

# Dioxin '97, Indianapolis, Indiana, USA

## The Congener Profiles of Anthropogenic Sources of Chlorinated Dibenzo-p-Dioxins and Chlorinated Dibenzofurans in the United States

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### Abstract

Anthropogenic sources of CDDs and CDFs in the U.S. are broadly classified as combustion/incineration sources, and chemical manufacturing/processing sources. It is postulated here that each source type favors the formation and environmental release of certain mixtures of CDDs and CDFs. These mixtures can be translated into what are termed 'congener profiles' which represent the distribution of total CDDs and CDFs present in the mixture. A congener profile may serve as a signature of the types of CDDs and CDFs associated with particular environmental sources of these compounds. Such source-specific profiles may aid researchers in explaining source contributions to environmental measurements in various matrices. This paper presents the congener profiles of the following sources of CDDs and CDFs to the U.S. environment: municipal, medical and hazardous waste incineration; cement kilns burning and not burning hazardous waste; industrial oil-fired boilers; industrial/coal and wood combustors; unleaded fuel combustion in vehicles; diesel fuel combustion in trucks; secondary aluminum smelters; secondary lead smelters; sewage sludge incineration; bleached chlorine paper pulp; technical pentachlorophenol, and 2,4-D salts and esters.

### Introduction

The United States Environmental Protection Agency (EPA) has been evaluating sources of environmental releases of CDDs and CDFs for the purpose of constructing a national inventory of emissions. This is in support of EPA's Dioxin Reassessment, and when completed will be included in the final version of, *Estimating Exposures to Dioxin-Like Compounds*.<sup>1</sup> This marks the first time that the EPA has comprehensively examined combustion and non-combustion dioxin source activity and derived estimates of annual emissions to the U.S. environment. When completed, the national inventory will be supported by an electronic database, which facilitates the development of congener profiles. Although there exist uncertainties, these congener profiles may assist researchers in: (1) identification of specific combustion source contributions to near field air measurements of CDDs/CDFs; (2) comparing sources in terms of discerning differences in the types and amplitude of CDD/CDF congeners emitted; and (3) providing insights on formation of CDDs and CDFs in various sources and chemicals.

### Method

Congener profiles are the fractional distribution of CDD/CDF congeners in an environmental release, in an environmental sample, or in a biological sample. There are numerous procedures one

could elect to use to derive a congener profile, and there is no single agreed-upon convention<sup>2,3</sup>. In this paper, congener profiles were developed using the ratio of specific 2,3,7,8-substituted CDDs and CDFs to the total ( $Cl_4 - Cl_8$ ) CDDs/CDFs. With respect to combustion sources, the profiles were derived by: (a) averaging congener-specific stack gas concentrations for the 17 TEQ compounds for each tested facility; (b) averaging congener profiles for each tested facility by dividing the congener-specific stack gas concentration by the average total ( $Cl_4 - Cl_8$ ) CDD/CDF stack gas concentration; and (c) averaging all congener profiles developed for all tested facilities within the combustor type. For chemical processes and commercial chemicals, CDD/CDF profiles were generated from average concentrations (ppt) in the chemical. These data were limited in several ways. First, when viewing the congener profile for 2,4-D it is important to note that OCDD/OCDF were not analyzed for in the chemical. Secondly, only the 2,3,7,8-substituted congeners were analyzed for in 2,4-D. Thus, the congener profile for 2,4-D was derived by dividing the concentration of the individual 2,3,7,8-substituted congener by the sum of the average concentration of 2,3,7,8-substituted CDDs/CDFs. The profile for bleached chlorine wood pulp is based on median concentrations of the detected congeners, and not the average.

The sources selected for analysis in this paper were those where it was judged that sufficient data were available to derive profiles with reasonable confidence. For combustion sources this includes: municipal, medical and hazardous waste incinerators; cement kilns burning and not burning hazardous waste; industrial oil-fired boilers; industrial/coal and wood combustors; unleaded fuel combustion in automobiles; diesel fuel combustion in trucks; secondary aluminum smelters; secondary lead smelters, and sewage sludge incinerators. For non-combustion sources this includes: bleached chlorine paper pulp; technical pentachlorophenol, and 2,4-D salts and esters. The profiles are plotted in Figure 1.

