CORRELATION OF CHLORINE IN FEEDSTOCK WITH DIOXIN EMISSION FACTORS FROM VARIOUS FORMS OF COMBUSTION. A REANALYSIS.

William F. Carroll, Jr.
Chlorine Chemistry Council, 1300 Wilson Boulevard. Arlington, VA USA 22209

Abstract

The relationship or lack thereof between chlorine content in combusted materials and PCDD/F generated during combustion has been explored for nearly twenty years. A recent article by Thomas and Spiro hypothesizes a positive log-log correlation between chlorine content and dioxin generation. No statistical methods are employed. When individual data points are tested by means of Spearman Rank Test, materials containing more than 14 ppm chlorine show no significant correlation between chlorine content and emission factors for PCDD/F.

Introduction

In recent years inventories of dioxin generation have been published for a number of countries. Most are European including the United Kingdom [1,2], Sweden [3], the Netherlands [4], and Germany [5,6]. Two have been published for the United States (US): one by the Environmental Protection Agency (EPA) [7] and one by Thomas and Spiro [8,9]. EPA's Draft Dioxin Reassessment gives ranges of estimates in Toxicity Equivalency (TEQ). Thomas and Spiro report a larger number of sources as the sum of PCDD and PCDF.

Thomas and Spiro include a graph of chlorine feedstock content vs. dioxin emission factor (Figure 1), with data gleaned from other publications. Results by combustion type are shown as ranges. The authors conclude that rising emission factors, particularly for "poor" combustion correlate with increasing chlorine. This conclusion is at odds with those of other authors [10, 11] who find no correlation in most individual combustors and no similar global correlation. Despite the apparent paradox harmonization is possible; however, a reanalysis of the raw data presented by Thomas and Spiro is necessary.

Results

The dataset collected by Thomas and Spiro is presented in Table 1. These data are extracted from the original text or taken from Figure 1 in reference 8. In cases where a specific chlorine concentration in feedstock was not measured a typical value reported by the authors for a type of fuel is used. The number of data points reported in the original text is preserved so as to retain degrees of freedom for statistical analysis, although in some cases doing so required redundancy of data points.

The raw data of Table 1 are plotted in Figure 2 on the same scale as Figure 1. Simple linear regression of all the data yields a weakly positive correlation; however, poorly fitting points are found at the low extreme of chlorine concentration. Statistical treatment of the data reveals that when all 81 data points are included in Spearman rank the data are just significant at 95% (0.242 vs 0.219) in a two-sided test; sequential removal of the lowest chlorine concentrations yields progressively lower correlation, and at chlorine content greater than 14 ppm shows no significant correlation (0.150 vs 0.223). If only non-redundant points are considered (n=65) there is no statistical significance even to the lowest levels of chlorine (0.181 vs 0.245)

Discussion

The search for the role of chlorine in dioxin formation has occupied numerous researchers over the past twenty years. Fly ash is an important locus for formation of dioxins in most types of controlled combustion. Metals on the solid phase catalyze the reaction. Within the solid-phase mechanism at least two submechanisms are possible: formation by assembly of small molecules [12] and formation by functionalization of carbon black with subsequent oxidative cleavage of dioxin molecules from the carbon matrix [13]. The role of the chlorine source, whether organic or inorganic, has been explored as well [14, 15].

The possible effects of differences in types of combustion within the categories presented by Thomas and Spiro and presence or absence of catalytic metals have been pointed out previously [16]. Clearly, given the low statistical significance without controlling for these well-known variables, no overall correlation can be reasonably inferred from these data. Moreover, for controlled combustion, the type and design of the combustor and particularly the air pollution control systems are overriding considerations for any discussion of feedstock-related mechanism.

Stoichiometrically, chlorine must be involved in dioxin formation to at least a very small degree; however, chlorine in most fuels greatly exceeds the stoichiometric requirements. Moreover, chlorine in ambient air has been shown to be stoichiometrically significant considering the small concentrations of dioxins in emitted gases [10,16]. Townsend has explored the relationship between chlorine and dioxin formation in three conceptual domains: chlorine-limited, chlorine plentiful, and carbon-limited [17]. Rigo's work analyzes mainly the middle domain; Marklund's work on unleaded gasoline reproduced in Thomas and Spiro might be effectively in the chlorine-limited domain (ca. 10 ppm Cl in feedstock); however, fly ash, the locus for solid-phase dioxin formation is virtually nonexistent in combustion of gasoline and the presence of catalytic metal sites and residence time at favorable temperature for dioxin formation may also be low.

Conclusion

The inventory of dioxin emission factors collected by Thomas and Spiro has been of value for comparison with other inventories done in the US and Europe. The appearance of a correlation between chlorine input and dioxin formation across divergent processes seems to be an artifact of data grouping techniques used in the original article. The correlation becomes substantially weaker when the data themselves are regressed and statistically insignificant when combustor design or the possibility of changes in formation mechanisms are considered.

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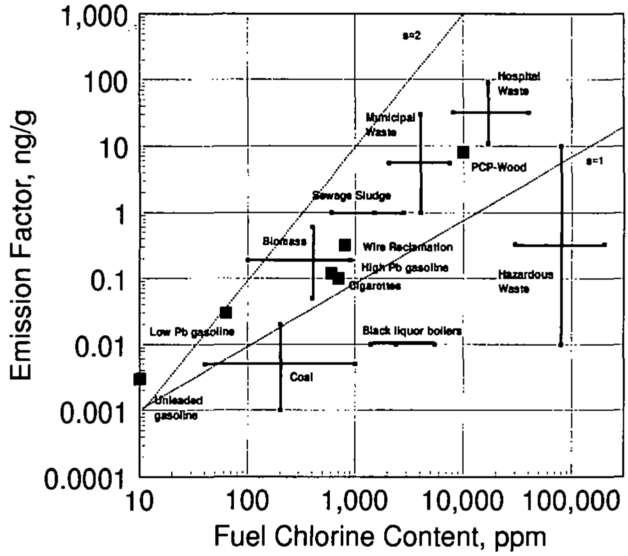

Figure 1. Reproduction of Figure 1 from Thomas and Spiro, Reference 8.

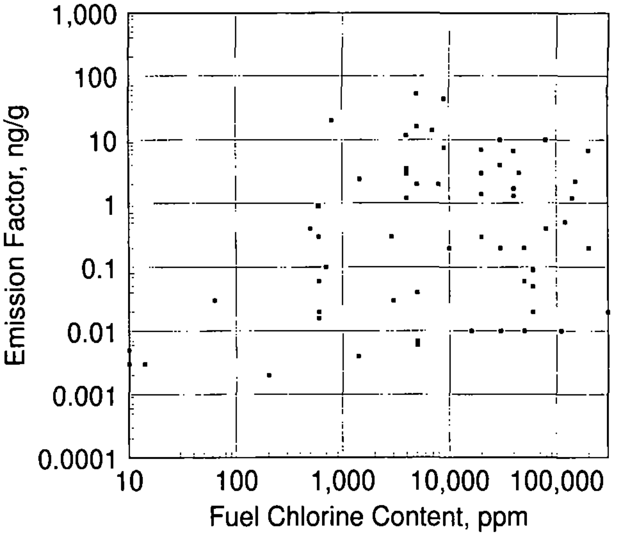

Figure 2. Original data points used to generate Figure 1.

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