attached to this report were collected by independent certified, stack testing contractors working at each facility. Stack testing was done in accordance with EPA Method 23 or Environment Canada “Reference Method for Source Testing: Measurement of Releases of Selected Semi-Volatile Organic Compounds from Stationary Sources, EPS 1/RM/2, June 1989. Each sampling run was typically 3 or 4 hours long. Quality assurance and quality control (QA/QC) evaluation of the PCDD/F data was based on three sets of analyses: (1) recoveries from pre-spike standards prior to sampling;

(2) analysis of laboratory control samples for the 17 PCDD/F isomers listed in EPA Method 23; and (3) analysis of field and trip blank samples for PCDD/Fs. All samples and tests, except those for Mill RFA in Appendix D (see page D-1), met the pre-test QA/QC criteria. In all cases, the concentrations for non-detect congeners were set equal to zero as currently recommended by EPA for sources with very low emissions. In determining averages and medians for a given unit operation, the averages for each series of tests on a given boiler or kiln were used. If more than one boiler was tested at a given mill, the results for each boiler were included in the determination of average and median emissions. The averages for a boiler with 8 stack tests were, however, given no more weighting than those for a boiler with only one or two tests.

3.1 Power Boilers Burning Clean Wood-Waste (With or Without Wastewater Effluent Treatment Plant Sludges):

As dioxin and furan emissions from power boilers burning clean wood waste can vary dramatically due to co-firing of wood product residues, plywood or even agricultural wastes (see Table 2.1.1), only emission data for wood waste power boilers at pulp and paper facilities will be used to estimate a suitable emission factor for these boilers. Appendix A contains dioxin and furan emission data, compiled by NCASI for the four non-pulp and paper boilers in the CARB studies [1990a – d] and for 21 tests on 10 pulp and paper industry boilers in the U. S. As NCASI did not have data on the boiler firing rates, but did have accurate flue gas flow rate data, they have estimated the hog firing rate by assuming a wood heating value and a flue gas flow per million BTU of input heat, corrected to 12 % CO_2. All 10 boilers were equipped with multiclones for particulate emission control. Three of the boilers were also equipped with dry electrostatic precipitators (ESP), four with wet scrubbers and one with a wet scrubber followed by a wet ESP. Two had only multiclones for PM control. While the four boilers with wet scrubbers generally had lower dioxin and furan emissions, NCASI researchers found it difficult to conclude that the final PM control device had any effect on the total PCDD/F emissions, because of the wide range of emissions for a given boiler and between boilers.

Table 3.1: Dioxin and Furan Congeners Included in the NPRI Dioxins/Furans Group

Compound	*TEF*
2,3,7,8-tetrachlorodibenzo-*p*-dioxin	1.0
1,2,3,7,8-pentachlorodibenzo-*p*-dioxin	0.5
1,2,3,4,7,8-hexachlorodibenzo-*p*-dioxin	0.1
1,2,3,6,7,8-hexachlorodibenzo-*p*-dioxin	0.1
1,2,3,7,8,9-hexachlorodibenzo-*p*-dioxin	0.1
1,2,3,4,6,7,8-heptachlorodibenzo-*p*-dioxin	0.01
Octachlorodibenzo-*p*-dioxin	0.001
2,3,7,8-tetrachlorodibenzofuran	0.1
1,2,3,7,8-pentachlorodibenzofuran	0.05
2,3,4,7,8-pentachlorodibenzofuran	0.5
1,2,3,4,7,8-hexachlorodibenzofuran	0.1
1,2,3,6,7,8-hexachlorodibenzofuran	0.1
1,2,3,7,8,9-hexachlorodibenzofuran	0.1
2,3,4,6,7,8-hexachlorodibenzofuran	0.1
1,2,3,4,6,7,8-heptachlorodibenzofuran	0.01
1,2,3,4,7,8,9-heptachlorodibenzofuran	0.01
Octachlorodibenzofuran	0.001

Appendix B contains dioxin and furan emission data, compiled by Paprican, for 16 tests on 5 additional Canadian pulp and paper industry boilers. The mills in this data set provided Paprican with estimates of the hog firing rates based on the amount of steam produced from hog fuel during each stack test or average hog firing rates for each boiler. As most of these tests were done during permit compliance testing and the boilers are required to operate at 85 % or better of their typical loading during compliance testing, the average hog firing rates should reasonably approximate the firing rates during the stack tests. The data compiled by Paprican is normalized to 8 % O_2 as this is the standard in many provincial permits for combustion sources. We have assumed that emissions at 12 % CO_2 in NCASI's data base are comparable to those at 8 % O_2 in Paprican's data base. In both data sets, the concentrations of non-detect congeners were set equal to zero as currently recommended by EPA. Both sets of data are summarized in Table 3.2.

