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IS THERE A MEANINGFUL DIOXIN:CHLORINE LINK IN COMMERCIAL SCALE SYSTEM FLUE GASES?

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ABSTRACT

An extensive database including more than 1,900 PCDD/F test runs at different types of waste combustors was assembled and analyzed. A series of increasingly sophisticated statistical techniques found that for the vast majority of the data sets, the effect of feed chlorine content on PCDD/F emissions cannot be differentiated from normal variability. The small number of data sets that showed an effect displayed conflicting results. The quantity of PCDD/F increased in some cases and decreased in others. Whatever effect chlorine feed rate has on PCDD/F in the products of combustion, it is not discernible against the background. Consequently, mandatory chlorine reduction programs are unlikely to produce any measurable reduction in the quality or quantity of PCDD/F emissions from commercial scale waste combustors.

INTRODUCTION

Since polychlorinated dibenzo-p-dioxins and dibenzo furans [PCDD/F] are organochlorides, they clearly cannot be found in the products of combustion when there is no chlorine. On the other hand, atmospheric measurements demonstrate that air contains enough chlorine to produce about 2,500 ng/dsm^3 of 2,3,7,8 TCDD and laboratory experience indicates that intrinsic PCDD/F might pass through the flame zone under poor combustion conditions or be formed throughout the combustion system via a complex series of interacting gas phase, surface catalyzed and solid phase reactions. Laboratory work also shows that PCDD/F formation is strongly influenced by combustor design and operating conditions. This leads to the question, which effects predominate PCDD/F emissions at commercial scale facilities? Is a change--discernible in some laboratory experiments--a meaningful factor in full scale system operation?

FOCUS & LIMITATIONS

This paper summarizes some of the key findings of the effort directed by the Subcommittee on The Relationship between Chlorine in Waste Streams and Dioxin Emissions from Combustors of the ASME Research Committee on Industrial and Municipal Waste to examine the impact of waste feed chlorine content on PCDD/F emissions from waste combustion systems. The effort focused primarily on the acquisition, review and analysis of stack emissions data from the municipal, medical, hazardous and agricultural (biomass) commercial waste management segments. Seminal data from laboratory, pilot and small-scale test facilities were used to provide understanding of mechanisms and provide a framework for examining full-scale facility performance.

The full report (Rigo, Chandler & Lanier, 1995) provides an analysis of the data, a discussion of the statistical techniques employed, and a standardized listing of the pertinent data so that others may perform independent analyses. There is a wealth of information in the main body of the report and Appendix D that can be used to address other PCDD/F formation questions and assess air pollution control system [APCS] performance. Others are encouraged to use this reference work as a starting point to verify the following conclusions and observations and to extend the assessment to address other questions.

Neither this paper nor the underlying study, however, address changes in the PCDD/F characteristics of residues and liquid effluents leaving commercial scale waste combustion facilities. This limitation does not seriously reduce the utility of the effort since multipathway health risk assessments find stack emissions predominating the PCDD/F risk contribution; the other effluents have a negligible effect. This is not surprising since testing at Stapelfeld, Germany (1985) and Montgomery County, Ohio (Radian, 1989) found little PCDD/F in scrubber effluents and routine TCLP testing finds that whatever PCDD/F is in combustor residue, it is not leached. This study properly emphasized the area where an environmentally significant relationship is most likely to be found.

APPROACH

Data Acquisition

Information in Rigo & Rigo Associates, Inc.'s proprietary emissions database and the emissions database assembled by Energy & Environmental Research Corp. [EER] in support of the Combustion Emissions Technology Resource Document (EPA, 1994) was augmented by data gleaned primarily from complete emissions test reports and occasionally from summary reports obtained from plant owners, researchers and regulators predominantly in the United States, Canada and Europe. Previously unpublished results were provided and utilized. In total, more than 1,900 PCDD/F measurements taken along waste combustion system gas paths were databased and utilized. The data were assembled along with facility characteristics, test methods, plant operating data and an indication of chlorine feed rate (e.g., uncontrolled HCl measurements in the flue gas or an indication of waste composition).

