

Is There a Meaningful Relationship Between Chlorine Feed and Non-Dioxin Stack Emissions?

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INTRODUCTION

The American Society of Mechanical Engineers' Center for Research and Technology Development (ASME/CRTD) published an extensive analysis and tabulation of available dioxin and chlorine in late 1995¹. The preponderance of that data produced no meaningful relationship between dioxin stack emissions and chlorine feed across a broad range of commercial waste combustor types. In the Preamble to the April 1996 proposed Hazardous Waste Combustor Rule, EPA acknowledged that changes in chlorine feed have little effect on dioxin emissions², but the text goes on to speculate that reducing chlorine input is still a good idea because fewer metals and chlorinated organics might be emitted.

Given that the conventional wisdom — reducing chlorine input to full scale facilities will reduce dioxin emissions — proved groundless when the available data were examined in a consistent manner, what does the available data tell us about the relationship between chlorine feed rate and municipal waste combustor (MWC) stack emissions in general? Product substitution and waste component diversion programs are expensive and economically disruptive at current levels. So, the likelihood of achieving any benefit needs to be determined before public policy changes are made. If there is no significant relationship between chlorine feed rate and stack emissions, then efforts to reduce chlorine feed are unlikely to reduce the trace levels of contaminants that leave state-of-the-art MWCs. Interventions to reduce chlorine feed rate would simply cause society to squander its scarce resources chasing ghosts.

APPROACH

The ASME/CRTD analysis used a segment of a much larger emissions database that contains emitted concentrations for a host of non-dioxin pollutants. These data can be subjected to the same analysis used in the ASME/CRTD report to determine if there is a meaningful relationship between chlorine input and MWC stack emissions.

Database Characteristics

All database entries are from the most reliable information available. Whenever possible, emitted concentrations are calculated directly from analytic laboratory reports and field data sheets to avoid intermediate transcription, rounding and interpretation problems. The databased values are brought to USEPA standard reference conditions (dry, 20°C, 1 atmosphere, 7% O₂) and compared to reported concentrations as a quality assurance check. In addition, the database is routinely screened for outliers — unusually large or small results. Potentially aberrant results are checked and corrected whenever possible. Remaining outliers are flagged so that their effect on subsequent data analysis can be determined.

Metals, volatile and semivolatile organics and criteria pollutant concentrations are covered to varying degrees in the database. The metals include those in the Clean Air Act Sections 112 and 129 lists along with additional environmentally sensitive metals listed in 40 CFR 266, the Boiler and Industrial Furnace Rule, and the European Union standards. Trace organics include much of the Section 112 Organic Hazardous Air Pollutants (HAPs) list along with data on other trace organics collected as part of broad-scope emissions assessments and research programs.

Below Analytic Laboratory Detection Limits Results

Much of the trace organics data are below analytic laboratory detection limits (ADL). Traditional analytic laboratory practice involves establishing the detection limit for their instruments. An instrument response that is less than 2.5 to 3 times the noise (variability) established by repeatedly analyzing samples without the pollutant present is not distinguishable from a sample with the pollutant absent. Analytic laboratories report these values as below detection limits (BDL). Some labs go a step further

following ASTM³ practice and identify results between the ADL and a value 3.33 times higher as tentative since the variability is too large to provide reasonable assurance that the measured value is within 30 percent of the true value. When the ADL is converted into an equivalent emitted concentration using standard data reduction procedures, it is called the analytic laboratory detection limit equivalent concentration or ADLE.

When two below ADLE results are compared, source characteristics are not involved. Rather the comparison is between the low level quantitation capabilities of the instruments and laboratories involved. Such results must be excluded from the statistical data analysis since they provide no useful information on the relationship between MWC stack emissions and chlorine. Below ADLE results are excluded so that relationships are neither caused nor hidden by laboratory detection limit differences and random chance.

A fully correct analysis should also exclude data that are below the Reference Method Practical Quantitation Limit (RMPQL). The ADL inherently considers only analytic laboratory procedures and instrument responses. Emitted concentrations, on the other hand, have a whole host of additional sources of variability — for example, spatial differences within the stack, velocity pressure and flue gas molecular weight determination errors, residual sampling train contamination, recovery losses, matrix differences, sample volume and diluent measurement errors, laboratory concentration procedure and sample clean-up errors, etc. — in addition to the instrument limitations considered by the ADL. These sources of variability raise the concentration that can be accurately quantified.

