

Dioxin Surrogates — Are There Any Meaningful Ones?

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INTRODUCTION

A number of easily measured pollutants have been offered up as dioxin surrogates—easily measured pollutants or process variables that consistently parallel dioxin emissions. Surrogates are a very attractive concept because the expense of direct dioxin measurement could be avoided. Also, the public can be assured that as long as easily and potentially continuously measured surrogates are within acceptable limits, people are not being exposed to excessive amounts of pollution. The question remains, however, is there a meaningful surrogate at conventionally regulated levels? Or, perhaps more importantly, at elevated levels that provide a comfortable margin of safety between normal operations and the conditions likely to represent elevated dioxin emissions?

For example, the preamble to the April 16, 1996 proposed Hazardous Waste Combustor Rule, states that particulates are a surrogate for trace organic HAPs, yet the supporting documents in the docket pronounce that “the plots between organic emissions and PM... .. show no apparent trends for cement kilns or other systems...”¹ U.S. Environmental Protection Agency (EPA) found no statistically significant correlation between particulates and trace organics. Further, EPA’s surrogate analysis concludes that “...PM are not good surrogates” (for SVOC and VOC)². As the following analysis shows, MWC data buttresses EPA’s supporting documentation, not the rhetoric in the Preamble. The suppositions provide a good starting point for evaluating the efficacy of various surrogates. However, in the course of developing the regulations or providing public assurance, peer-reviewed hypothesis and not unproved theories should be the basis of surrogate selection. It is particularly discouraging to realize that surrogates are sometimes offered even though the EPA has test data that can be used to test hypothesized relationships.

APPROACH

The following steps were undertaken to perform the analysis:

- Express all concentrations in common units and at the same diluent concentration.
- Check the database against laboratory and field data sheets to minimize errors and examine the database to identify outliers which much be corrected or flagged for inclusion and exclusion in the analysis.
- Use only values that exceed the reference method practical quantitation limit (RMPQL) in statistical procedures —relationships between values less than the RMPQL and higher values are meaningless since RMPQL results have an uncertainty of ± 30 percent. Relationships between pairs with at least one concentration below the analytic (laboratory) detection limit equivalent concentrations (ADLE) or the RMPQL concentration are simply due to chance. Table 1 is a summary of the results of a recent methods validation study conducted as an add-on to the DOE/NREL sponsored performance demonstration test at EAC/Pittsfield³. In this test, reference method testing was conducted using a quad-train. 40 CFR 63 Method 301⁴ method validation criteria were used to calculate the method’s practical quantitation limit, “the lowest concentration which can be accurately measured”⁵.
- Use International Toxic Equivalent (ITEQ) dioxin concentrations. The general linearity of tetra-through octa-dioxin and furan homologue totals and ITEQ has been established⁶. Given the international interpretability and trend toward summarizing complex dioxin and furan mixtures as an equivalent amount of 2,3,7,8 tetrachlorodibenzo-p-dioxin using the international weighting scheme, this approach has been selected even though it is at variance with current EPA MWC regulations.

- Use localized regression (loess) curves to identify the potential for relationships between paired variables. Loess curves are good for identifying the general shape of a trend through data. They are calculated, in this case, using the 30 or 50 percent of the data that surrounds each point and represent the curve drawn through the center of what is effectively a rolling average. When there are two or more underlying relationships in the data, the loess curves are shaped like hockey sticks. Forcing a straight line through such data is incorrect. A trial and error approach can be used to establish the breakpoint between various segments or splines. Absent such an extensive effort, statistical significance cannot be assigned to any particular inflection point or curve segment.
- Employ Spearman Rank-Correlation techniques when the use of individual scattergrams becomes unduly burdensome (such as in the analysis of the relationship between particulates and a plethora of trace organic HAPs) so that the underlying form of the distribution does not affect the comparisons of data above the RMPQL. Also, since this is really an exploratory data analysis — we cannot assume any specific hypothesis is true before analyzing the data — use multiple comparison statistics to identify significant results.

ANALYSIS OF POTENTIAL SURROGATES

A number of potential dioxin surrogates have been suggested. The relationship between air pollution control system (APCS) operating temperature, carbon monoxide and total hydrocarbons and dioxins are explored. Additional relationships between trace contaminants that may be less expensive to monitor, such as chlorobenzenes and dioxins, are explored. Surrogate relationships between dioxins, particulates and a host of additional trace organics that EPA has hypothesized are associated with particulates are also investigated using the techniques just described.