Standard USEPA regulatory units--PPMdv for gases, such as HCl; mg/dsm^3 for particulates; and ng/dsm^3 for PCDD/F congeners and homologues--were used. The data were standardized to 20°C, 762 mm Hg, dry and 7% O_2 conditions.

Data quality was assessed for each data set (i.e., test report or publication). In addition to verifying that the tests used standard test procedures and adhered to an established QA/QC protocol, the data were reviewed to identify data that did not meet QA requirements and outliers. Apparent outliers were traced back and, where errors were found, the appropriate corrections were made. Remaining outliers were flagged so that the effect of possibly aberrant data could be considered during interpretation.

Data Analysis

The overall question of whether chlorine affects PCDD/F stack emissions was broken down into a set of testable questions so that objective statistical methods could be consistently used to determine if there is a discernible effect of waste feed chlorine content on PCDD/F emissions at commercial waste combustion facilities. Two questions were used to ascertain if there is an effect since changes in chlorine feed rate might affect either :

1. the composition, or
2. the quantity of PCDD/F emissions.

The composition question was addressed by determining if the PCDD/F profile measured at various locations within a facility, or between facilities, was more different than experimental variability could explain. The quantity question was addressed using a number of correlation based tools and Analysis of Variance [ANOVA] techniques. If no relationship was found between chlorine and either composition or quantity of PCDD/Fs in the gases, then it was concluded that there was no overall effect.

Many ways of characterizing PCDD/F profiles have been proposed and utilized. This effort compared as many of the following three descriptor sets as could be computed using the available information:

- the fraction congener, defined as the ratio of the 2,3,7,8 Substituted Congeners grouped by equal International Toxicity Equivalence Factor [ITEF] within a homologue to the sum of all 2,3,7,8 Substituted Congeners (A-J);
- the fraction homologue, defined as the ratio of each homologue total to the Total PCDD/F (K); and
- the 2,3,7,8 Ratio, defined as the sum of all 2,3,7,8 Substituted Congeners to the Total PCDD/F (L-U).

Each of the above was calculated on a molar rather than on a mass basis to avoid camouflaging changes induced by substituting a few molecules of heavier congeners for more molecules of lighter, more toxic congeners. Figure 1 displays the signatures developed for several types of waste combustors using complete data sets (e.g., sets that did not include below detection limits [BDL] data points).

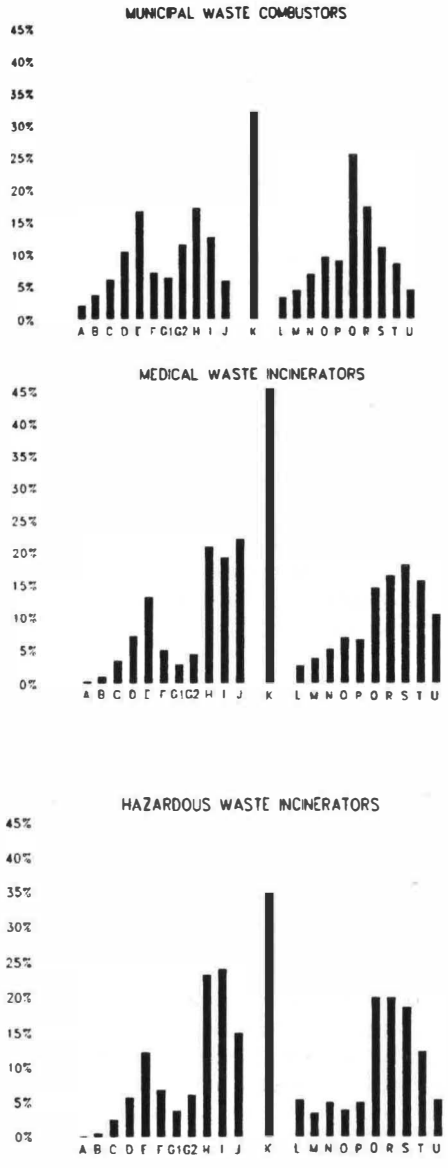

Figure 1. PCDD/F PROFILES FOR SEVERAL TYPES OF COMMERCIAL WASTE COMBUSTION SYSTEMS.