EPA Method 301⁴ describes the practical quantitation limit (PQL) as “the lowest level above which quantitative results may be obtained with an acceptable degree of confidence.” A reasonable degree of confidence is defined in Method 301 as 99 percent of replicated results being within 30 percent of the average value. The PQL is determined by analyzing paired test results obtained by operating, recovering and analyzing two or more simultaneous sampling trains. The “lower limit of the test method” is, by definition, equal to the PQL.

Results that are between the ADLE and the PQL are too variable to provide any meaningful information. They are so noisy that any relationships uncovered between the ADLE and the PQL are as likely to be attributed to data noise (random chance) as they are to the phenomena being investigated. Unfortunately, EPA has not determined the PQL for Methods 23, 26 and 29. Consequently, all results above the ADLE have been treated as valid numbers in this analysis.

Analysis of dual and quad train testing sponsored in part by the ASME Research Committee on Municipal and Industrial Waste indicates that the median PQL to ADLE ratios are 10, 3,000 and 120 for Methods 23 (dioxins, chlorobenzenes, PAHs and other semivolatile compounds); 26 (HCl, Cl₂, HF and HBr); and 29 (Section 112, BIF and EU) results respectively. The controlled metals data are probably sufficiently accurate for this analysis; the uncontrolled HCl and trace Organic HAPs analyzed may be sufficiently noisy that really firm conclusions are not possible.

Chlorine Input

Determining the chlorine concentration of a particular batch of MSW burned during a test run is virtually impossible. Previous analysis of MWC data shows, however, that there is a strong correlation between chlorine feed measurements and uncontrolled flue gas HCl concentrations. The starting amount of chlorine available for participation in organic chlorination reactions and formation of metal chlorides is the amount released from the MSW (not bound up with the bottom ash). Also, the uncontrolled HCl concentration is usually large compared to the amount of chlorine that is associated with uncontrolled MWC fly ash. Consequently, uncontrolled HCl is used as a proxy for chlorine feed rate.

Statistical Techniques

The techniques used in the ASME/CRTD study to investigate the relationship between dioxin feed rate and dioxin stack emissions can be applied to these as well. Those analyses included: Spearman Rank-Order and Partial Correlation Analysis, Analysis of Variance (ANOVA) and Factor Analysis to find whatever relationship might exist between chlorine input and stack dioxin concentrations.

The major parametric studies which required ANOVA techniques to sort out confounding effects do not generally include metal or other trace organics emissions. Instead, partial correlation techniques were employed to sort out the effect of readily discernible differences like the type of air pollution control device (APCD) and designed interventions (e.g., purposely running the afterburner at low temperature for research purposes), from whatever effect chlorine feed might have on non-dioxin pollutant emissions. Factor Analyses were not performed due to the sparse nature of the data. To be reliable, Factor Analysis requires that all the parameters being investigated be complete. When there are significant data gaps, the analysis can still be mathematically performed, but the interaction terms are not fully characterized and the results can be misleading.

Spearman Rank-Order Correlation techniques were used to perform most of the analyses. Here, rank orders rather than absolute values of data sets are compared. This method has the advantage of not requiring precise knowledge of the underlying data distribution. Regardless of whether the data are normally, lognormally or otherwise distributed, the rank order of each data point remains the same. Sidestepping the distribution type question simplifies the analysis without losing any ability to uncover a relationship if one exists. Whenever Spearman Rank-Order Correlations could not be performed, the natural logarithms of the data were used, since it is well known that emissions data are usually lognormally distributed.

Statistically significant correlations are ones whose significance level are less than 5 percent. This is a way of saying that we are 95 percent confident that the correlation is significant. Since this is an exploratory data analysis, we have to be aware that one in 20 comparisons will be “significant” due to chance alone. To avoid the problem of finding false positive results while minimizing the chance of declaring there is no relationship when one is really present, we used the False Discovery Rate (FDR) procedure⁵. This is a refinement of Bonferroni which scales the significance level from $\alpha = 0.05$ found in most EPA regulations by the total number of comparisons (n) to be made and the rank order (i) of the significance level determined for a specific comparison:

$$\alpha^* = i\alpha/n \quad (1)$$

The FDR criteria effectively increases the required level of significance as the number of less significant comparisons already made increases. The advantage compared to other techniques that use a single threshold value is an increased potential for finding meaningful relationships that could otherwise be lost using a more conservative screening criteria while still avoiding the problem of finding a large number of false positives.

Just because a relationship is statistically significant does not mean that it is practically significant. The amount of change seen in one variable as a result of a change in the other is explained by the square of the correlation coefficient. As a result, with large data sets, statistically significant relationships can explain practically inconsequential portions of the total observed response.