## Results and Discussion

On the basis of inspection and comparisons of the average CDD/CDF congener profiles across combustion and non-combustion sources, the following observations are made: (These generalizations are derived from this data set, and their application beyond these data is uncertain).

- i. It appears that combustion sources emit all 2,3,7,8-substituted CDDs and CDFs, although in varying percentages of total CDD/CDF.
- ii. In combustion source emissions, 2,3,7,8-TCDD is usually 0.1 to 1.0% of total CDD/CDF. The exception to this is the stack emission from industrial oil-fired boilers where 2,3,7,8-TCDD constitutes an average of 7% of total CDD/CDF emissions.
- iii. It cannot be concluded that OCDD is the dominant congener for all combustion generated emissions of CDDs/CDFs. OCDD dominates total emissions from mass burn municipal solid waste incineration (MSWI) that have dry scrubbers and fabric filters (DS/FF) for dioxin controls; from industrial oil-fired sum of boilers; from industrial wood-fired boilers; from unleaded gasoline combustion; from diesel fuel combustion in trucks; and from sewage sludge incinerators. The dominant congeners for other combustion sources are: 1,2,3,4,6,7,8-HpCDF in emissions from mass burn MSWIs equipped with hot-sided electrostatic precipitators (ESPs); OCDF in emissions from medical waste incineration; 1,2,3,4,6,7,8-HpCDF in hazardous waste incinerators; 2,3,4,7,8-PeCDF in cement kilns burning hazardous waste; 2,3,7,8-TCDF in cement kilns not burning hazardous waste; OCDF in industrial/utility coal-fired boilers; 1,2,3,4,6,7,8-HpCDF in secondary aluminum smelters; 2,3,7,8-TCDF in secondary lead smelters.
- iv. The 1,2,3,4,6,7,8-HpCDF appears to be the dominant congener in the following sources: secondary aluminum smelters; MSWIs equipped with hot-sided ESPs; hazardous waste incinerators; and 2,4-D salts and esters.