Dioxins Versus APCS Operating Temperature

Figure 1 is a plot of the ITEQ dioxin data collected from more than 150 MWCs since 1976. The loess line shows that there is no meaningful relationship between dioxins and APCS operating temperature below about 300 °F. Above that temperature, there is a generally linear relationship showing increasing dioxins with increasing APCS operating temperature. This supports EPA's finding underpinning the regulatory requirement to keep APCS temperature at no more than 30°F above the highest temperature demonstrated during the most recent compliance demonstration. Looking at the detailed data underlying this scattergram, it becomes apparent that the slope of the ITEQ dioxin — APCS operating temperature line for each facility is generally similar as long as emitted concentrations are above the RMPQL. That is, they are measured with reasonable precision. There is considerable scatter among plants indicating that more than APCS operating temperature is involved in determining dioxin emissions from MWCs.

Dioxins Versus Carbon Monoxide

Figure 2 is a scattergram relating dioxin emissions and carbon monoxide. Again the loess plot displays the hockey-stick pattern characteristic of emissions that are unrelated below a trigger concentration and linearly related above that level. Carbon monoxide (CO) becomes a meaningful surrogate for dioxins when its concentration exceeds 200-400 ppm_{dv} @ 7% O₂. Below that level, there is no meaningful relationship. Consequently, a facility that exceeds EPA's CO emissions standard of 100 ppm_{dv} @ 7% O₂ <4-hr average> for MWCs or up to 250 ppm_{dv} @ 7% O₂ <24-hour average> for other sources is unlikely to emit increased dioxins until sustained levels above 300-500 ppm_{dv} @ 7% O₂ are realized.

This finding is generally consistent with the mid-1980's data underpinning EPA's Good Combustion Practices. Back then, sustained operation under furnace conditions conducive to comparatively elevated dioxin emissions were standard, although rapidly becoming antiquated. Modern facilities generally operate at much lower sustained CO concentrations. Environmental impairment is not indicated when EPA's regulatory levels are exceeded for most plants. Only when emissions approach two to three times the permitted levels for sustained periods of time does the potential for a problem appear.

Note that these data were not analyzed using statistical techniques that account for confounding factors such as design and operating differences. If a surrogate is to be generally useful, it must be robust. That is, it must represent what it is supposed to be true in general and not just in special cases or under specific conditions. Examination of the loess curve and data points in Figure 2 indicate that when the curve breaks upward, the dioxins are generally below the levels found to produce theoretical multi-pathway health risk levels that trigger superfund site cleanups.

Dioxin Versus Total Hydrocarbons

Figure 3 is a scattergram showing the relationship between dioxins and total hydrocarbons. Interestingly, the loess line is essentially horizontal indicating no relationship for all the data. When the dioxin data are trimmed to eliminate concentrations below the RMPQL, the loess line is again a clear hockey stick with an inflection point in the vicinity of 10-20 ppm_{dv} @ 7% O₂. In fairness, it must be pointed out that THC data are available over a comparatively restricted range and a stronger relationship might exist at higher THC concentrations. On the other hand, these results are from operating facilities, and even with the operational abuse imposed on some of them during research efforts and performance demonstrations, it is unlikely that higher concentrations will be observed at commercial installations.

Carbon Monoxide Versus Total Hydrocarbons

Since both CO and THC monitors are commercially available (although some would quickly point out that THC monitors are unreliable without extraordinary care), the question arises which analyzer should be employed. Figure 4 is a scattergram showing the relationship between CO and THC. The loess curve displays the same hockey stick pattern that characterizes the relationship between dioxin and CO. In fact, the break point is the same CO concentration. This indicates that either CO or THC could be used as a dioxin surrogate at "high" emitted surrogate concentrations.

Dioxins Versus Chlorobenzenes

For many years, researchers have been using chlorobenzenes as a surrogate for dioxins, arguing that when they affect a change in chlorobenzenes they affect a similar change in dioxin emissions. Figure 5 is a scattergram relating dioxins and total chlorobenzenes (homologue totals — mono- through penta-chlorobenzenes). Once again, the loess curve shows the hockey-stick pattern that characterizes a change in formation mechanisms, or simply a shift from highly uncertain data to comparatively accurately known concentrations. In this case, below about 2,000 µg/dsm³ @ 7% O₂ of chlorobenzene, there is no co-trending. Above that level, a relationship begins to emerge.