For each statistically significant relationship, a scattergram was produced and a loess line — a localized regression fit through the nearest 25 percent of the data on each side of an uncontrolled HCl concentration — was added to determine if a threshold is apparent. A loess line that is flat at one end

followed by rapid rising is evidence of a threshold effect. When the loess line flattens out again, this is an indication that different mechanisms are at work. A continuing straight line indicates the relationship is valid over the data range. Separate loess lines were fit through data from facilities equipped with high efficiency particulate control devices and those that were not to separate that effect in the plots.

RESULTS

The 28 databased HAPs and pollutants found in other country's regulations with enough simultaneous uncontrolled HCl and emitted concentration data to support analysis are tabulated in Table 1. The number of paired data points and the strength of the relationship (squared partial correlation coefficient) with uncontrolled HCl as a chlorine feed surrogate are included along with available melting and boiling temperatures for metal chlorides.

Scatterplots contrasting Section 112 HAP and uncontrolled HCl emissions are provided for all pollutants displaying a statistically significant relationship.

Metal Emissions

Figures 1 through 7 are scatterplots for analyzable Section 112 and 129 metal emissions versus uncontrolled HCl concentrations that show a statistically significant relationship. In each plot, data collected at facilities equipped with high efficiency particulate control devices (fabric filters and large electrostatic precipitators) are plotted as solid points. The balance of the data, principally from low efficiency electrostatic precipitators, are plotted using open symbols. While some plots show roughly an order of magnitude difference between these two data sets, the majority of the results are interleaved. This indicates that either the volatilization and condensation mechanism often ascribed to chlorine is not applicable to commercial scale systems or state-of-the-art air pollution control devices are efficient enough that this mechanism becomes essentially irrelevant.

The lack of applicability of the volatilization mechanism to MWCs is illustrated by the metal chloride boiling point data in Table 1. For metals showing a statistically significant relationship with uncontrolled HCl, after controlling for known confounding factors, the metal chlorides boil between 130 and $>1,600^{\circ}\text{C}$ while those that show no such relationship have metal chloride boiling points between 12 and $1,560^{\circ}\text{C}$. There is no obvious relationship between increased releases and the metal chloride boiling point.

Most of the loess curves show either a hockey stick or a S-type pattern. Metal concentrations are initially flat, rising rapidly between 600-800 ppm_{dv} @ 7% O₂ uncontrolled HCl concentrations and then flatten again. This indicates that there is either a change in mechanism taking place or, alternatively, this effect could be a data artifact. A data artifact could be caused by distinct plant or test method differences above and below 600-800 ppm_{dv} @ 7% O₂.

Inspection of source descriptions and test reports indicates that design differences are probably not the cause, but the possibility cannot be ruled out. Interestingly, the majority of the higher uncontrolled HCl data tend to be from European MWCs. Thus, sampling method variations are a credible explanation. For the purposes of this paper, this possibility will be ignored.

Even though statistically significant relationships exist between chlorine and some metals, those relationships are not practically significant. For example, only 11 percent of the variability in cadmium concentrations, the most strongly related Section 129 HAP, is explained by changes in uncontrolled HCl concentration after design and location differences were accounted for in the partial correlation analysis. For lead, only 7 percent of the variability is accounted. Mercury is not statistically related to

uncontrolled HCl concentrations in this data set even though it is believed that mercury chloride is more readily captured than elemental mercury. These observations provide a strong indication that other mechanisms predominate.

Turning to the other Section 112 metals, antimony and selenium are the most strongly related. Here around 50 percent of the variability is explained by changes in uncontrolled HCl concentrations. The other Section 112 metals exhibiting statistically significant relationships also have practically insignificant relationships.

Trace Organic HAPs

Figures 7 and 8 display the simultaneous data for Section 112 trace organic HAPs that are statistically significantly related to uncontrolled HCl concentrations. The strongest relationship is for 1,4 dichlorobenzene, and that relationship is negative. That is, increasing uncontrolled HCl concentrations is associated with reduced 1,4 dichlorobenzene concentrations. This entire relationship could be nonsense since 1,4 dichlorobenzene is a contaminant in the North American supply of dichloromethane used in the laboratory extraction and clean-up technique.

Total chlorobenzenes, as a surrogate for the Section 112 HAP monochlorobenzene, on the other hand, are statistically significantly related to uncontrolled HCl concentrations after accounting for confounding effects. As a practical matter, however, they are found at environmentally insignificant stack concentrations and only 24 percent of the variability in this pollutant is explained by changes in uncontrolled HCl. Interestingly, 2,3,7,8 TCDD shows neither a statistically significant (significance level 0.2 for a statistical confidence level of 80 percent) nor a practically significant relationship (5 percent of the variance is explained after controlling for confounding factors) to uncontrolled HCl. So, while total chlorobenzenes are sometimes used as surrogates for dioxin emissions, they probably should not be.