Table 3.2: Dioxin and Furan Emission Data for Pulp and Paper Industry Wood Waste Boilers

	In NCASI's Data Set	In Paprican's Data Set	For the Combine Data Set
Number of Boilers Tested	10	5	15
Total Number of Stack Tests	21	16	37
Stack Emissions, pg TEQ/dscm*			
Range	0.4 – 339.2	0.8 – 86.5	0.4 – 339.2
Average	81.5	20.2	58.5
Median	3.7	5.7	4.7
Estimated Emission Factor, ng TEQ/BDt of hog			
Range	3.3 – 2799	10.2 – 247.3	3.3 – 2799
Average	672	84.2	451.6
Median	30.4	46.6	38.5

* at 12 % CO_2 for the NCASI data set and at 8 % O_2 for the Paprican data set

Only four of the 10 boilers in NCASI's data set (see page A–17), and only one of the five boilers in Paprican's data set (see page B-7), had average dioxin and furan emissions exceeding Environment Canada's LOQ of 32 pg TEQ/dscm. In addition, the second test on wood fired boiler G (WFBG) in NCASI's data set gave dioxin and furan emissions that were a factor of 10 lower than those observed in test 1, suggesting that either very poor combustion conditions existed during the first test or that treated wood or processed wood residues (plywood, chipboard, fibreboard, etc.) may have been burned during the first test. Only 2 of the 16 stack tests on the five boilers at Canadian mills in Paprican's data set showed dioxin emissions that were marginally greater than the average emission (81.5 pg TEQ/dscm) for the power boilers in the NCASI data set. This strongly suggests that treated wood or wood product wastes were likely burned in many of the wood waste boilers in NCASI's data set.

It should be noted that one high or low test result can significantly skew the average of a small data set, as evidenced by the large differences between the average and median test results in both data sets. If the results for boiler G in NCASI's data set are disregarded, the average stack emission drops by 35 %, from 81.5 to 52.9 pg TEQ/dscm, and the average emission factor for the NCASI data set drops from 672 to 435.7 ng TEQ/BDt of hog. Similarly, if the single highest test result (test 2 at Mill D) is excluded from Paprican's data set, the average emission factor for the five boilers in Paprican's data set drops by 13 %, from 84.2 to 73.3 ng TEQ/BDt of hog fuel. Since the median stack emissions and emission factors are much closer than the averages in the two data sets, use of an emission factor close to the mean emission factor of 38.5 ng/BD tonne of hog fuel burned is recommended to estimate dioxin and furan emissions from this source.

3.2 Power Boilers Burning a Combination of Clean Wood-Waste (With or Without Wastewater Effluent Treatment Plant Sludges) and De-inking Process Sludges:

Appendix C contains dioxin and furan emission data, compiled by Paprican, for 21 tests on all 5 of the Canadian pulp and paper industry boilers that burn de-inking sludge. The coding for the boilers in Appendices B and C are identical, allowing the reader to compare boiler emissions with and without the co-firing of de-inking sludges. The mills in this data set again provided Paprican with estimates of the hog firing rates based on the amount of steam produced from hog fuel during each stack test or average hog firing rates for each boiler. As most of these tests were done during permit compliance testing and the boilers are required to operate at 85 % or better of their typical loading during compliance testing, the average hog firing rates should reasonably approximate the firing rates during the stack tests.

Mill O (see page C-10) has been excluded from the summary table and data set because we could not find a reasonable way to appropriate the dioxin emissions measured for the power boiler stack. The mill has four power boilers discharging through one common stack. One (30,000 lbs/hr maximum steam production capacity) burns wood waste. Two (each producing up to 60,000 lbs/hr of steam) burn only coal. The fourth and largest (165,000 lbs/hr maximum steam production) burns coal and sludge from both the de-inking process and the waste water treatment plant. The mill conducted one stack test when there was no de-inking sludge fired (5.6 pg TEQ/dscm) and two tests when firing deinking sludge (average emission- 22.3 pg TEQ/dscm). The mill burnt 3.9 to 10 BDMT per day of bark, 31.1 to 33.3 BDMT per day of wastewater treatment plant sludges, 1.8 to 28.5 BDMT per day of de-inking plant sludge and 44.4 to 120.4 ADMT per day of coal during the three stack tests. The better than 3 fold increase in dioxin emissions when firing deinking sludge is consistent with the data for the other mills (compare test results for mills C and E on pages B-7 and C-9). Since the amount of hog fired in the four boilers at Mill O was relatively small, however, and we could not reasonably allocate the proportion of dioxins produced from hog, sludges and coal, we decided to drop the mill from the averaging exercise.