Additional insight can be obtained by looking at the simultaneous dioxin and chlorobenzene data collected during the recent EAC/Pittsfield testing, the testing conducted at Davis County⁷ and the ongoing compliance testing performed at the Peel Resource Recovery Incorporated (PRRI) facility in Brampton, Ontario, Canada. Each of these test programs involved splitting the Method 23 catch at the analytic laboratory and analyzing dioxins and chlorobenzenes in the parent samples. Also, these samples

were all taken by the same field teams and analyzed by the same analytic laboratory so that between-team and between-laboratory variance sources are eliminated.

Figure 6 shows that EAC/Pittsfield and PRRI display no relationship between dioxins and chlorobenzenes. At Davis County, however, a relationship becomes apparent when the total chlorobenzene concentration exceeds 6-8,000 $\mu\text{g}/\text{dsm}^3$ @ 7% O_2 . Interestingly, the chlorobenzene concentrations at Davis County are characterized by a single normal distribution, but the dioxins fall into two groups. This is not surprising since activated carbon was used to reduce dioxin and mercury emissions during the Davis County demonstration test. The lack of change in chlorobenzenes is an indication that activated carbon does not affect chlorobenzene emissions. Also, when the simultaneous data from these three plants are considered as a single group as in Figure 7, the same 2-4,000 $\mu\text{g}/\text{dsm}^3$ @ 7% O_2 inflection point that characterizes the entire data set is indicated by the loess curve. This indicates that chlorobenzenes may be a good surrogate at high dioxin concentrations, but the relationship has no utility at the below MDPQL levels that characterize today's MWCs and probably is non-existent at facilities using powdered activated carbon to reduce dioxin concentrations. It also issues the caution that laboratory studies analyzing chlorobenzene levels are reached and conclusions drawn by such studies must be taken as tentative.

Dioxins and Other Trace Organic HAPs

Because of the number involved, the relationship between dioxins and a plethora of other potential surrogates and less exactly measurable parameters was investigated using multiple Spearman Rank-Order Correlation techniques. The following statistically significant relationships between ITEQ dioxins greater than the RMPQL and the potential surrogates were identified:

- Hexachlorobenzene
- Pentachlorophenol
- Total PAHs (California list)
- Acetanaphthylene
- Total Chlorobenzenes
- Phenanthrene
- Particulates
- Carbon Monoxide
- Total Hydrocarbons

Only hexachlorobenzene accounts for more than 50 percent of the simultaneous change in dioxin concentrations. That is, even though there is a statistically significant relationship between dioxins and the other listed parameters, the amount of change in dioxins explained by a change in the other is too small to be practically significant and explain an important amount of the variability.

Below RMPQL dioxin data were eliminated from this analysis, so the above correlations are for concentrations that are likely to be representative of actual emissions. Analysis of the scatter plots for CO, THC and Total Chlorobenzenes demonstrate that there is a critical level below which no meaningful relationship exists. Further analysis and exclusion of low level concentrations without apparent relationships might produce stronger correlations. For example, for CO concentrations above 250 ppm_{dv} @ 7% O_2 , the amount of dioxin change explained rises from 7% to 26%. Further improvement could be realized by optimizing the breakpoint. The result of this sort of analysis is identification of concentrations above which a meaningful surrogate relationship exists so that exceedances are indicative of an increase in dioxins.

Particulates With Organic HAPs

During the development of the proposed HWC Rule⁸, EPA suggested that particulates were a surrogate for dioxins and other trace organic HAPs. The following statistically significant correlations were found with particulates for all data sets characterized by dioxin concentrations above the RMPQL:

- Phenanthrene
- Naphthalene (a contaminant in Method 23 recovery chemicals)
- Pentachlorophenol, and
- Acenaphthylene

Interestingly, the vast majority of the trace organic HAPs investigated, another 48 Section 112 organic HAPs for which we also have simultaneous particulate data, show no relationship with particulates. Consequently, having low emitted particulate concentrations does not provide assurance that trace organic HAPs emissions are also low; there is no obvious relationship.

CONCLUSION

A statistical review of more than 1000 dioxin test runs conducted at MWCs indicates that conventional regulatory and permitted levels of surrogates like CO and THC are not associated with increased dioxin emissions. The variables identified by EPA's good combustion practice strategy (CO and THC) are sufficiently related that keeping CO below say 250-500 ppm_{dv} @ 7% O₂ <4-hr average>, and THC below 20 ppm_{dv} @ 7% O₂ <4-hr average>, provides reasonable assurance that dioxin emissions are not increasing.