CONCLUSION

The same techniques that found no statistically significant relationship between dioxin and chlorine in combustor stack emissions have found a transition in emitted concentrations when uncontrolled chlorine concentrations are around 600 ppm_{dv} @ 7% O₂. On either side of this bound, there is no significant relationship. Since there is no theoretical reason to expect a step-type threshold effect, these conclusions may be a data artifact caused by differences in European (much of the high uncontrolled HCl concentration data) and North American (much of the low uncontrolled HCl concentration data). In any case, the metals showing a statistically significant relationship that is also practically meaningful are not environmentally significant. So, interventions to reduce MSW's chlorine content for the purpose of reducing metal emissions are unlikely to improve the environment. The same finding is reached for trace organic HAPs.

Analysis of the information in our database and review of the Regulatory Docket for the 1995 Emissions Guidelines indicates that current uncontrolled North American HCl concentrations are on the order of 550 ppm_{dv} @ 7% O₂. Consequently, it appears that little benefit would result from interventions to reduce the chlorine content of MSW, even if there were a meaningful chlorine—HAP link. No intervention for the purpose of reducing metal or trace organic HAPs emissions is indicated.

It must be realized, however, that the database employed in this analysis, as extensive as it is, only has a small amount of applicable data. Further work is needed to reach very strong conclusions. The available

information indicates that such an effort is unlikely to discover that significant reductions in metal emissions will be realized by reducing the level of chlorine in North American MSW. Nevertheless, such research is encouraged to minimize the chance that erroneous public perceptions rather than sound science will drive regulatory efforts.

REFERENCES

1. H.G. Rigo, A.J. Chandler, and W.S. Lanier, The Relationship Between Chlorine in Waste Streams and Dioxin Emissions from Waste Combustor Stacks, ASME, CRTD-36, August 1995.
2. Federal Register, V. 61 NO77, April 19, 1996.
3. ASTM, Method D4210-83, Standard practice for Interlaboratory Quality Control Procedures and a Discussion on Reporting Low-Level Data.
4. Method 301—40 CFR 63, 9.1.2, Appendix A. Method 301 Field Validation of Pollutant Measurement Methods from Various Waste Media.
5. V. Williams, L. Jones and J. Tukey, "Controlling Error in Multiple Comparisons," with Special Attention to the National Assessment of Educational Progress, National Institute of Statistical Sciences, Technical Report, #33, December 1994.

Table 1. Correlation results for uncontrolled HCl versus metals and HAPs.

Pollutant	n	significance (2-tail)	RDF significance criteria	result significant?	signed squared correlation coefficient	metal chloride melting point	metal chloride boiling point
Silver	36	0.0028	0.013	yes	25%	455	1500
Aluminum	34	0.0000	0.005	yes	52%		177.8
Arsenic	52	0.0124	0.021	yes	13%	-8.5	130.2
Boron	37	0.0533	0.027	no	11%	-107.5	12.5
Barium	35	0.4391	0.043	no	-2%	963	1560
Beryllium	14	0.6528	0.046	no	-2%	405	520
Calcium	23	0.0000	0.007	yes	64%	752	>1600
Cadmium	65	0.0149	0.023	yes	11%	568	960
Cobalt	25	0.7109	0.048	no	1%	742	1049
Chromium	62	0.0031	0.014	yes	15%	824	
Copper	38	0.1109	0.032	no	8%	620	993
Iron	37	0.0000	0.002	yes	69%	674	
Mercury	101	0.0955	0.030	no	3%	276	302
Nickel	56	0.0099	0.020	yes	13%	1001	976
Lead	83	0.0222	0.025	yes	7%	501	950
Antimony	35	0.0000	0.004	yes	54%	283	602
Selenium	25	0.0004	0.011	yes	43%	305	288
Tin	26	0.0000	0.009	yes	54%	246	652
Zinc	93	0.1981	0.039	no	2%	283	732
Total Chlorobenzenes	35	0.0056	0.016	yes	24%		
1,2 Dichlorobenzene	12	0.1616	0.034	no	26%		
1,3 Dichlorobenzene	18	0.9718	0.050	no	0%		
1,4 Dichlorobenzene	17	0.0069	0.018	yes	-44%		
Total Hexachlorobenzene	33	0.5454	0.045	no	1%		
4 Methylphenol	11	0.1937	0.038	no	18%		
Napthalene	13	0.0694	0.029	no	32%		
Total Pentachlorophenol	33	0.2294	0.041	no	5%		
2,3,7,8 Tetrachlorodibenzo-p-dioxin	44	0.1899	0.036	no	-5%		

Figure 1. Relationship between antimony and uncontrolled HCl concentrations.