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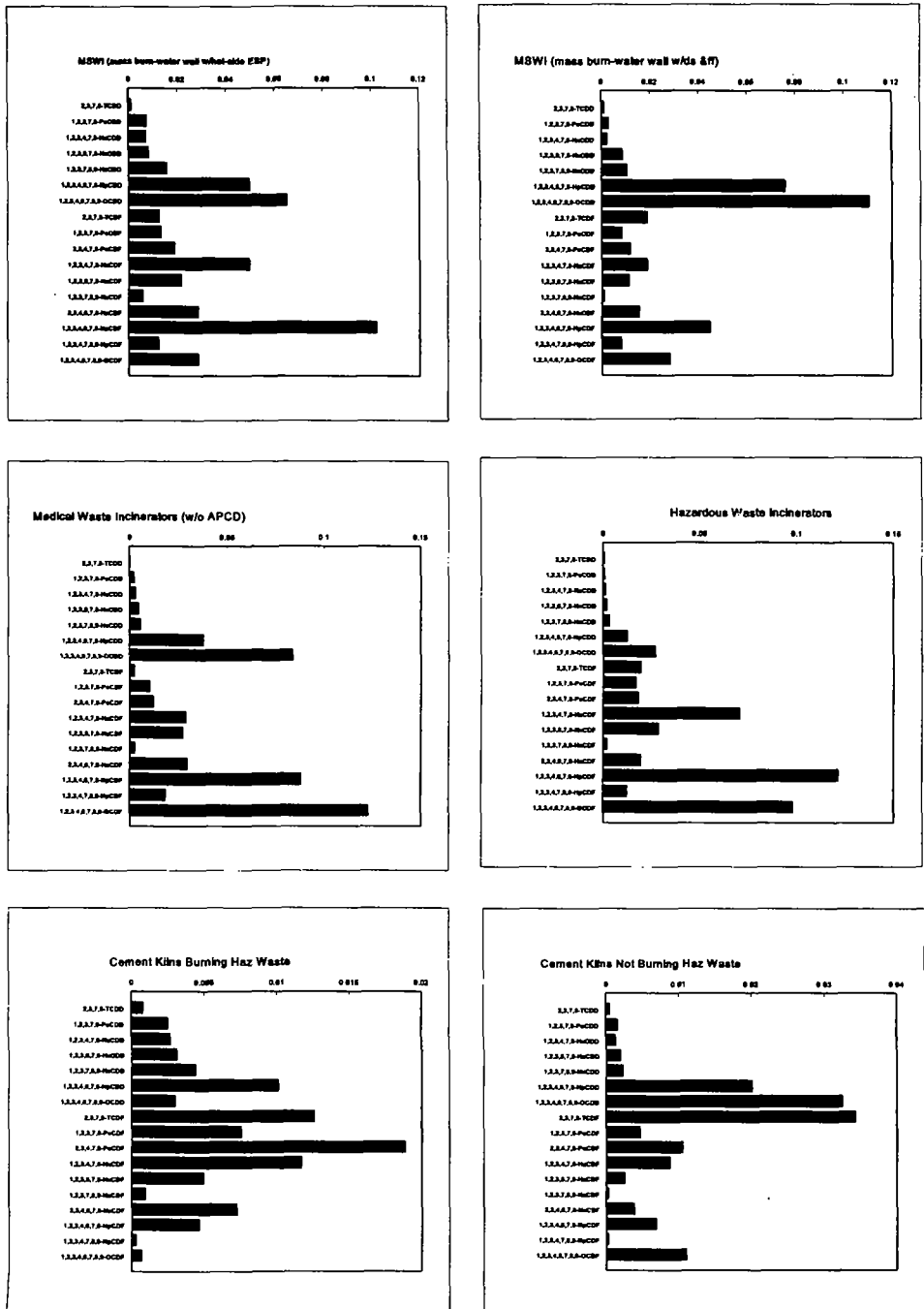
- v. Evidence for a shift in the congener patterns potentially caused by the application of different air pollution control systems within a combustion source-type can be seen in the case of mass burn MSWIs. For mass burn MSWIs equipped with hot-sided ESPs, the most prevalent CDD/CDF congeners are: 1,2,3,4,6,7,8-HpCDF; OCDD; 1,2,3,4,6,7,8-HpCDD/1,2,3,4,7,8-HxCDF; 2,3,4,6,7,8-HxCDF/OCDF; 1,2,3,6,7,8-HxCDF. The most prevalent congeners emitted from MSWIs equipped with DS/FF are: OCDD; 1,2,3,4,6,7,8-HpCDD; 1,2,3,4,6,7,8-HpCDF; OCDF; 2,3,7,8-TCDF/1,2,3,4,7,8-HxCDD; 2,3,4,6,7,8-HxCDF.
- vi. There is evidence of marked differences in the distribution of CDD/CDF congeners between cement kilns burning and not burning hazardous waste. When not burning hazardous waste as supplemental fuel, the dominant congeners appear to be 2,3,7,8-TCDF; OCDD; 1,2,3,4,6,7,8-HpCDD, and OCDF. When burning hazardous waste, the dominant congeners are: 2,3,7,8-PeCDF; 2,3,7,8-TCDF; 1,2,3,4,7,8-HxCDF; 1,2,3,4,6,7,8-HpCDD. When burning hazardous waste, OCDD and OCDF are minor constituents of stack emissions.
- vii. The congener profile of 2,4-D salts and esters seems to mimic a combustion source profile in the number of congeners represented, and in the minimal amount of 2,3,7,8-TCDD relative to all 2,3,7,8-substituted congeners. A major difference is the prevalence of 1,2,3,7,8-PeCDD in 2,4-D, e.g. 14%, which is not seen in any other combustion or non-combustion sources presented here.
- viii. There are similarities in the congener profiles of pentachlorophenol (PCP), diesel truck emissions, unleaded gasoline vehicle emissions, and industrial wood combustors. In these sources, OCDD dominates total emissions, but the relative ratio of 1,2,3,4,6,7,8-HpCDD to OCDD is also quite similar.
- ix. The congener profiles between the direct measurement of diesel truck exhaust and air measurements from a tunnel study<sup>4</sup> of diesel traffic are quite similar.