An increase in dioxin emissions begins to occur when the APCS operating temperature rises above 300-400°F; but below that operating temperature window, dioxin emissions are below the RMPQL. So, imposing an incremental temperature restriction on low temperature systems is not environmentally beneficial. Whatever relationship that might be found is likely the result of chance relationships among variables. At the upper limit of the available data, however, a meaningful relationship probably exists.

The surrogate relationship is not apparent, or even necessarily incipient, at current regulatory levels. Consequently, it is incumbent upon regulators, operators and the public to realize that violating extremely restrictive combustion-related emissions restrictions is not equivalent to belching unregulated pollutants.

Particulates are not good surrogates for dioxins or other trace organic HAPs emissions. Consequently, monitoring particulates with a continuous particulate monitor would not provide any additional assurance that these emissions are being minimized.

Public assurances of continuous compliance can be provided, however, by a second, much higher limit for the surrogates. Arbitrarily restricting surrogates to low levels simply does not enhance environmental protection. Concentration limitations for surrogates should be based on the potential of each pollutant to do environmental harm.

Annex A - Statistical Considerations

When multiple comparisons are done in an exploratory effort, there is a great risk of chance findings. When working at the 95% statistical confidence level (α , the statistical significance level, is 0.05), 5 percent or one out of 20 comparisons, are expected to be "statistically significant" when there is nothing significant to be found. To get around this problem, multiple comparison techniques are used. There is

little dispute that if the significance level is greater than the Bonferroni significance level of $\alpha/\{n(n-1)/2\}$ for the n variables being compared, then a significant finding has been uncovered. For significance levels between α and the Bonferroni level, individual critical levels for each comparison should be based on the False Discovery Rate (FDR) level of $i\alpha/\{n(n-1)/2\}$ where i is the rank order from least to most significant of the comparison.

Dual-train calibration type analysis to establish the RMPQL is slightly complicated because the RMPQL is established by comparing two simultaneous, but unknown results. Unlike the implicit assumptions in Method 301 that the average of a pair of results is its true value, the field testing cannot achieve that goal because there is no "reference method" known to produce true values and no way to guarantee that slight spatial deviations do not produce real differences. Consequently, either member of a twin pair of results could be considered first and the other second. Fisher's symmetrical table approach aligns each pair first with one member to the left and then again with it to the right in a duplicate pair used, an upper bound for the RMPQL is produced. If the data are aligned with the largest of each pair on the same side, the minimum residual variance lowest likely RMPQL is produced. EPA's Method 301 method of calculating data variability produces a number between the two limiting values.

Given that the underlying experiment used the same sampling team and analytic laboratory, the upper limits are probably more representative of the true RMPQL than the lower limit. So, concentrations larger than the RMPQL calculated using Fisher's symmetrical table were taken as probably exceeding the RMPQL and accurately measured in this assessment.

REFERENCES

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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.
6. H.G. Rigo and A.J. Chandler Retrofit of Waste-to-Energy Facilities Equipped with Electrostatic Precipitators, (Phase I--Davis County), an ASME Research Report, CRTD-39, April 1996.
7. H.G. Rigo, A.J. Chandler, and W.S. Lanier The Relationship Between Chlorine in Waste Streams and Dioxin Emissions from Waste Combustor Stacks, an ASME Research Report, CRTD-36, August 1995.
8. Federal Register, V. 61 No. 77, April 19, 1996.

Table 1. Reference Method Practical Quantitation Limits for Method 23,26 and 29 measurable parameters.

pollutant	units	nominal sample volume (dsm ³)	Analytic (Laboratory) Detection Limit Equivalent Concentration ADLE	Reference Method Quantitation Limit RMPQL
HCl	ppm _{dv} @ 7% O ₂	1.800	0.006	126 to 218
Cl ₂	ppm _{dv} @ 7% O ₂	1.800	0.003	9 to 11
HBr	ppm _{dv} @ 7% O ₂	1.800	0.016	0.4 to 0.7
HF	ppm _{dv} @ 7% O ₂	1.800	0.005	5 to 15
Particulates (Front-Half)	gr/dsft ³ @ 7% O ₂	3.714	0.001	0.11 to 0.058
Cd	µg/dsm ³ @ 7% O ₂	3.714	0.5	46 to 77
Hg	µg/dsm ³ @ 7% O ₂	3.714	0.008	47 to 74
Pb	µg/dsm ³ @ 7% O ₂	3.714	5	825 to 1,700
ITEQ	ng/dsm ³ @ 7% O ₂	3.714	0.19	0.22 to 0.47
Dioxins			(0.03)	
Total Dioxins	ng/dsm ³ @ 7% O ₂	3.714	0.84	10.9 to 19.6
			(0.03)	

Note: The ADLE is based on the laboratory DL and the stated sample size. The upper two tailed tolerance limit provides 99 percent coverage of future tests at the 95 percent statistical confidence level within 30 percent for the measured value. The duplicate Method 23 and 29 results and quadruplicate Method 26 results were analyzed using statistical calibration techniques. Given that this testing was done by one field team, at one site, using one analytic laboratory, the upper bound of the RMPQL is probably most representative.