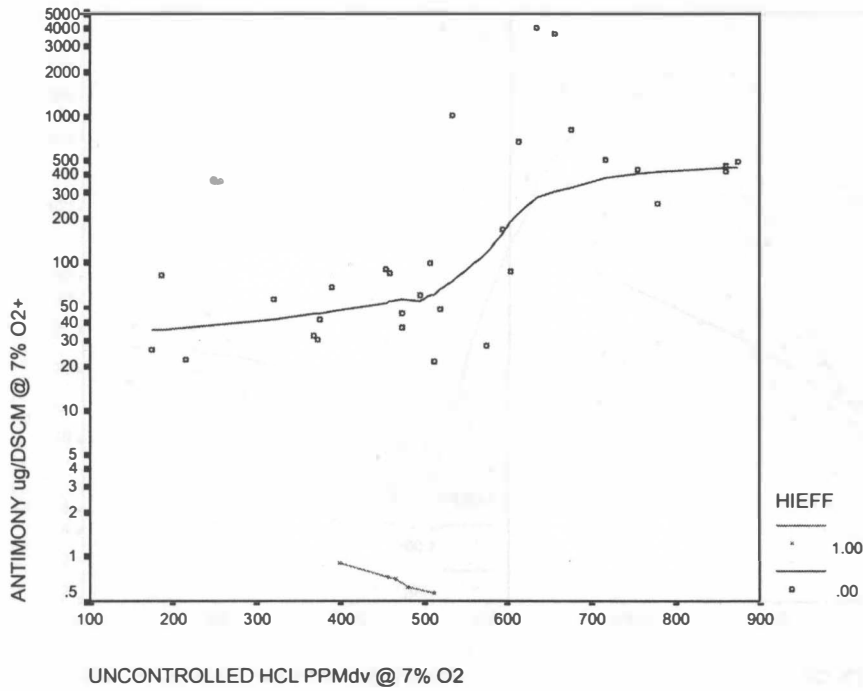


Figure 2. Relationship between selenium and uncontrolled HCl.

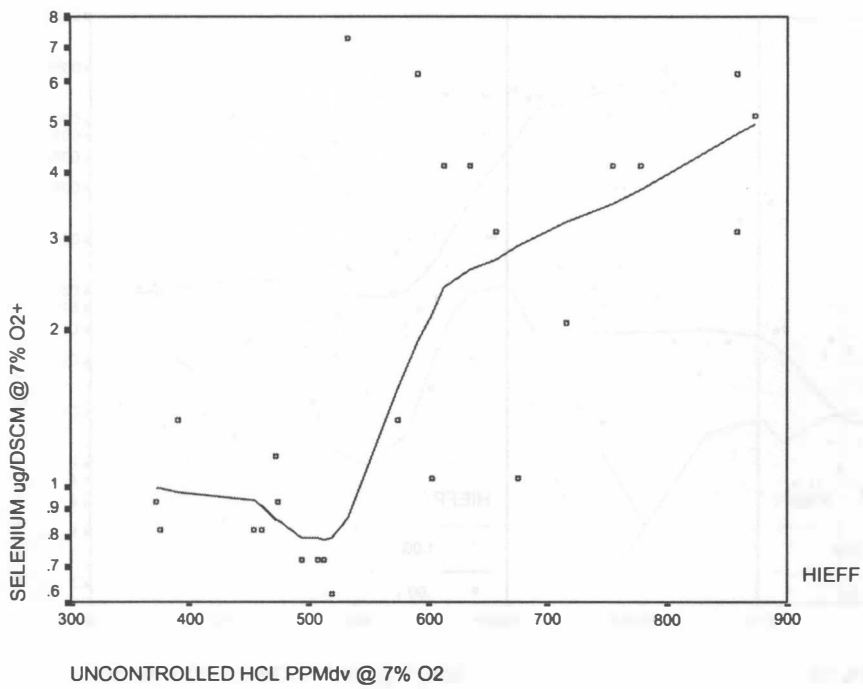


Figure 3. Relationship between chromium and uncontrolled HCl.

