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Ms. Ellen Porter
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OCTOBER 21, 2019

Dear Ellen,

This letter and accompanying white paper serve as a follow-up to your request for NCASI's assessment on the potential for formation of polychlorinated dibenzo-p-dioxins / furans (PCDD/F) in boilers with suspension burners, direct-fired dryers and lumber kilns.

The combustion conditions in boilers with suspension burners, direct-fired dryers and lumber kilns are unlike those in wood-fired stoker boilers as these wood-products sources fire dry wood fuels like sanderdust and sawdust in suspension and therefore have very robust combustion. More details on the implications of robust combustion on the formation of products of incomplete combustion (PICs) (long-chain organic intermediates within the combustion zone) – the precursors for dioxin/furan formation – are provided in the attached technical paper, prepared by Dr. Arun Someshwar, with support from Messrs. Rob Crawford and Ric Law.

Please do not hesitate to contact me if you have additional questions on this information.

Sincerely,

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cc: Arun Someshwar, Rob Crawford and Ric Law, NCASI

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Potential for Dioxin/Furan Formation and Emissions from Suspension Burners burning dry wood fuel, Direct-Fired Wood Products Dryers and Lumber Kilns

NCASI was recently made aware that there are questions about the potential for PCDD/F formation and emissions from boilers with suspension burners that burn dry wood fuel, direct-fired dryers and lumber kilns. Based on an understanding of the formation mechanisms and the robust combustion conditions prevalent in suspension firing of dry wood fuels, it is NCASI's assessment that there is limited potential for formation and emissions of PCDD/F from combustion sources and process equipment in the wood products industry.

Background on Dioxin Formation and Emissions from Combustion

Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), collectively known as dioxins, are formed in minor quantities and emitted from industrial wood-fired boilers. For most, if not all, of the cases where dioxins were reported on the ICR, the congener-specific PCDD/F emissions rates were derived from tests on 31 wood-fired boilers that principally burned wood residues. These test results are summarized in NCASI Technical Bulletin No. 1013 (NCASI 2013).

There is a vast amount of published literature dealing with the mechanisms of dioxin/furan formation in thermal and combustion operations. For example, the paper by Huang and Buekens (1995) "On the mechanism of dioxin formation in combustion processes" and another by Altarawneh and Mulder (2009) "Mechanisms for formation, chlorination, de-chlorination and destruction of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs)" provide excellent reviews on this subject. In their extensive review, Altarawneh and Mulder (2009) state that "PCDD/Fs are formed through ***homogeneous and heterogeneous pathways.*** The homogeneous pathway involves reaction of structurally related precursors in the gas phase, at temperatures between 400 and 800°C. A large number of compounds can serve as potential precursors for the formation of PCDD/Fs, including compounds as simple as propene (Jarmohamed et al. 1994) and as complex as permethrin (Tame et al. 2007); though the most important and direct precursors are monocyclic aromatic compounds such as chlorinated phenols and chlorobenzenes. Recently, quinones have attracted attention as possible important precursors. Heterogeneous pathways involve two routes. The first is the so called de novo process, which proceeds through burnoff of a carbonaceous matrix with simultaneous oxidation and chlorination at temperatures between 200 and 400°C in the presence of oxygen (Stieglitz 1998). The second takes place by catalytic-assisted coupling of precursors, also in the temperature window of 200–400°C. It is widely accepted that transition-metal species, especially copper compounds, have a strong catalytic effect – compared with no added copper compounds – on the formation of PCDD/Fs through the two heterogeneous pathways." In a European study, Everaert and Baeyens (2002) review extensive amounts of PCDD/F emissions data from various thermal processes including municipal solid waste incinerators, wood and solid waste combustors and coal-fired power plants and boilers. They conclude that the ESP temperature was the most important factor for PCDD/F formation in their review and that PCDD/F concentrations increased with temperatures in the range up to about 280°C. They recommend that ESP temperatures should be maintained between the range of 180 and 200°C where the prevalence of de novo synthesis is reduced, and PCDD/Fs are increasingly absorbed on the fly ash.