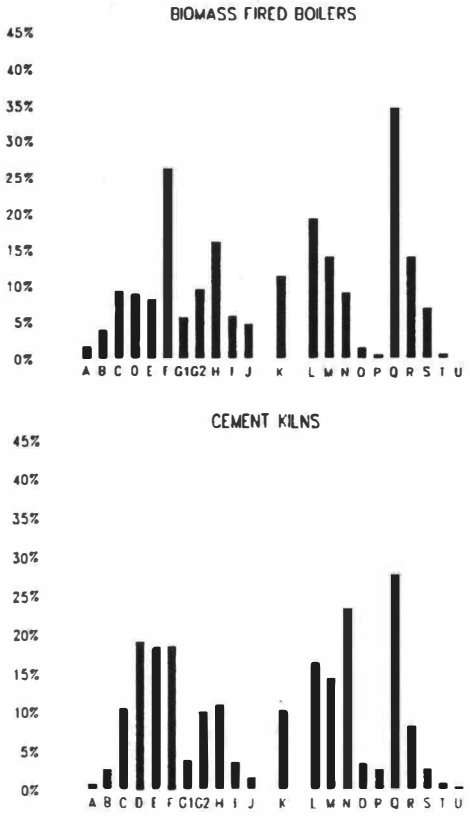

FIGURE 1(CONT'D). PCDD/F PROFILES FOR SEVERAL COMMERCIAL WASTE COMBUSTION SYSTEMS.

First, for individual facilities and subsequently facility averages, cluster analysis was used to compare the relative congener and homologue signatures. Cluster analysis is a technique that compares entire patterns. The Squared Euclidean Distance is the sum of the squares of the differences between each signature component (shown graphically in Figure 2). It was used to make this comparison since it could be compared to the imprecision of the PCDD/F measurement methods to distinguish real signature differences from happenstance. A statistically significant difference at the 95 percent confidence level is likely to be found 5 percent of the time when the comparisons are made from a common data set due to data noise alone. Since this effort involves analyzing more than 1,900 sets of PCDD/F results, the number of false conclusions likely to be found by not starting with method imprecision is in excess of 2 million due to chance. The number of false positives was minimized in this effort by using multiple means comparison techniques such as using the Studentized Maxim Modulus statistic instead of the t-statistic when developing critical values for differences[1].

[1] Another technique is to simply use the Bonifonini approximation and do all comparisons at the α/k statistical significance level instead of the α level when k comparisons are being made. For example, when 4 averages are compared, six unique paired comparisons will be made (k). So, if the 95 percent statistical confidence level is desired, tabulated values for 1-.05/6 or 99.2 (say 99) percent confidence level should be used. Obviously, larger differences are needed to identify significant differences, but this is a natural consequence of using a data set to do more than one comparison.

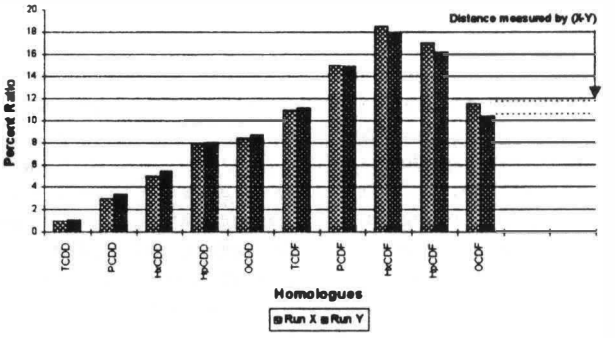

FIGURE 2. DIFFERENCES BETWEEN SIGNATURE COMPONENTS USED TO ESTIMATE THE SQUARED EUCLIDIAN DISTANCE.