Stack dioxin emissions increased significantly in power boilers burning de-inking sludge (compare test results for mills C and E in Table 3.3 and for Mill O on page C-10). This is consistent with reports that while mechanical dewatering can reduce the moisture content of de-inking sludge to 40 – 60 %, the high inert content of these materials make them difficult to burn on conventional stoker grates [Douglas, 1997]. De-inking sludges have also been found to contain a number of metals and chlorine compounds [Douglas, 1997] that can catalyse dioxin and furan formation during combustion. When co-firing de-inking sludge, average stack dioxin emissions at the 4 mills ranged from 15.9 to 182 pg TEQ/dscm at 8 % O_2 in the 20 stack tests. Average and median stack emissions for the 4 boilers were 87.9 and 76.9 pg TEQ/dscm at 8 % O_2. When co-firing de-inking sludges, average emission factors for the four boilers ranged from 118 to 1576 ng TEQ/BD tonne of hog fuel. Average and median emissions for the four boilers tested were 791 and 735 ng TEQ/BD tonne of hog fuel, respectively. Use of the median emission factor of 735 ng TEQ/BD tonne of hog fuel is recommended to estimate dioxin and furan emissions from this source.

3.3 Recovery Boilers Burning Black Liquor:

Appendix D contains dioxin and furan emission data, complied by NCASI, for 36 stack tests on 11 chemical recovery boilers in 11 kraft mills in the U. S. As NCASI did not have data on the boiler firing rates, but did have accurate flue gas flow rate data, they have estimated the black liquor firing rate by assuming a liquor heating value and a flue gas flow per million BTU of input heat (see page D-10). Appendix E contains dioxin and furan emission data, compiled by Paprican, for 9 tests on 2 chemical recovery boilers at two British Columbia coastal kraft mills. The mills in this data set provided Paprican with estimates of the liquor firing rates from their normally logged data on liquor flow and fired liquor solids content. Both sets of data are summarized in Table 3.3.

Average dioxin emissions never exceeded Environment Canada's LOQ for any of the thirteen recovery boilers tested and included in the two data sets (see page D-1). Based on the data summarized in Table 3.3, the median emission factor of 0.015 ng/kg of dry fired black liquor solids (0.0068 ng TEQ/lb of dry BLS fired), calculated for the combined data sets, is recommended to estimate dioxin and furan emissions from this source. The proposed emission factor is about half of the emission factor of 0.028 ng TEQ/kg of dry black liquor solids recommended for use by EPA [1998]. Even the average emission factor for the two data sets is about 30 % lower than that recommended by EPA [1998].

Table 3.3: Stack Dioxin and Furan Emissions Tests on Power Boilers With and Without Burning of De-inking Process Sludges

Mill	Type of Furnace	Fuel Mix	Particulate Control System	Number of Tests	Range of Stack Particulate Emissions (Average) mg/Rm^3 @ 11% O_2	Range of Stack Dioxins Emissions (Average) pg TEQ/Rm^3 @ 8% O_2	Emission Factor ng TEQ/BDt of hog (ng TEQ/t wet hog) low/high/avg	Emission Factor ng TEQ/BDt hog & sludge (ng/wet tonne) low/high/avg.	Fuel Firing Rates BDtph (moisture content)
C – does not normally burn deinking sludge	Riley Stoker travelling grate	Hog & gas (1996)	ESP	5 (on 2 boilers)	3.1 – 47.9 (averages for each boiler)	4.9 – 6.5 (5.7) (averages for each boiler)	40.0 / 53.1 / 46.6 (19.2 / 30.2 / 24.4)	40.0 / 53.1 / 46.6 (19.2 / 30.2 / 24.4)	10.4 – 10.8 hog (43 - 52 %)
		Hog, primary, secondary and deink sludge & gas		3 (on 1 boilers)	1.4 - 21.0	10.8 – 19.1 (15.9)	79.9 / 141.4 / 117.7 (38.3 / 80.6 / 67.1)	73.8 / 132.2/ 110.0 (34.9 / 72.9 / 61.1)	10.2 – 10.5 hog (43 – 52%) 0.75 deink (35%)
E – no longer burns deinking sludge	Stoker (PB #1)	Hog & deink sludge (1997)	Venturi scrubber	3	44.8 – 89.3 (74.0)	47.2 – 280.2 (182.1)	408.5 / 2425.0 / 1576.0 (183.8 / 1091.3 / 709.2)	389.6 / 2312.8 / 1503.1 (177.2 / 1053.3 / 684.6)	18.6 hog (55%), 0.9 deink (41%)
	Stoker (PB #2)	Hog & effluent sludge (1999)	2-stage multiclone plus an ESP	3	3.2 – 7.1 (4.7)	2.2 – 9.2 (6.5)	35.7 / 149.3 / 105.5 (16.1 / 74.7 / 50.2)	30.7 / 128.3 / 90.7 (13.1 / 60.5 / 40.7)	31.25 Bark (50%) 3.8 Primary sludge (65%) 1.3 Secondary sludge (65%)
F	Stoker boiler with vibrating grate	Bark/hog , primary, secondary and deinking sludges	ESP	5	27 – 41 (32)	23.4 – 266.4 (108.2)	204.2 / 2325 / 944.4 (102.1 / 1162.6 / 472.2)	139.8 / 1589.2 / 646.5 (63.4 / 724.2 / 293.2)	13.5 Bark (50%) 3.75 Deink (58.1%) 2.5 P&S Sludge (66.1%)
G	3 KMW combustors into three Renteck boilers (1999)	Hog , primary, secondary and deink sludges	Cyclones on each boiler to common ESP	3	(7.6)	2.3 – 111.4 (40.4)	26.5 / 1281.1 / 464.7 (13.0 / 630.4 / 228.7)	21.0 / 1015.1 / 368.2 (9.8 / 474.3 / 172.0)	12.4 Hog (50.8%) 3.25 Sludge (60.2%) 29 % deinking sludge
	3 Fuel Cells (1997) – now burn only gas	Hog, primary, secondary and deinking sludges & gas	Multiclones	6	717 – 942	7.2 – 142.8 (50.8)	82.9 / 1643.6 / 584.7 (39.7 / 639.6 / 227.5)	65.8 / 1345.0 / 471.4 (28.1 / 495.0 / 90.5)	5.2 – 8.3 Hog (51.9 – 61.1%) 1.4 – 1.9 Sludge (70.4%) – 33 % deink