The gist of current understanding on PCDD/F formation is that there are two principal pathways through which dioxins can be formed and emitted from industrial boilers: ***precursor formation and de novo synthesis***.

> ***Precursor formation*** *is relevant in cases where the fuels used for combustion contain significant levels of organic compounds which would be considered precursors for dioxin formation in the boiler combustion zone. This homogenous pathway is generally discounted as being largely irrelevant today because fuels tend to undergo increased scrutiny relative to contaminants, such as those which could potentially be dioxin precursors.*
>
> ***The de novo synthesis*** pathway is operative in the low temperature post-combustion zones of boilers/incinerators, typically in the range of 250 to 400°C. It involves heterogeneous catalytic reactions in the flue gas - fly ash environment. It is generally agreed upon today that dioxin formation in industrial boilers is predominantly a "post-combustion" phenomenon through the de novo synthesis pathway. The reactions involve a catalytic surface (typically fly ash), products of incomplete combustion (PICs) and chlorine atoms, all within the temperature zone of 250 to 400°C. Here, the PICs refer to long chain hydrocarbon byproducts (including phenols and benzenes) that get chlorinated by Cl atoms in the post-combustion zone, thus becoming available as chlorophenols and chlorobenzenes for dioxin formation in the post economizer temperature zone of 250 to 400°C.

It is worth reiterating that all these prerequisites, i.e., fly ash, the appropriate temperature zone and the concurrent presence of PICs along with adequate levels of atomic chlorine need to be present for PCDD/F to be formed.

Dioxin Formation and Emissions from Suspension Burners in Boilers, Direct-fired Dryers and Lumber Kilns

The above prerequisites for PCDD/F formation are not prevalent in boilers with suspension burners that burn dry wood fuel or in direct-fired dryers or lumber kilns in the wood products industry. The types of wood residues and the manner in which they are fired to generate hot flue gases for drying wood chips or lumber, differ from the combustion of wood residues on grates in most industrial stoker boilers. These differences are expected to result in much lower levels of PIC formation in direct-fired dryers and lumber kilns than in industrial stoker boilers.

Suspension Burners

Suspension burners that burn dry wood fuel typically combust very fine, dry wood such as sawdust and sanderdust. Many boilers have, and most direct-fired dryers are heated by, 100% suspension burners. This type of burner is designed to rapidly combust the fuel to completion. The rapid combustion, along with the resulting high temperatures around 1000^{o}C, is expected to produce drastically lower levels of PICs (the precursors for PCDD/F formation) than the combustion of wet fuel on the grates of industrial stokers. It should be noted that, occasionally, the sanderdust fuel may originate from wood products operations that use resins containing elevated levels of chloride. While elevated levels of Cl in wood fuels beyond a certain threshold (typically 0.2% Cl as in salt-laden wood) is associated with high levels of PCDD/F formation during combustion, the extremely low levels of organic PICs generated during sanderdust combustion in suspension burners is likely to minimize the formation of PCDD/Fs for which the presence of PICs is essential.

The role played by de novo synthesis and, potentially PICs, is illustrated in Figure 1 that provides a look at PCDD/F emissions as measured in ng WHO-TEF/2005 TEQ/m^3 @7% O_2 for 30 wood-fired stokers in the U.S. and a single U.S. suspension burner burning sanderdust. These data were extracted from Boiler MACT reports submitted to EPA as a part of the Industrial Coordinated Rulemaking effort and summarized by NCASI. Figure 1 illustrates that PCDD/F emissions can be quite variable in traditional biomass stokers. All other prerequisites being equal (temperature, fly ash, and Cl levels), this can be attributed to variability in combustion quality and the resulting potential for formation of PICs. It is difficult to achieve consistent combustion in stokers burning wood residues due to variable fuel quality and resulting changes in combustion conditions. On the other hand, combustion quality is expected to be more controllable and robust in suspension burners; Figure 1 illustrates (albeit with limited data) that PCDD/F emissions from suspension burners burning sanderdust would generally be expected to very low, at the low end of the range for wood-fired stokers. This is primarily due to the absence of PICs, even if the requisite post combustion temperature range for heterogenous de novo synthesis could be present.