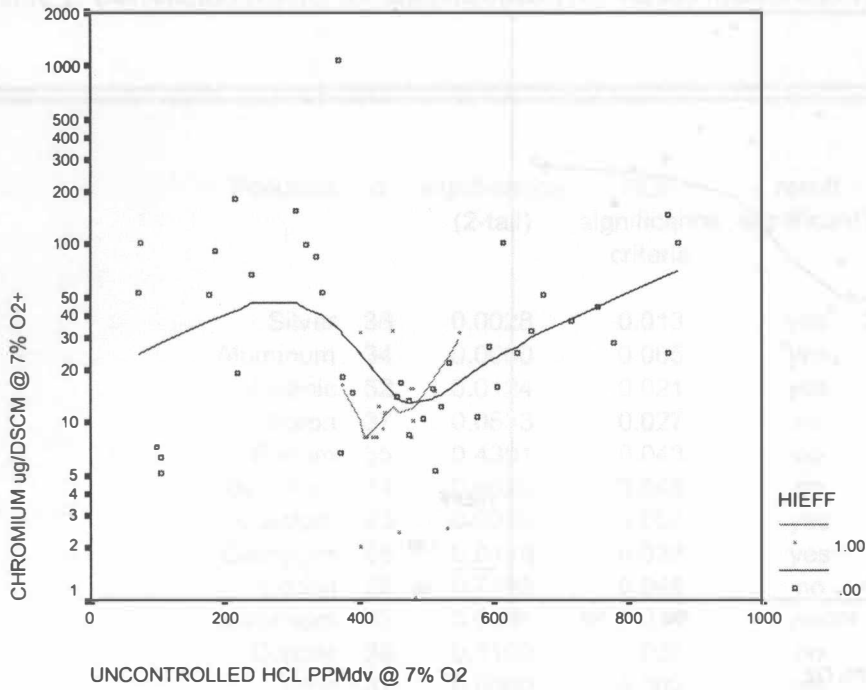


Figure 4. Relationship between arsenic and uncontrolled HCl.

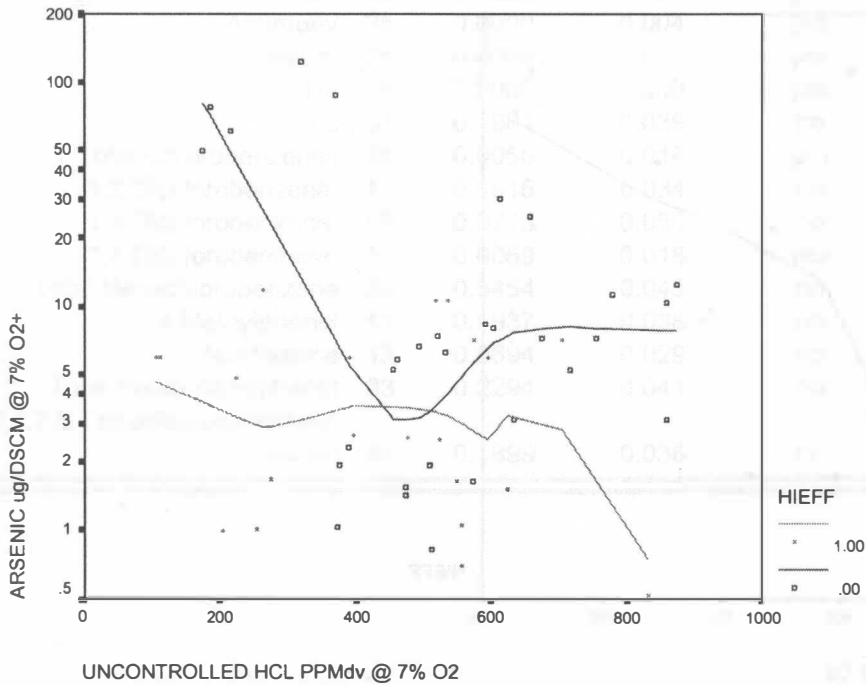


Figure 5. Relationship between nickel and uncontrolled HCl.

