ABSTRACT

The Relationship Between Chlorine in Waste Streams and Dioxin Emissions from Waste Combustor Stacks

This study investigated the impact that waste feed chlorine content and waste stream components, including PVC plastics and salts, have on PCDD/F concentrations in the flue gases at waste combustion facilities. The effort was not intended to develop emission factors, evaluate control system performance or assess PCDD/F relationships in liquid effluents or solid residues. The data were mostly obtained from full-scale tests. Seminal laboratory studies were used to suggest the form relationships might take and help identify significant confounding factors which must be taken into account.

Over 1,900 Municipal Waste Combustor [MWC], Hazardous Waste Incinerator [HWI], Medical Waste Incinerator [MWI], Hazardous Waste Fired Boiler [HWB], Cement Kiln [CK], Biomass Combustor [BMC], and Laboratory- Bench- and Pilot-Scale Combustor [LBP] test results from 169 facilities, many with multiple units, were analyzed to determine whether there is a relationship between stack gas PCDD/F concentrations and chlorine input or uncontrolled gas phase chlorine concentration as a surrogate. Chlorine feed concentration ranged from less than 0.1 percent for many BMC up to 80 percent for some HWI. The chlorine feed concentration was between these two extremes for most of the other sources and generally spanned an 8: 1 range in each category .

The data were carefully checked to identify errors and statistical outliers, standardized to common reference conditions and analyzed to determine if there were any changes in either the signature (composition) or quantity of PCDD/F concentrations. Changes that were greater than measurement method imprecision were studied to determine whether they were related to differences in waste stream or flue gas chlorine content.

Detailed analysis of the signatures was done using Cluster Analysis. Signatures for data collected at the same sampling point within a combustor family (i.e., MWC, HWI, etc.) were all the same unless the run produced a significant number of below detection limit values. Some facilities displayed signature differences exceeding PCDD/F measurement method imprecision between sampling locations. No observable changes in PCDD/F profile were associated with differences in chlorine content.
A general review, using a combination of Canonical Correlation Analysis and simple Linear Regression, found no statistically significant relationship between chlorine input and PCDD/F stack gas concentrations for the majority (80 percent) of the 90 facilities which had sufficient simultaneous data to detecT a statisfically significant trend. Eleven percent displayed an in- crease; 9 percent of the facilities displayed decreasing PCDD/F concentrations with increasing chlorine.

Analysis of Variance [ANOV A] and combustion engineering models were combined using Multivariant Linear and Autoregressive Regression to analyze three major controlled experiments at Municipal Waste Combustors during which PVC, mixed

plastics or salt was spiked into the feed. No statistically significant relationship was found between PCDD/F concentrations and chlorine in two of the experiments. In the third, a relationship was found when the PVC was sufficient to raise the chlorine content to about 10 times that normally found in MWC's. This data set displays severe autocorrelation (run-to-run memory effects), so the ob- served effect may be due to something other than the spiking.

Similar techniques were employed to analyze the results of the major parametric MWC studies conducted under the auspices of Environment Canada, Environmental Protection Agency, New York State Energy Research and Development Authority and the Great Lakes Regional council of Governors. No statistically significant relationship between PCDD/F concentrations in the products of combustion and chlorine input was found in the data from these studies.

The same mixed picture is found for MWI's with 15 percent showing an increase and 7 per- cent showing a decrease in PCDD/F concentrations in the stack gases with increasing chlorine feed.

HWI's taken as a whole show no observable relationship between PCDD/F and chlorine concentrations in the waste being burned. Examination of individual facilities reveals that some have been tested over a 10: 1 range of chlorine contents, \!P to almost 80 percent chlorine, and display no discernible relationship. Eighteen percent of the HWnacilities, however, showed an increase, while 18 percent showed a decrease with increasing chlorine feed.

Cement Kilns displayed no apparent stack gas PCDD/F concentration increase with increasing chlorine feed rate. This is not surprising, since chlorine is frequently added to remove natural alkalis and produce Portland cement meeting federal and state construction standards.
The waste fired boilers showed decreasing PCDD/F concentrations with increasing chlorine, but boiler design and cofiring fuel differences confound this finding.

Biomass combustors produce PCDD/F, but there is too little simultaneous PCDD/F and chlorine data to determine if there is a general trend. One test replacing salt laden wood with higher chlorine sludge displayed reduced PCDD/F concentrations in the stack gases.

While some laboratory experiments show that there is a functional relationship between chlorine input and PCDD/F concentrations in the products of combustion under certain conditions, the effect is much smaller than the effect of confounders like combustor design, operating practices and the normal variability found in emission measurements made at commercial scale systems.

Whatever effect chlorine has on stack gas PCDD/F concentrations from waste combustors is masked by these other variables. Discernible changes and consistent

improvements in PCDD/F waste combustor stack concentrations are unlikely to be realized by reducing waste chlorine content.