- Average emission factor for mills burning deinking sludges (20 tests on 5 boiler stacks) = 790.7 ng TEQ/BD tonne of hog fuel burned.
  Median emission factor for mills burning deinking sludges (20 tests on 5 boiler stacks) = 734.5 ng TEQ/BD tonne of hog fuel burned.

Table 3.4: Dioxin and Furan Emission Data* for Kraft Chemical Recovery Boilers

	In NCASI's Data Set	In Paprican's Data Set	For the Combined Data Set
Number of Boilers Tested	11	2	13
Total Number of Stack Tests	36	9	45
Stack Emissions, pg TEQ/dscm*			
Range	0.016 – 10	4 - 6	0.016 – 10
Average	3.3	5.0	3.6
Median	2.3	5.0	2.6
Estimated Emission Factor, Ng/kg of BLS			
Range	8.7×10^{-5} – 0.055	0.022 – 0.033	8.7×10^{-5} – 0.055
Average	0.018	0.028	0.020
Median	0.013	0.028	0.015

* at 8 % O_2 for both the NCASI data and Paprican data sets

3.4 Lime Kilns Fired With Natural Gas and/or Heavy Fuel Oil:

Appendix F contains dioxin and furan emission data, complied by NCASI, for 6 stack tests on 4 lime kilns at 4 kraft mills in the U. S. As NCASI did not have data on the kiln production rates, but did have accurate flue gas flow rate data, they have estimated the kiln production rate by assuming a required heat input of 6 million BTU for the calcination of one tonne of lime and respective flue gas flow rates per million BTU of input heat for both gas and oil. Three oil-fired kilns and one gas-fired kiln were tested. While the dioxin and furan emissions from the gas-fired kiln were about 50 % higher than those from any of the oil-fired kilns (see page F-4), one set of tests is insufficient to set a separate emission factor for gas-fired kilns. As expected, dioxin and furan emissions were very low in all the tests. Stack emissions ranged from zero to 3.3 pg TEQ/dscm at 12 % CO_2 in the 4 tested facilities and never exceeded Environment Canada's LOQ. Estimated emission factors ranged from zero to 17.5 ng TEQ/tonne of lime (CaO) produced (see page F-5), significantly lower that the emission factor of 290 ng/tonne of product recommended by EPA for cement kilns not burning hazardous waste [EPA/600/P-98/002Aa, April 1998]. Average and median emission factors were estimated at 8.9 and 9.1 ng TEQ/tonne of product lime. An emission factor of 9 ng TEQ/tonne of product lime is, therefore, recommended to estimate emissions from this source.

3.4 Smelt Dissolving Tanks:

There is no data available in the open literature on dioxin and furan emissions from smelt dissolving tanks. Dioxin emissions from recovery boilers are generally quite low, 0.016 – 10 pg TEQ/dscm (see Table 3.3 above). As smelt from the recovery boiler is rapidly quenched from 700 – 800 C to less than 100 C in a dissolving tank, eliminating the possibility of forming dioxins and furans by de novo synthesis in the 200 – 500 C temperature range, dioxin emissions from the dissolving tank vent would be expected to be even lower than those from the recovery boiler stack. Dioxin and furan concentrations on two raw (unclarified) green liquor samples and on one green liquor dregs sample (the suspended solids removed from the green liquor exiting the dissolving tank) are reviewed in Appendix G and used to estimate potential emission factors for this unit operation. Estimated vent stack emissions, using this very limited data set, range from 0.0072 to 1.08

pg TEQ/dscm, far below Environment Canada's LOQ of 32 pg TEQ/dscm. Estimated emission factors range from 3.6 to 540.6 pg TEQ/t of dry fired black liquor solids (DBLS). The maximum estimated emission factor of 550 pg TEQ/t DBLS or 0.00055 ng/kg of dry fired black liquor solids is, therefore, a factor of 36 lower than the emission factor estimated for kraft chemical recovery boilers in section 3.3 above.