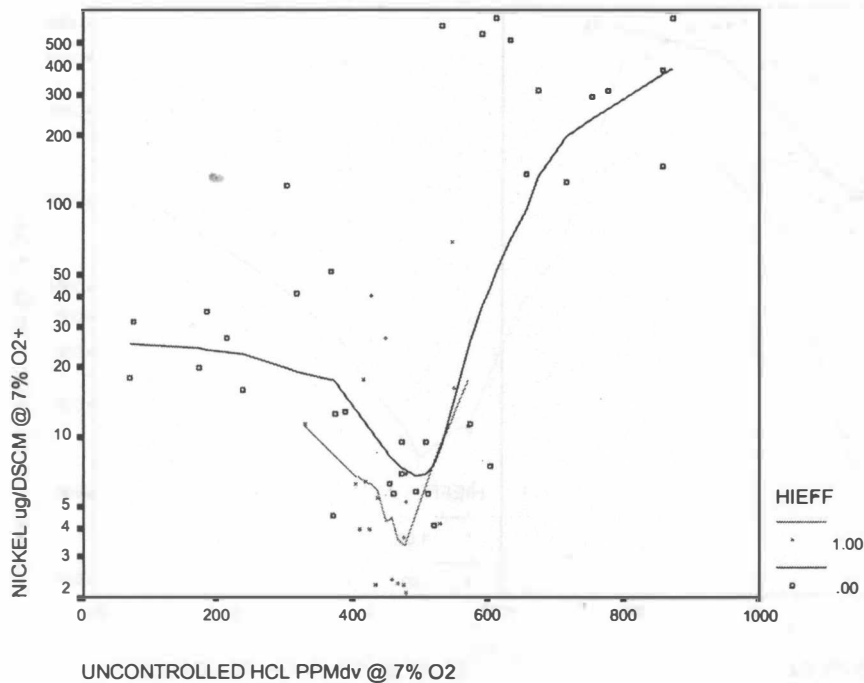


Figure 6. Relationship between cadmium and uncontrolled HCl.

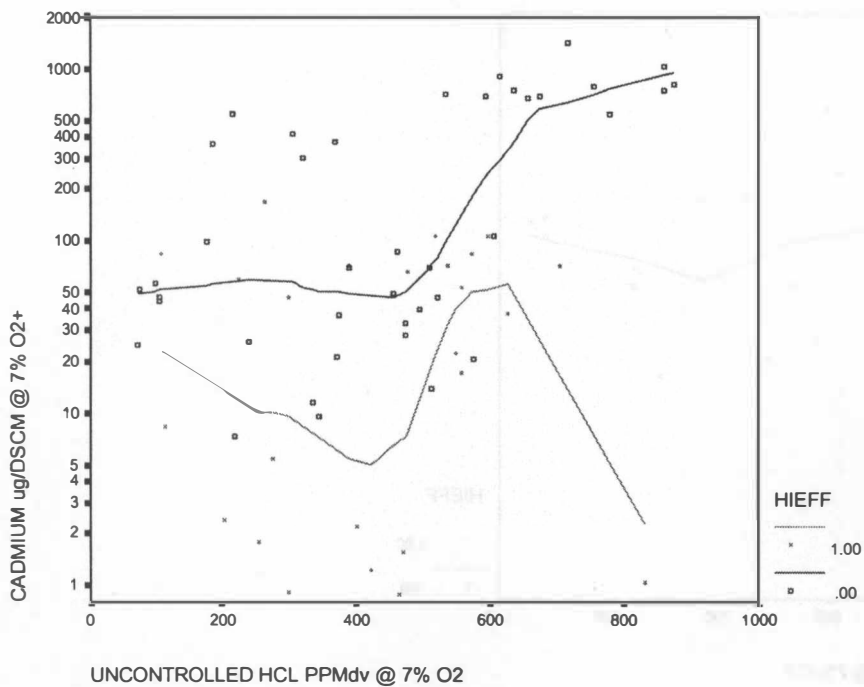


Figure 7. Relationship between lead and uncontrolled HCl.