Other clustering techniques could have been chosen, but method imprecision would not have been as cleanly addressed. A Criterion to distinguish Squared Euclidean Distances that exceed PCDD/F measurement method imprecision from normal data variability was developed by combining the expected signatures in Figure 1 with estimated method imprecision estimates for individual isomers (Rugenthaler, 1994) in a Monte Carlo simulation. If the Squared Euclidean Distance is less then the Criterion, then the individual signatures are the same and changes in chlorine feed rate could not have had a measurable effect. Also, if the signatures are the same, then a summary quantity measure like total PCDD/F concentration can be used to assess quantity changes since changes in the summary statistic and each individual component are related with observed differences being less than method variability. Hence, these differences and are attributable to chance.

The database includes 87 variables for each of the more than 1,900 PCDD/F runs recorded. It is difficult to meaningfully inspect such extensive data and identify and separate systematic variations from data noise. Correlation methods, including principal component analysis [PCA], canonical correlation and scatter plots of one variable against another with linear regression line overlays provide a quick way to identify potentially meaningful relationships, but cannot account for collinear and confounding factors. Designed experiments that purposely varied operating parameters (parametric tests), collinearity (variables responding together like a scrubber lowering the flue gas temperature) and confounding factors (different sampling locations or combining data from different units or time frames) however, are readily handled using regression based ANOVA techniques. Continuous variables, like flue gas temperature and oxygen content, can be combined with discrete blocking variables, which take on a value of 1 when a condition is true (a 5%

PVC spike, for example) and a value of 0 when it is false (normal MSW being burned) in an ordinary least squares or robust least median square regression. Statistically significant regression coefficients indicate that the continuous variable or the condition represented by the blocking variable has an effect; otherwise, they do not. ANOVA enables identification of significant discrete effects and the sorting out of complex industrial experiments where several things are changed simultaneously.

A combination of all these techniques, applied in a consistent manner to all the available data, is required to identify which data sets contain differences. Further statistical and technical data analysis is then used to determine whether changes in feed chlorine affected the composition of the emitted PCDD/Fs (e.g., did the changes induce shifts in the congener and homologue distributions?) or the amount of PCDD/F emitted. If the answer to both of these questions is no--chlorine changed neither the character nor the amount of the PCDD/F emissions--it is concluded that there is no effect of changes in chlorine feed rate on PCDD/F emissions. If a change is noted, it is compared to other experiments and tests with positive results. The same effect must be found in the majority of similar experiments to assign causality because even with the application of techniques designed to minimize the number of chance findings in multiple comparisons, happenstance can still produce a few significant results when there is really nothing there.

FINDINGS

Municipal Waste Combustors [MWC]

Data from 59 MWC facilities, taken at various points throughout the system, were used in this portion of the study. Parametric tests were conducted at several facilities to address the significance of potential PCDD/F formation mechanisms. Furthermore, spiking tests were performed where lime, mixed plastics, PVC and salt were added to or removed from the normal feed to determine the relationship between PCDD/F concentrations and chlorine. Many of these tests included some measurement of chlorine feed rate. For spiking tests without measured uncontrolled HCl concentrations (i.e., HCl data before the acid gas control system), the parametric changes in feed composition were used in the analysis.

Comparison of the individual signatures obtained from each facility found that some test runs apparently differ from the bulk of the test runs by more than nominal method imprecision. These differences were usually caused by a large number of below detection limits [BDL] isomer results which means that the signature was reflecting method limitations rather than actual composition information. The remaining signature differences are associated with varying sampling location (i.e., boiler outlet, stack, etc.). After accounting for these differences, there is no indication that either the normal range of operating conditions or wide variations in feed material, including spiking runs with elevated or depressed chlorine content, cause any measurable change in PCDD/F signatures.

Parametric and spiking studies are helpful in examining the effect of varying feed chlorine content on the quantity of PCDD/Fs emitted by MWC facilities. Figure 3 displays the aggregated stack test results with each facility represented by a unique symbol (see Rigo, Chandler & Lanier, 1995, for specific plant characteristics and identification). The data from major emissions inventory efforts in Denmark and the Netherlands have been aggregated to develop predictive equations that include HCl. When the modeling was repeated using the logarithmic form of the chemical kinetic equations and accounting for the collinear effect of scrubbers on HCl concentrations and air pollution control system operating temperatures, the HCl effect disappeared.