3.5 Sulphite Process Recovery Boilers:

Appendix H contains dioxin and furan emission data, compiled by NCASI, for 5 stack tests on 2 sulphite recovery boilers in the U. S. For both of these boilers, NCASI had liquor firing rate data and was , therefore, able to estimate emission factors directly from the flue gas flow rate and PCDD/F concentrations. As sulphur dioxide concentrations are exceedingly high in sulphite recovery boilers, and sulphur dioxide has been shown to attenuate dioxins formation in power boilers burning salt laden hog fuel [Luthe, 1998b], in kraft chemical recovery boilers burning black liquor contaminated with high concentrations of sodium chloride [Luthe, 1995; McCubbin, 1997] and in municipal waste incinerators [Griffin, 1994, Lindbauer, 1992, Frankenhaeuser, 1994], dioxin and furan emissions from sulphite recovery boilers would be expected to be very low.

As expected, dioxin and furan emissions were very low in all the tests. Stack emissions ranged from 0.18 to 0.41 pg TEQ/dscm at 8 % O_2, and averaged 0.21 pg TEQ/dscm at 8 % O_2 in the two tested facilities. Estimated emission factors ranged from 0.00043 to 0.00053 ng TEQ/kg of fired red liquor solids. The average or mean emission factor was estimated at 0.00049 ng TEQ/kg of fired red liquor solids and an emission factor of 0.0005 ng TEQ/kg of fired red liquor solids is, therefore, recommended to estimate dioxin and furan emissions from this source.

4. Review of Power Boiler Ash Analyses and Development of Emission Factors:

As dioxin and furan emissions from power boilers burning clean wood waste can vary dramatically due to co-firing of wood product residues, plywood or even agricultural wastes (see Table 2.1), only emission data for wood waste power boilers at pulp and paper facilities should be used to estimate a suitable emission factor for these boilers. Appendix I contains dioxin and furan analyses, compiled by NCASI, for 63 ash samples taken from 27 different wood waste incinerators. Unfortunately, several of these incinerators were at wood processing plants, such as plywood mills, and may have burned wood residues in addition to clean wood (see section 3.1 above).

The first column under each sample (<ppt) shows the detection limit for each congener while the second column shows the concentrations of only those congeners which exceeded the detection limit in each ash sample. The toxic equivalents for all of the detected congers in each ash sample, as calculated using both the International Toxic Equivalency Factors (I-TEF) and the World Health Organization (WHO) Toxicity Equivalency Factors (TEF) are shown on the bottom two lines for each ash sample.

Two primary types of ash samples were collected at the different facilities:

Flyash – comprised of lightweight wood ash, salt, fine sand and partially burned residues, which are carried up with the combustion air, emitted from the furnace cavity and captured on heat transfer surfaces or by particulate emission control equipment. Flyash was broken down according to the type of particulate control device used to remove it from the flue gas – an electrostatic precipitator (ESP), a wet scrubber, or a multiclone (cyclone). In some cases, the collection system did not permit sampling of the particulate removed by each device and a only a combined flyash sample was available for analysis.

Bottom or grate ash – composed of coarse material, such as gravel and rocks from the incoming wood waste or hog fuel, and the ash residue from combustion, collected from the bottom of the boiler.

The NCASI data set contains grate ash analyses for 7 different wood waste burners, multiclone ash analyses for 22 different wood waste incinerators, and ESP, scrubber or combined flyash analyses for 16 different wood waste incinerators. As illustrated in Table 4.1, both the mean and median dioxin concentrations in the ash increased as the gas flowed through the boiler. Median concentrations increased from 0.02 pg TEQ/g for grate ash to 0.10 pg TEQ/g for multiclone ash to 1.47 pg/g for ESP, scrubber or combined flyash. A similar pattern was reported for power boilers burning salt-laden hog fuel [Luthe et al., 1996]. Unfortunately, several of the incinerators in the NCASI data set were at wood processing plants, such as plywood mills, and may have burned wood residues in addition to clean wood, which would result in higher dioxin and furan formation than that resulting from burning clean wood waste alone (see Table 2.1 and section 3.1 above).