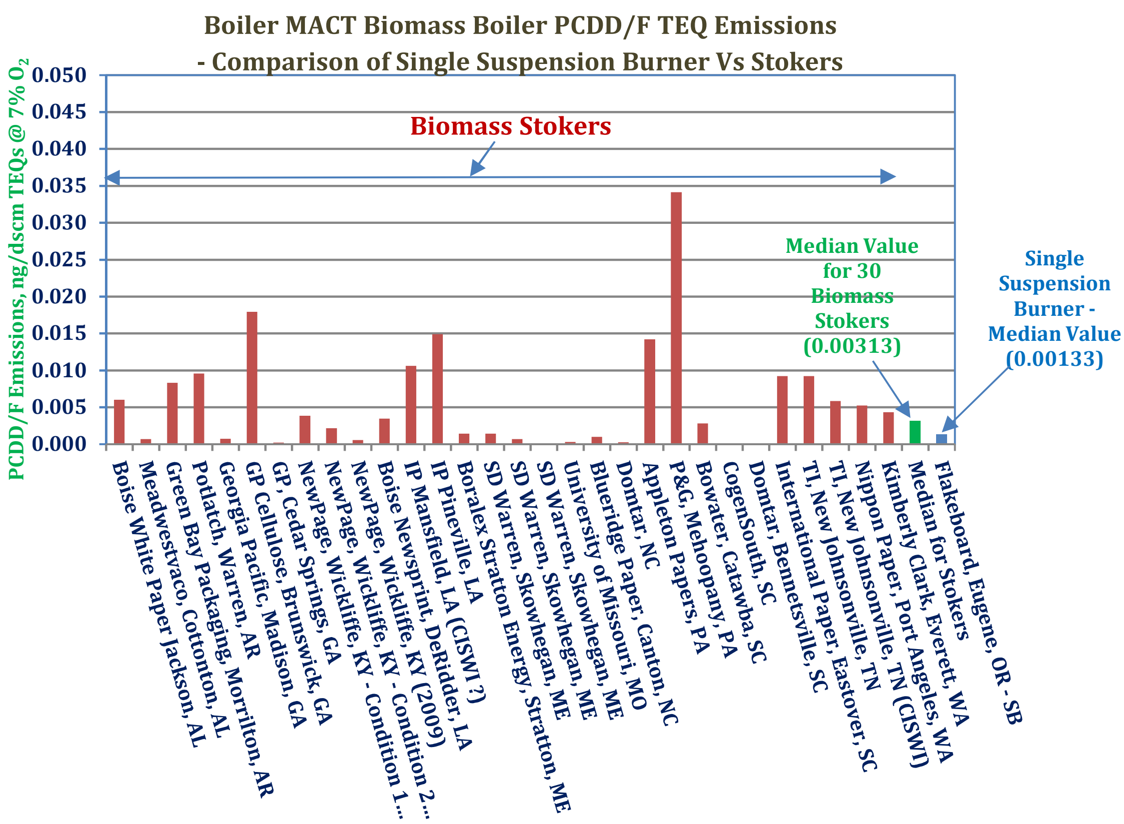

Figure 1. Boiler MACT PCDD/F Emissions Data for 30 Stokers & 1 Suspension Burner, All Burning 100% Biomass (ND = 0 per EPA guidance for PCDD/F)

Summary Conclusion
For the above stated reasons, it is our assessment that the conditions for formation of PCDD/F are not prevalent in suspension burners firing dry wood fuel and direct-fired process units in the wood products industry. The use of emission factors related to traditional biomass fired stoker boilers would therefore result in a significant overestimation of emissions.

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