Figure 1. Scatter plot displaying the relationship between dioxins and APCS operating temperature.

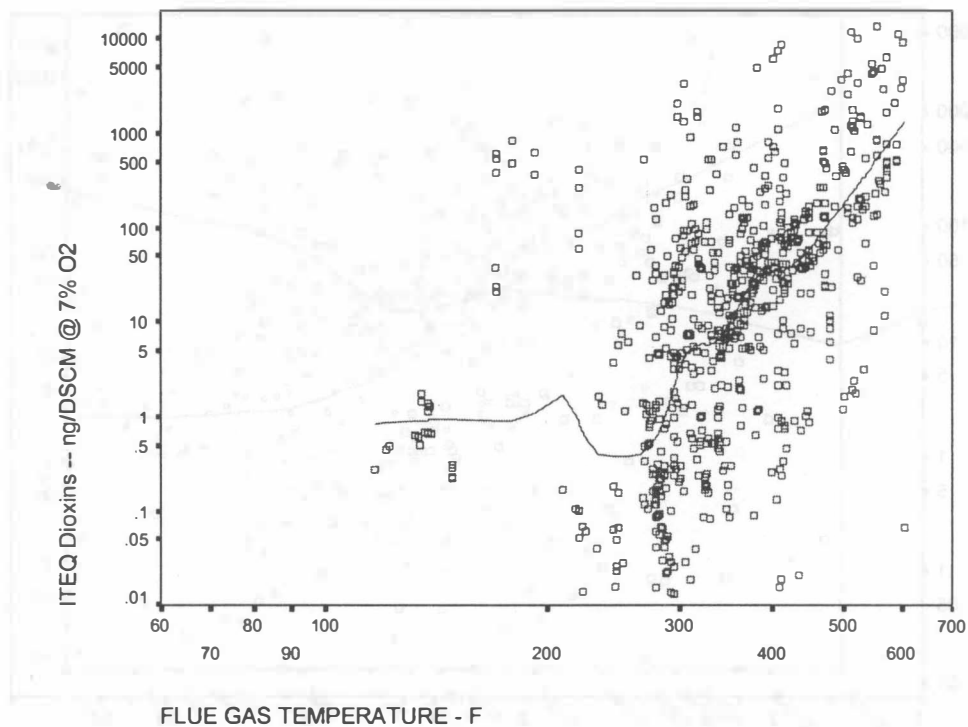


Figure 2. Scatter plot displaying the relationship between dioxins and CO.