Appendix J contains dioxin and furan analyses for 23 ash samples from 9 wood waste incinerators at Canadian forest product plants and pulp and paper mills, as compiled by Paprican, FPAC, AIFQ and AFPA. Only clean, raw wood waste, and no processed wood waste, was burnt in these facilities. The Canadian data set contains no data for grate ash and data for multicyclone ash from only one power boiler. While the median and mean concentrations of dioxins on flyash are much lower than the corresponding medians and means for the NCASI data set, the average for the multicyclone ash is much higher in the Canadian data set because multiclone ash from only one boiler was analysed.

Both sets of data are summarized in Appendix K and Table 4.1 below. Because of the lack of multiclone and grate ash samples in the Canadian data set, it is necessary to use the combined data set to obtain reasonable estimates of the emission factors for each type of ash. Again, these estimates are likely to be very conservative and safe as several of the incinerators in the NCASI data set were at wood processing plants, such as plywood mills, and may have burned wood residues in addition to clean wood. The median concentrations for the combined data set are, therefore, recommended for use in estimating dioxin and furan concentrations on landfilled boiler ashes.

Table 4.1: Summary of Power Boiler and Wood Waste Boiler Ash Dioxin and Furan Analysis

Data Source	Type of Ash	Number of Samples	Number of Facilities Tested	Minimum pg TEQ/g	Maximum pg TEQ/g	Mean pg TEQ/g	Median pg TEQ/g
NCASI	ESP/WS or combined MC/ESP - scrubber Ash	24	16	0.0	29.4	7.72	1.47
	Multiclone Ash	29	22	0.0	11.2	1.04	0.10
	Grate (Bottom) Ash	10	7	0.0	0.17	0.05	0.02
Paprican, FPAC, AIFQ and AFPA	ESP/WS or combined MC/ESP - scrubber Ash	19	8	0.0	3.65	0.62	0.20
	Multiclone Ash	4	1	0.0	3.93	1.84	1.72
Both data sets	ESP/WS or combined MC/ESP - scrubber Ash	43	24	0.0	29.4	5.35	0.46
	Multiclone Ash	33	23	0.0	11.2	1.07	0.10
	Grate (Bottom) Ash	10	7	0.0	0.17	0.05	0.02

If the total dioxin and furan emissions with ash need to be estimated for a boiler, the quantity of each type of ash generated can be measured either volumetrically or gravimetrically on several consecutive operating days. In the absence of measured data, the quantities of each type of ash can be estimated using data that Paprican has collected for power boilers burning salt-laden hog fuel. As both the ash and moisture content of salt-laden hog fuel is typically higher than that for interior, clean wood waste, these ash estimates are also very conservative. The quantities of ash from coastal power boilers burning salt-laden hog fuel are typically:

- 15 – 20 kg of grate ash/BD tonne of hog fuel burnt
- 12 – 16 kg of multicyclone ash/BD tonne of hog fuel burnt
- 18 – 41 kg of ESP or scrubber ash/BD tonne of hog fuel burnt

5. Conclusions:

Based on a review of the literature and emission data compiled by both NCASI and Paprican, the following emission factors are recommended to estimate stack dioxin and furan emissions from pulp mill combustion processes:

- For power boilers burning clean wood-waste (with or without wastewater effluent treatment plant sludges) – 40 ng TEQ/BDt of hog fuel burned.
- For power boilers burning a combination of clean wood-waste (with or without wastewater effluent treatment plant sludges) and de-inking process sludges – 750 ng TEQ/BDt of hog fuel burned.
- For kraft chemical recovery boilers burning black liquor – 15 ng TEQ/tonne of dry fired black liquor solids.
- For lime kilns fired with either natural gas and/or heavy fuel oil – 9 ng TEQ/tonne of product lime.
- For kraft mill smelt dissolving tanks – 0.55 ng TEQ/tonne of dry fired black liquor solids.
- For sulphite process recovery boilers – 0.5 ng TEQ/tonne of fired red liquor solids.

The concentrations of dioxins and furans on ashes from power boilers burning clean wood-waste (with or without wastewater treatment plant sludges), estimated from the medians for 76 ash samples from 54 different facilities, as compiled by both NCASI and Paprican, are :

- 0.02 pg TEQ/g for grate or bottom ash

- 0.10 pg TEQ /g for multicyclone ash
- 0.46 pg TEQ/g for ESP, scrubber or combined flyash

The amount of each type of ash can be estimated, in the absence of measured data, using data compiled by Paprican for coastal power boilers burning salt-laden hog fuel:

- 15 – 20 kg of grate ash/BD tonne of hog fuel burnt
- 12 – 16 kg of multicyclone ash/BD tonne of hog fuel burnt
- 18 – 41 kg of ESP or scrubber ash/BD tonne of hog fuel burnt

6. Acknowledgements:

The authors would like to thank all of the mills who generously provided both emission test data, operating data and ash analyses. Thanks also to Tim Whitford of ET Consulting, Louis Desilets of AIFQ, and Lucie Veilleux of FPAC who helped track down all of the Canadian mills that had dioxin emission test data and boiler ash analyses. Thanks to Arun Someshwar and John Pinkerton at NCASI who agreed to share the emission data and ash analyses compiled by NCASI for emission tests at pulp mills and wood processing facilities in the United States. Thanks finally to Environment Canada who provided funding which allowed us to compile and review all of the emission data and recommend scientifically-defensible emission factors for pulp and paper mill combustion sources.

