IS THERE A STRONG DIOXIN:CHLORINE LINK IN COMMERCIAL SCALE SYSTEMS?

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1. Introduction

Full scale dioxin emissions test results from municipal waste combustors [MWCs], medical and hazardous waste incinerators [MWIs & HWIs], cement kilns [CKs] and boilers and industrial furnaces [BIFs] burning chlorinated hazardous waste and biomass (e.g., wood and straw) combustors [BMCs] were assembled, put into common units and analyzed to determine if changes in feed chlorine content produced either statistically or practically discernible changes in dioxin isomer distribution or mass emission rate (total and ITEQ basis).

The full report[1)] provides an analysis of the data and a discussion of the statistical techniques employed; all the data employed are provided in appendices. Neither this paper nor the underlying study address PCDD/F in residues or liquid effluents. Multipathway health risk assessments usually find that stack emissions predominate the PCDD/F risk contribution. Consequently, the focus on the gaseous products of combustion is not believed to be a serious limitation.

2. Data Acquisition & Standardization

Information in Rigo & Rigo Associates, Inc.'s proprietary emissions database of more than 10,000 runs from more than 450 plants and up to 300 pollutants, and the emissions database assembled by Energy & Environmental Research Corp. [EER] in support of the Combustion Emissions Technology Resource Document[2)] was augmented by data gleaned from complete emissions test reports and summary reports provided by plant owners, researchers and regulators in the United States, Canada and Europe. More than 1,900 sets of PCDD/F measurements, taken along waste combustion system gas paths (e.g., furnace outlet, boiler outlet, economizer outlet, various points in the air pollution control system [APCS] and the stack) were used. Concentrations were expressed in USEPA regulatory units—ppm_{dv} for gases, such as HCl; mg/dsm^3 for particulates; and ng/dsm^3 for PCDD/F congeners and homologues—and standardized to 20°C, 760 mm Hg, dry and 7% O_2. Half the detection limit was used for below detection limit values [BDL] in calculations. PCDD/F concentrations were also expressed on a molar basis. Facility characteristics, test method descriptors, 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) were also databased.

3. Data Analysis

The same objective statistical methods were consistently applied to each data set to determine if a discernible effect of waste feed chlorine content on PCDD/F emissions at commercial waste combustion facilities could be found by considering the following two hypotheses:

- does composition (signature) change with chlorine, and
- does the quantity of PCDD/F emissions change with chlorine?

If no consistent, statistically significant relationship can be found between chlorine and either the composition or quantity of PCDD/Fs in the gases, then no overall effect is observable.

The composition signatures used as many of the following three descriptor sets as could be computed:

- the congener fractions, 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;
- the 2,3,7,8 ratio, defined as the sum of all 2,3,7,8 Substituted Congeners to the Total PCDD/F; and
- the homologue fractions, defined as the ratio of each homologue total to the Total PCDD/F.

Signatures were calculated on a molar basis.

Cluster analysis was used to compare the relative congener and homologue signatures for an individual facility and all similar facilities. Cluster analysis is a technique that compares entire patterns. The Squared Euclidean Distance (the sum of the squares of the differences between each signature component) was used. Monte Carlo simulation was used to calculate a criterion to identify signatures that exceed measurement method imprecision for individual isomers and homologues[3]. 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 involved 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. The number of false positives was minimized by using multiple means comparison techniques, such as using the Studentized Maximum Modulus Statistic instead of the t-statistic, when developing critical values for differences.

Townsend[4] summarized much of the seminal work and concluded that PCDD/F can be formed from precursors in the gas phase, be made on catalyzed surfaces or developed within the solids themselves. Once made, PCDD/F can partition to the solids removed in the APCS or be emitted with the flue gas. They can also be chlorinated or dechlorinated as they pass through the process system. Other work points to the importance of good combustion. All these mechanisms and phenomena work simultaneously. If relevant phenomena are ignored when looking at such complex data, causality can be misattributed. For example, Burns[5] reported a chlorine (PVC) link in some bench-scale testing. However, the original experimenters[6] observed that companion high PVC runs exhibited low PCDD/F concentrations and the high PCDD/F run was characterized by CO spiking which indicates upset combustion conditions. In short, collinear effects, like the simultaneous reduction in APCS operating temperature and gaseous HCl concentrations by scrubbers, or

abrupt changes in waste composition inducing formation mechanism changes, must be recognized and reconciled by the analysis to avoid false attributions of causality.

Designed experiments with varied operating parameters (parametric tests), collinearity (variables responding together like lower flue gas temperatures and scrubbing) and confounding factors (different sampling locations or combining data from different units or time frames) are readily handled using ANOVA techniques. Both continuous variables (e.g., flue gas temperature and oxygen content) and discrete binary variables (e.g., variables which take on a value of 1 when a condition is true—a 5% PVC spike, for example, or a value of 0 when it is false—normal MSW is being burned) are used to describe an experiment. Statistically significant coefficients indicate that the variable or condition being captured has an effect; otherwise, they do not.

4. Findings

Data from 59 **Municipal Waste Combustion** [MWC] facilities, taken at various points throughout the system, were analyzed. Comparison of the signatures within facility data sets found some test runs that differ from the bulk of the results by more than method imprecision. These differences were usually caused by a large number of BDL results which reflect sampling and analytic method limitations rather than composition. The remaining signature differences are associated with differing sampling locations (e.g., boiler outlet, stack, etc.). After accounting for sampling location effects, neither the normal range of operating conditions nor wide variations in feed material, including spiking runs with elevated or depressed chlorine content, caused any measurable change in PCDD/F signatures.