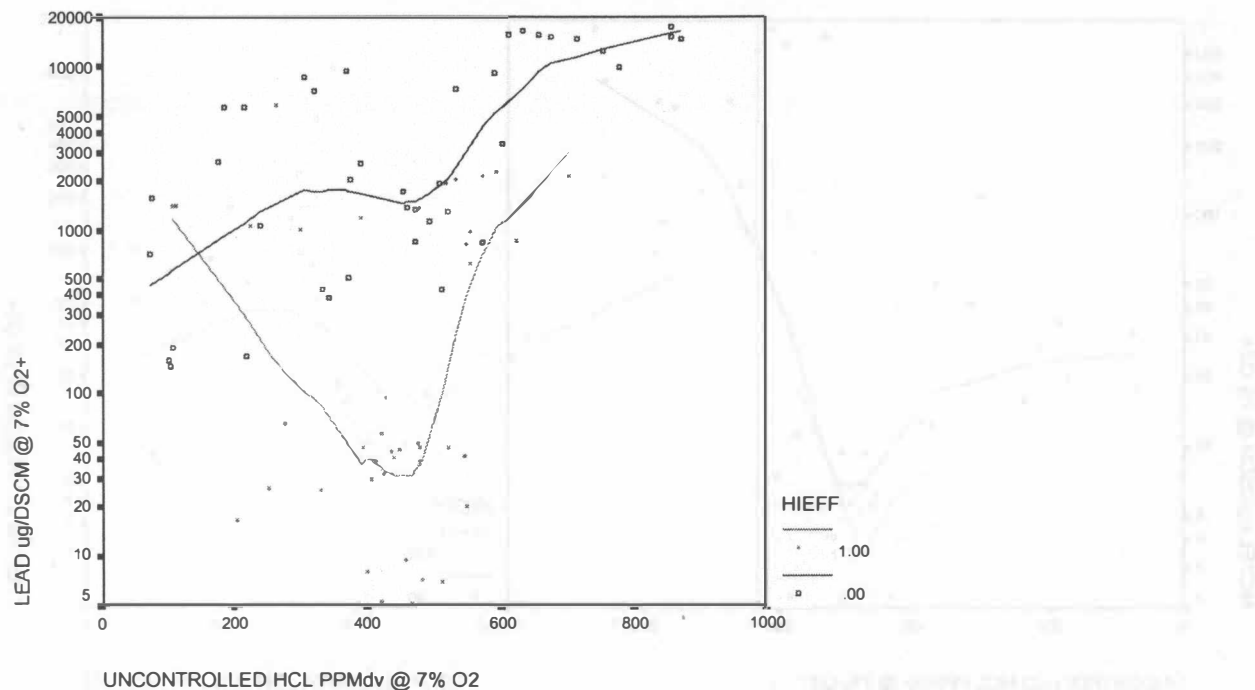


Figure 8. Relationship between total chlorobenzenes and uncontrolled HCl.

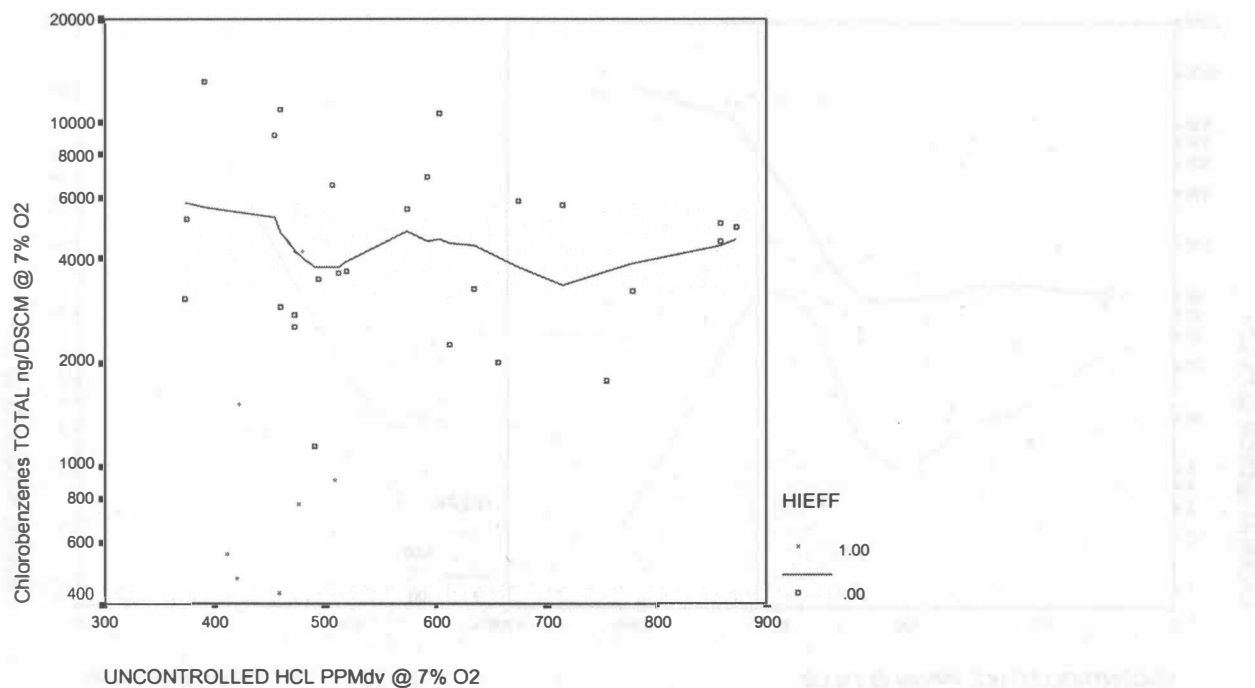


Figure 9. Relationship between 1,4 dichlorobenzene and uncontrolled HCl.