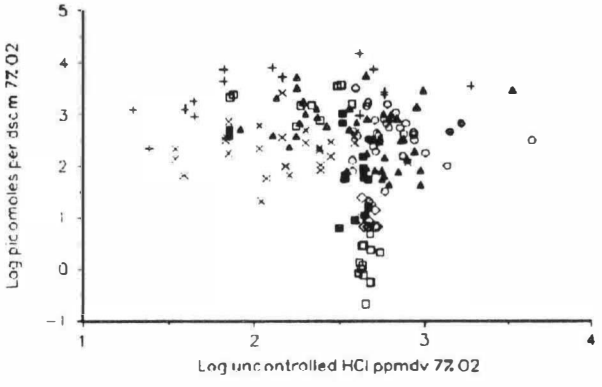

FIGURE 3. SCATTER PLOT SHOWING THE RELATIONSHIP BETWEEN PCDD/F AND UNCONTROLLED HCl CONCENTRATION.

The importance of accounting for APCS operating temperature is indicated by the relationship between the log of PCDD/F concentration and temperature. As the APCS temperature increases (inverse temperature decreases), stack gas PCDD/F concentrations increase. While there are many variables affecting

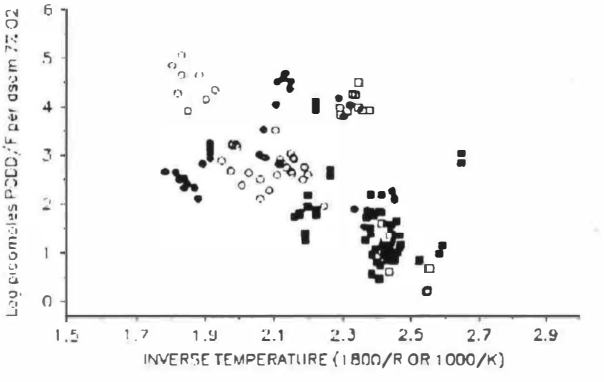

FIGURE 4. SCATTER PLOT SHOWING THE RELATIONSHIP BETWEEN PCDD/F CONCENTRATIONS AND APCS OPERATING TEMPERATURE.

PCDD/F emissions within an individual facility and between similar facilities, APCS operating temperature is a predominant factor.

Statistical analyses were conducted on the data from 18 facilities where parameters were intentionally varied to determine which, if any, had a significant effect. A full scale study was conducted at the state-of-the-art waste burning facility located in Würzburg, Germany (Mark, 1994). No difference was found between either the PCDD/F isomer profile or concentration when burning only MSW and burning MSW augmented with either 7.5 or 15 percent mixed plastics enriched to 10% PVC.

The Pittsfield experiment (MRI, 1987) is another study that looked for a relationship between feed PVC content and PCDD/F emissions. The combustion of PVC-"free" material produced the same PCDD/F levels as combustion of regular waste, PVC-spiked waste and PVC-"free" waste. It should be noted, however, that careful attention has to be paid to the design of the Pittsfield test since a simple plot of PCDD/F concentration versus measured HCl indicates correlation. This correlation, however, is the result of hidden variables--the parametric changes in incinerator operating conditions. Once these effects are accounted for, no chlorine effect remains. This points out the importance of considering all the variables in a designed experiment where each of the variables is intended to produce a PCDD/F response. Each variable must be considered, along with other confounders that come to light after the experiment is conducted, to produce a proper interpretation.

Trial burns using three types of densified Refuse Derived Fuels [dRDF] were performed at Sioux Center, Iowa (Pacific Environmental Services, 1989). There was no difference in PCDD/F emissions between fuel types even though the dRDF's ranged from plastics free through MSW to plastics augmented fuels.