7. Literature References:

Bodein, D., “Report concerning measurements in flue gas from recovery boiler 8 in Husum. Translation from Swedish, with supplementary calculations.” Report prepared by IVL (Bostrom, C., 1990) for MoDo (owners of the Husum mill). (1997).

Bostrom, C., “Report concerning measurements in flue gas from recovery boiler 8 in Husum.” Report prepared by IVL, Goteburg, Sweden. Original in Swedish, (1990) - refer to translation by Bodein.

Bovar-Concord Environmental, “Evaluation of Stack Emissions and Waste Streams from the Combined Burning of Pulp Mill Waste Residues and Hog Fuel in a Power Boiler”, prepared for Fletcher Challenge Canada Ltd. and Environment Canada (May 1994).

CARB (California Air Resources Board), Evaluation of a woodwaste fired incinerator at Koopers Company, Oroville, California. Test Report No. C-88-065. Engineering Evaluation Branch, Monitoring and Laboratory Division. (May 29, 1990a).

CARB (California Air Resources Board), Evaluation of a wood waste fired incinerator at Pacific Oroville Power Inc. Test Report No. C-88-050. Engineering Evaluation Branch, Monitoring and Laboratory Division. (May 29, 1990b).

CARB (California Air Resources Board), Evaluation test on twin fluidized bed wood waste fueled combustors located in Central California. Test Report No. C-87-042. Engineering Evaluation Branch, Monitoring and Laboratory Division. (February 7, 1990c).

CARB (California Air Resources Board), Evaluation of a wood waste fired incinerator at Louisiana Pacific Hardboard Plant, Oroville, CA. Test Report No. C-88-066. Engineering Evaluation Branch, Monitoring and Laboratory Division. (May 29, 1990d) - as reported in NCASI, 1995.

Douglas, M., Friedrich, F., Mortzavi, R., and Razbin, V., “Field Trials and Emission Testing of Paper De-Inking Solids (PDS)”. Proceedings of the 83rd Annual Meeting of the Technical Section of the Canadian Pulp and Paper Association. pp. B393 – 400. (January 1997).

Environment Canada, “Characterization of Organic Compounds from Selected Residential Wood Stoves and Fuels”, Environment Canada Emissions Research and Measurement Division, Report No. ERMD 2000-01 (December 2000).

EPA/600/P-98/002Aa, “The Inventory of Sources of Dioxin in the United States”, External Review Draft, (April 1998).

Frankenhaeuser, M., Hiltunen, M., Manninen, H., Palonen, J., Ruuskanen, J., and Vartiainen, T., “Emissions from Co-combustion of Used Packaging with Peat and Coal”, Chemosphere, 29(9 – 11): 2057 – 2066 (1994).

Griffin, R.D., “A New Theory of Dioxin Formation in Municipal Solid Waste Combustion”, Chemosphere, 15(9 – 12): 1987 - 1990 (1986).

Halonen, I., Tarhanen, J., Kopsa, T. Palonen, J., Vilokki, H., and Ruuskanen, J., “Formation of Polychlorinated Dioxins and Dibenzofurans in Incineration of Refuse Derived Fuel and Biosludge”, Chemosphere, 26(10): 1869 – 1880 (1993a).

Halonen, I., Tarhanen, J., Oksanen, J., Vilokki, H., Vartiainen, T. and Ruuskanen, J., “Formation of Organic Chlorinated Compounds in Incineration of Pulp and Paper Mill Biosludges”, Chemosphere, 27(7): 1253 – 1268 (1993b).

Kolenda, J., Gass, H., Jager, J., and Zeschmar-Lahr, B., “Determination of PCDD/F Emissions From Wood Burning Facilities”, Chemosphere 29(9-11): 1927 – 1938 (1994).

LC Engineering. “Detailed Report for Test Burns of Chlorophenol Contaminated Wood Wastes at Northwood Pulp Mill, Prince George, B.C.”, prepared for Environment Canada and the Ministry of Environment, Province of British Columbia (April 1989).

Lindbauer, R., Wurst, F., and Prey, T., “Combustion dioxin suppression in municipal solid waste incineration with sulphur additives”, Chemosphere, 25 (7 – 10): 1409 - 1414 (1992).