## Literature Cited

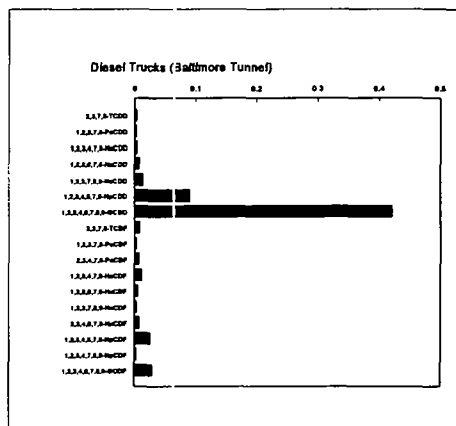
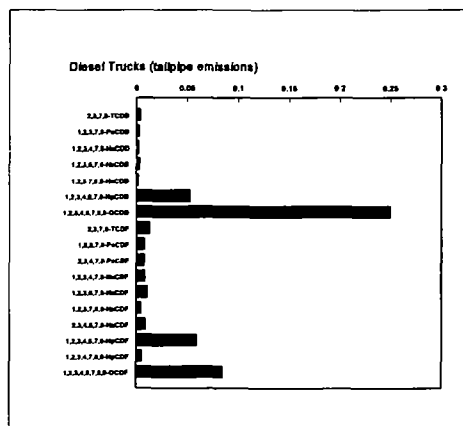
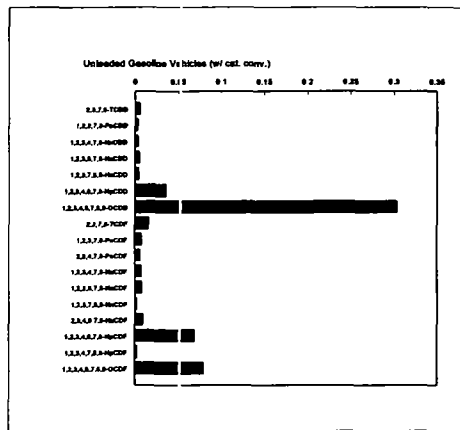
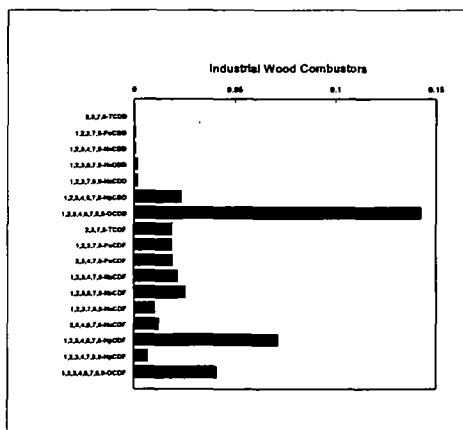
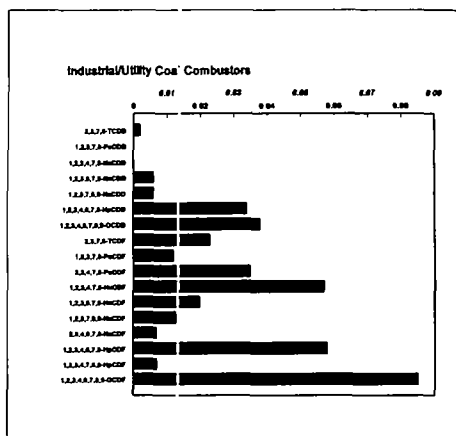
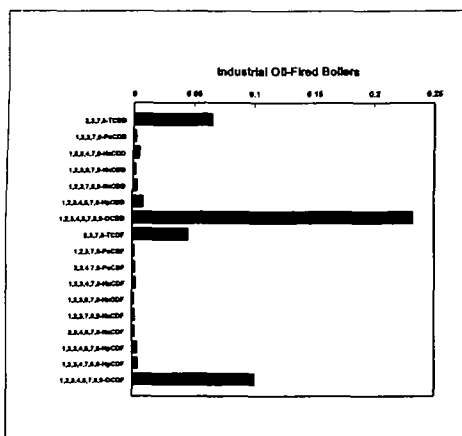
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# SOURCES

Figure 1. The Congener Profiles of Anthropogenic Sources of Chlorinated Dibenzo-p-Dioxins and Chlorinated Dibenzofurans in the United States



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# SOURCES