In the Hørsholm study (Miljoministeriet, 1989), PVC, salt and lime were spiked in a statistically designed, fractional factorial experiment. Analysis of the data revealed that too little time was allowed between experimental conditions. Consequently, each measurement is a complex mixture of the previous and intended experimental condition. Typical test days were 12 hours long during which 3 tests were run before the unit was restored to burning normal MSW for the next 12 hours. There was a gap in testing while the boiler was cleaned. The next two test days apparently had 4 and 5 runs each. The balance of testing then returned to the 3 run-per day pattern. Unfortunately, time series techniques cannot be applied to these data to compensate for the lagged effect since the runs were not conducted uniformly throughout the test period. Any conclusions drawn from this experiment are, therefore, unsupported by the data set. When the first runs of each day are considered (runs that should have minimum cross condition contamination), no effect of two levels of PVC spiking, one level of salt spiking or one level of lime addition can be discerned.

Neither normally observed changes in feed chlorine content nor intentionally induced increases or decreases (via adjusting the mixed plastics content of MSW, spiking with PVC and salt additions) significantly affected the PCDD/F concentrations in MWC flue gas. Since few chlorine-induced changes in either PCDD/F composition or quantity were found, spiking tests failed to illuminate a relationship and there is no consistent relationship between chlorine and PCDD/F in MWCs; the requirements for probable causality have not been met. Changes in chlorine content did not induce discernible changes in PCDD/F emissions from MWCs.

Medical Waste Incinerators [MWI]

The signatures were generally the same at individual sampling locations (uncontrolled secondary chamber outlet, air pollution control system [APCS] inlet and outlet) within each of the 24 MWI facilities in the database. The signatures before and after the air pollution control equipment were sometimes different; however, the changes were not related to changes in chlorine content of the feed.

No relationship was found between chlorine and PCDD/F stack concentrations at most MWIs as shown in Figure 5. One facility displayed an increase and one a decrease; the balance displayed no change. When the data from all MWIs in the database is combined using blocking variables to account for facility and sampling location differences, a statistically significant negative relationship is found between uncontrolled HCl concentrations and the natural logaritlun of molar PCDD/F concentration. If this relationship is true, increasing the chlorine fed to MWIs would decrease PCDD/F emissions. This negative relationship may be a data artifact and not a real effect, since current PCDD/F formation theories do not provide a scientifically defensible explanation for this finding.

This study found no statistically significant relationship between the composition or amount of PCDD/F emitted from MWIs and the level of chlorine in the waste feed.

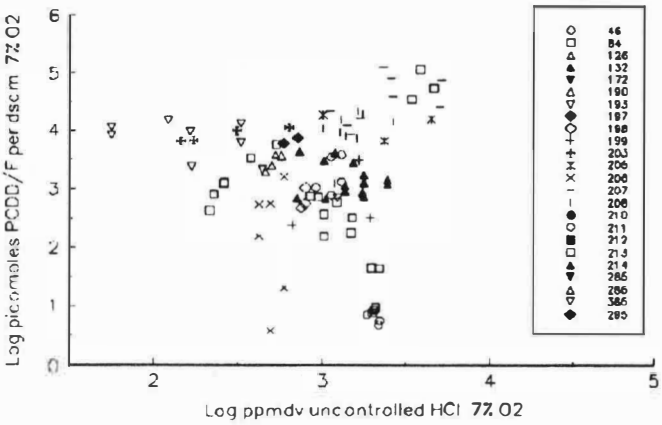

FIGURE 5. SCATTER PLOT SHOWING THE LOG OF PCDD/F MOLAR CONCENTRATION VERSUS UNCONTROLLED HCl CONCENTRATIONS.

Hazardous Waste Combustors [HWC]

The complete dioxin signatures are essentially the same for all Hazardous Waste Incinerators [HWIs] regardless of design, the APCS employed, or the chlorine concentration in the incinerator feed. Chlorine feed concentrations in the waste ranged from virtually zero to about 80 percent.

A few signatures are different. These differences are mostly attributable to different numbers of congeners with BDL values

in individual signatures and represent characteristic method limitations rather than real information about the isomer distribution. There was no relationship found between chlorine and arrangement of signatures that differed by more than method variability.