Luthe, C.E., Karidio, I., and Uloth, V.C., "Controlling Dioxin Emissions in Coastal Power Boilers: A Status Report", Pulp and Paper Canada, 97(9): T320-T326 (1996).

Luthe, C.E., Karidio, I., Uloth, V.C. and Wearing, J. T., "Are Salt-Laden Recovery Boilers a Significant Source of Dioxins?", Tappi Journal, 80(2): 165- 169 (1997a).

Luthe, C.E., Karidio, I., and Uloth, V.C., "Towards Controlling Dioxins Emissions From Power Boilers Fueled with Salt-laden Wood Waste. Part I.", Chemosphere, 35(3): 557-574 (1997b).

Luthe, C.E., Karidio, I., and Uloth, V.C., "Dioxins Formation in Salt-laden Power Boilers: a Mass Balance", Chemosphere, 36(2): 231-250 (1998a).

Luthe, C.E., Strang, A., Uloth, V.C., Karidio, I., Prescott, B. and Wearing, J., "Sulphur Addition to Control Dioxins Formation in Salt-Laden Power Boilers", Pulp and Paper Canada, 99(11): T391-T395 (1998b).

Luthe, C., Uloth, V. and Karidio, I., "Characterizing Polycyclic Aromatic Hydrocarbon Emissions from Hog Fuel Boilers", Pulp and Paper Canada, 99(12): T423-T429 (1998c).

Maatila, H., Virtanen, T., Vartiainen, T., and Ruuskanen, J., “Emissions of Polychlorinated Dibenzo-P-Dioxins and Dibenzofurans in Flue Gas from Co-Combustion of Mixed Plastics with Coal and Bark”, Chemosphere, 25(11): 1599 – 1609 (1992).

McCubbin, N., Preliminary Report on the Relationship Between Dioxin Emissions from Kraft Recovery Boilers and the Chloride Content of the Fuel”, Prepared for the U. S. Environmental Protection Agency Office of Science and Technology. (November 1997).

Nakao, T., Aozasa, O., Ohta, S., and Miyata, H., “Formation of Dioxin Analogs by Open-air Incineration of Waste Wood and by Fire of Buildings and Houses Concerning Hanshin Great Earthquake in Japan”, Chemosphere, 46:429 – 437 (2002).

NCASI (National Council of the Paper Industry for Air and Stream Improvement), “NCASI summary of PCDD/F emission from wood residue and black liquor combustion. Attachment 2 to comments submitted on January 13, 1995, to EPA’s Office of Health and Environmental Assessment concerning the draft document entitled “Estimating Exposure to Dioxin-Like Compounds”. (1995).

Oehme, M. and Mueller, M., “Levels and Congener Patterns of Polychlorinated Dibenzo-P-Dioxins and Dibenzofurans in Solid Residues from Wood-fired Boilers. Influence of Combustion Conditions and Fuel Type”, Chemosphere, 30 (8): 1527 – 1539 (1995).

Pandompatam, B., Kumar, Y., Guo, I., and Liem, A. J., “Comparison of PCDD and PCDF Emissions from Hog Fuel Boilers and Hospital Waste Incinerators”, Chemosphere, 34(5 – 7): 1065 – 1073 (1997).

Pinkerton, J. “Differences in the Reporting of Persistent Bioaccumulative Toxics Under the TRI and NPRI Programs”, NCASI National Meeting, Charlotte, NC (2001).

Schatowitz, B., Brandt, G., Gafner, F., Schlumpf, E., Buhler, R., Hasler, P., and Nussbaumer, T., “Dioxin Emissions from Wood Combustion”, Chemosphere, 29 (9-11): 2005 – 2013 (1994).

Umweltbundesamt, “Determination of requirements to limit emissions of dioxins and furans”. Report from the Working Group of the Subcommittee on Air/Technology of the Federal Government/Federal States Emission Control Committee. Berlin, Germany (1996).

Valttila, O., “Combustion of Biosludge” in the Leikki Combustion Research Program Technical Review, 1988 – 1992. Abo Akademi. (1993).

Vesterinen, R. and Flyktman, M., “Organic Emissions from Co-Combustion of RDF with Wood Chips and Milled Peat in a Bubbling Fluid Bed Boiler”, Chemosphere, 32(4): 681 – 689 (1996).

Zimmerman, R., Blumenstock, M., Heger, H., Schramm, K., and Kettrup, A., “Emission of Nonchlorinated and Chlorinated Aromatics in the Flue Gas of Incineration Plants During and After Disturbances of Combustion Conditions: Delayed Emission Effects”, Environmental Science and Technology, 35: 1019 – 1030 (2001).

To obtain Appendices A - K, contact your nearest NPRI Regional Office.