Parametric and spiking studies shed light on the effect of varying feed chlorine content on the quantity of PCDD/Fs emitted by MWC facilities. Aggregated meta analysis of the data from the Danish and Dutch emissions inventories has been used to develop predictive equations that include HCl. When the confounding effects of APCS temperature are not considered, PCDD/F is shown to increase with increasing HCl and sulfur dioxide (a known PCDD/F formation retardant)[7].

In the full scale study at Würzburg, Germany[8], a state-of-the-art waste burning facility, no difference was found between either the PCDD/F isomer profile or concentration when burning only MSW or MSW augmented with either 7.5 or 15 percent mixed plastics enriched to 10% PVC.

The Pittsfield experiment[9] looked for a relationship between PVC feed content and PCDD/F emissions. The combustion of PVC-"free" material, regular waste and PVC-spiked waste all produced the same PCDD/F levels and concentrations. The design of the Pittsfield test must be considered since a simple plot of PCDD/F concentration versus measured HCl indicates a correlation which is the result of hidden variables—parametric changes in incinerator operating conditions. Once these effects are accounted for, no chlorine effect remains.

Trial burns using three types of densified Refuse Derived Fuels [dRDF], ranging from plastics-free through MSW to plastics-augmented fuels, were conducted at Sioux Center, Iowa[10]. There was no difference in PCDD/F emissions between fuel types.

In the Hørsholm study[11], PVC, salt and lime were spiked in a statistically designed, fractional factorial experiment. 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 also a gap in testing while the boiler was cleaned. Two test days apparently had 4 and 5 runs each. Analysis of the data revealed that too little time was allowed between changes in experimental conditions; each measurement is a complex mixture of an unknown number of previous conditions and the intended experi-

ment. Unfortunately, time series techniques cannot be applied to these data to compensate for the lagged effect; the runs were not conducted uniformly throughout the test period. When the first runs of each day are considered (runs that should have minimum cross-condition contamination), there is no effect of two levels of PVC spiking, one level of salt spiking or one level of lime addition.

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 or 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 do not induce discernible changes in PCDD/F emissions from MWCs.

The signatures were generally the same at individual sampling locations (uncontrolled secondary chamber outlet, APCS inlet and outlet) within each of the 24 **Medical Waste Incinerators [MWIs]** 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. One facility displayed an increase and one a decrease; the balance displayed no change. When the data from all MWIs in the database are 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 logarithm of molar PCDD/F concentration. If this relationship is true, increasing the chlorine fed to MWIs would decrease PCDD/F emissions. 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.

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. The chlorine feed concentrations ranged from virtually zero to about 80 percent.

A few signatures are different due to varying numbers of congeners with BDL values in the individual signatures. 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 PCDD/F emitted and percent chlorine in the feed: 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 suggest a decrease in PCDD/F concentration with increasing chlorine feed. These results point out the complexity of the PCDD/F:chlorine question.

Signatures for the four **Hazardous Waste Fired Boilers [HWBs]** 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. A plot of PCDD/F versus chlorine in the feed 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.

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Manual sampling methods cannot be used to accurately estimate HCl concentrations for **Cement Kilns [CKs]** because the measured chloride levels can be easily attributed to ammonium and cations that penetrate the filter and are caught in the impingers[12]. Because chlorine is cycled 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 CKs. 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 CKs. CKs generally display a negative relationship 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.

The limited **BioMass Combustor [BMC]** data in the database show that neither PCDD/F composition nor concentration are related to chlorine content in the feed. Deliberate 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 be drawn from these tests.

5. Conclusions

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 the 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 finding 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 emissions in commercial scale systems 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 does not have a discernible impact on PCDD/F emissions from waste combustors.

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References

1) Rigo, H. G., A. J. Chandler and W. S. Lanier (1995): The relationship between chlorine in waste streams and dioxin emissions from combustors. ASME-CRTD-Vol. 36.

2) USEPA (1994): Combustion emissions technical resource document (CETRED). EPA530-R-94-014.

3) Ruggenthaler, P., G. Kahr and T. Steiner (1994): Innovations in permanent monitoring of PCDD/PCDF from hazardous waste incinerators. Dioxin '94, Vol. 19, p. 45-48.

4) Townsend, D. I., J. D. Wilson and C. N. Park (1995): Mechanisms and formation and options for control of emissions of PCDD's/PCDF's from incineration. International Incineration Conference Proceedings.

5) Burns, D. B. (1993): Final report, consolidated incineration facility metals partitioning test(U). Savannah River Technology Center. WSRC-TR-93-00623.

6) Hassel, G. R., B. R. Springsteen, T. P. McGrath and R. G. Rizeq (1992): Rotary kiln simulator metals partitioning study. EER Contract Report for Westinghouse Savannah River Technical Center.

7) Huang, H. and A. Buekens (1995): Analyzing dioxin measurement data in municipal waste incineration using multiple regression analysis. Dioxin '95, Vol. 23, p. 455.

8) Mark, F. (1994): Energy recovery through co-combustion of mixed plastics waste and municipal solid waste. PWMI, European Centre for Plastics in the Environment.

9) Midwest Research Institute (1987): Results of the combustion and emissions research project at the Vicon incinerator facility in Pittsfield, Massachusetts. Prepared for New York State Energy Research and Development Authority.

10) Pacific Environmental Services, Inc. (1989): Results of emissions testing while burning densified refuse derived fuel, Dordt College, Sioux Center, Iowa. Prepared for Council of Great Lakes Governors.

11) Miljoministeriet Miljostyrelsen (1989): Klorkilders betydning for dioxindannelse ved forbaending. Miljoprojekt n. 118.

12) Entropy Environmentalists, Inc. (1994): FTIR and Method 26 emission test, Southdown Incorporated, Dixie Cement Plant, Mail Kiln Stack, Knoxville, Tennessee. Prepared for Southdown, Inc.