Scatter plots with regression overlays were used to display the relationship between total moles of dioxins emitted and percent chlorine in the feed. The overall plot (Figure 6) shows the variable behavior found for each combustor: 17 of 32 facilities display no relationship; 5 facilities show an increase in PCDD/F concentration with increased chlorine in the feed; and 5 facilities show a decrease with increasing feed chlorine concentration. Overall, the data suggests a decrease in PCDD/F concentration with increasing chlorine feed. These results point out the complexity of the PCDD/F:chlorine question.

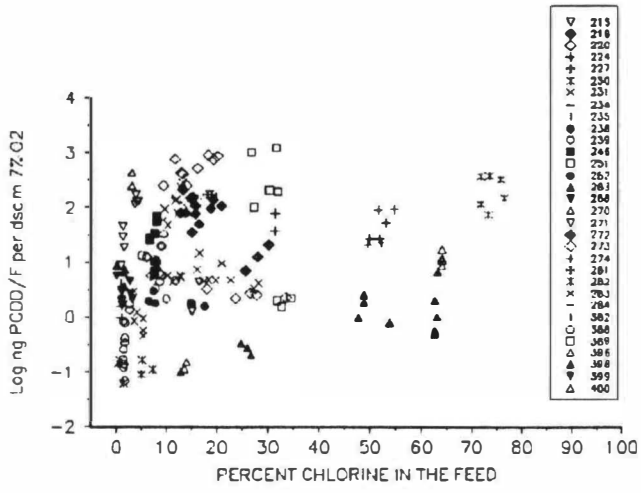

FIGURE 6. SCATTER PLOT SHOWING THE LACK OF RELATIONSHIP BETWEEN PERCENT CHLORINE FEED AND MASS OF PCDD/F EMITTED.

Signatures for the four hazardous waste fired boiler units [HWB] in the database were separated by plant. Since these boilers range from modified package boilers firing only hazardous waste to a pulverized coal-fired boiler with 10 percent liquid hazardous waste co-firing, the separation is probably the result of combustor design differences. Figure 7 is a scatter plot of the natural logaritlun of molar PCDD/F concentration versus percent chlorine in the feed. It displays a statistically significant decrease in PCDD/F with chlorine in the feed. Given the differences in boiler design, this is probably a data artifact as there is presently no PCDD/F formation or destruction theory to explain this behavior.

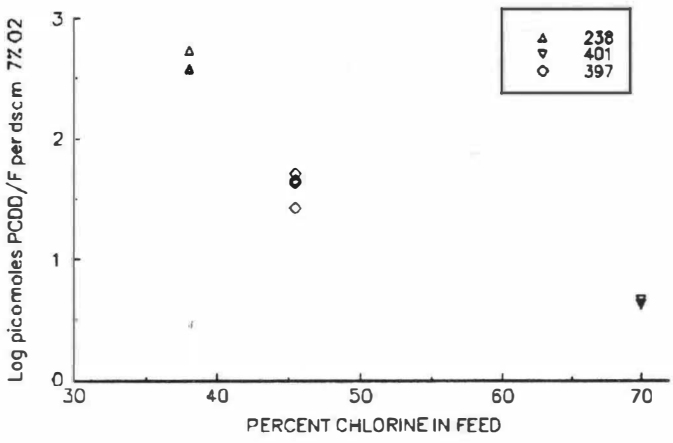

FIGURE 7. SCATTER PLOT SHOWING THE RELATIONSHIP BETWEEN MOLAR PCDD/F CONCENTRATION AND THE PERCENT CHLORINE IN THE BIOMASS BURNED.

Method 26 cannot be used to accurately estimate HCl concentrations for cement kilns [CK] because sufficient ammonium and cations penetrate the filter and are caught in the impingers to account for the measured chlorides. Because chlorine cycles within cement kilns--volatilized metal chlorides condense on the counter current feed and are reintroduced into the very hot burning zone where they again volatilize-- the chlorine feed cannot equal the gas phase chlorine under steady state conditions. However, it is proportional. The relative chlorine feed rate, pounds chlorine per ton of clinker produced, was used to characterize chlorine feed rate to CK. The signatures for some different CK types are separated by a greater Squared Euclidean Distance coefficient than method imprecision explains indicating that there may be different fundamental PCDD/F formation mechanisms involved in different types of CK. CK generally display a negative relationship, as shown in Figure 8,

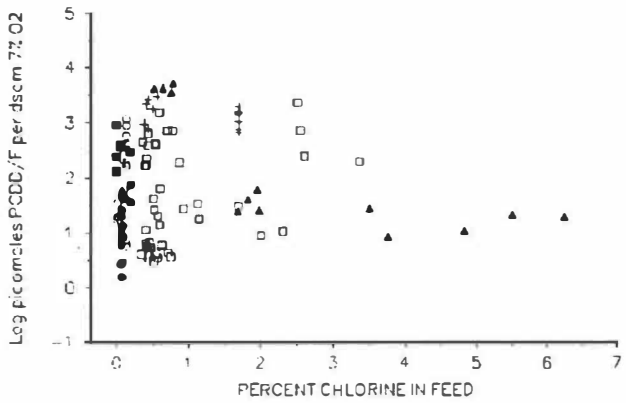

FIGURE 8. SCATTER PLOT SHOWING THE RELATIONSHIP BETWEEN PCDD/F CONCENTRATIONS AND CHLORINE FEED RATE IN CK.

between relative chlorine feed rate and dioxin emissions. The one plant that showed any chlorine effect displayed a statistically significant reduction in PCDD/F concentration with increasing relative chlorine feed rate.

HWCs generally show no relationship between PCDD/F and chlorine, but some individual HWI facilities display either an increase or decrease with increased chlorine in the feed. HWBs show a decrease in PCDD/F with increased chlorine which may be due to boiler design differences rather than a real phenomenon. CKs display either no relationship or decreasing PCDD/F with increasing chlorine.

Biomass Combustors [BMC]

The limited BMC data in the database show that neither PCDD/F composition nor concentration are related to chlorine content in the feed. Deliberately spiking with Pentachlorophenol [PCP] at Northwood, B.C. produced only two detectable PCDD/F homologues at the highest spiking levels. At Elk Falls, when salt laden wood chip was augmented with even higher chlorine content pulp mill sludge, PCDD/F emissions decreased. Data from the other BMCs show comparable PCDD/F emission levels; however, neither the chlorine content of the biomass fuel nor HCl was measured. No firm conclusions can, therefore, be drawn from these tests.

OVERALL FINDINGS

This effort brought together much of the available information on PCDD/Fs and chlorine in waste combustion systems. It was assembled in a database in consistent units and analyzed in a consistent, statistically and technically valid fashion. This effort evaluated the relationship between PCDD/F concentrations in flue gas streams with feed chlorine concentration. It was not designed to address the relationship between chlorine and PCDD/F in liquid effluents like residue quench waters and wet scrubber blowdown or solid residues leaving facilities. These questions could be addressed to determine if removal processes explain the lack of an observed relationship in the gas streams.

Drastic changes in waste stream and flue gas chlorine content only produced a few differences in PCDD/F composition that exceeded measurement method imprecision. These differences were generally explained by sample location or number of BDL values in the signature. Quantity differences were uncovered, but they were so inconsistent and contradictory that it is impossible to conclude that increasing chlorine content is associated with increasing PCDD/F concentrations in commercial facilities. In fact, given that the scientific method relies on counter examples to disprove theories, the failure to find simultaneous increases in most cases and the finding of inverse relationships in a few indicates that any effect chlorine has on PCDD/F emissions is smaller than the influence of other causative factors. That is, whatever effect chlorine has on PCDD/F in commercial scale system gaseous combustion products is masked by the effect of APCS temperature, ash chemistry, combustion conditions including localized flow stratification, and measurement imprecision. Changing the amount of chlorine in waste streams did not have a discernible impact on PCDD/F emissions from waste combustors.

ACKNOWLEDGMENT

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