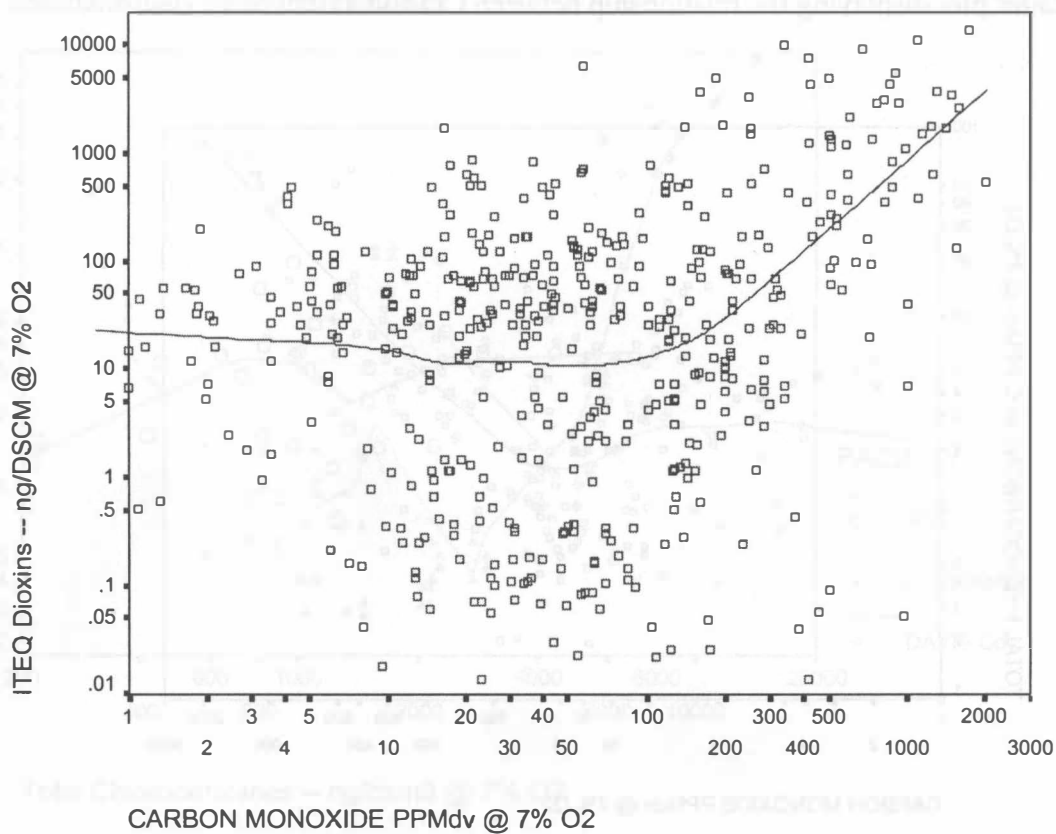


Figure 3. Scatter plot displaying the relationship between dioxins and THC.

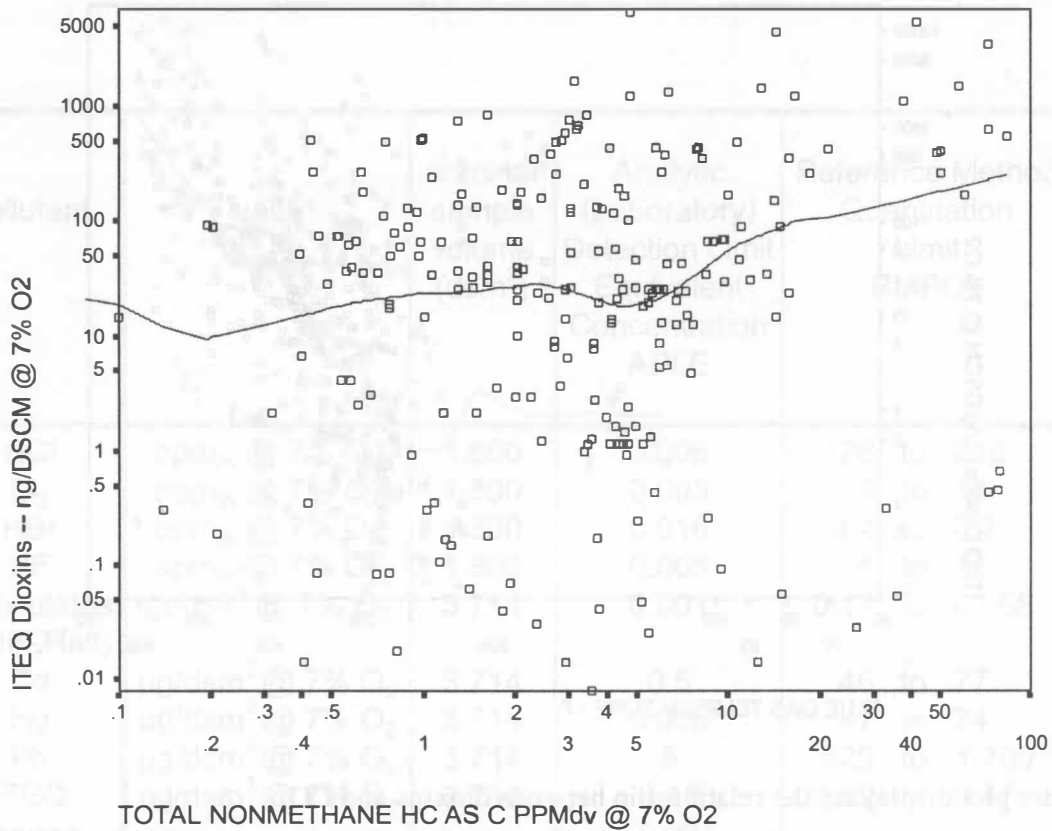


Figure 4. Scatter plot displaying the relationship between CO and THC.

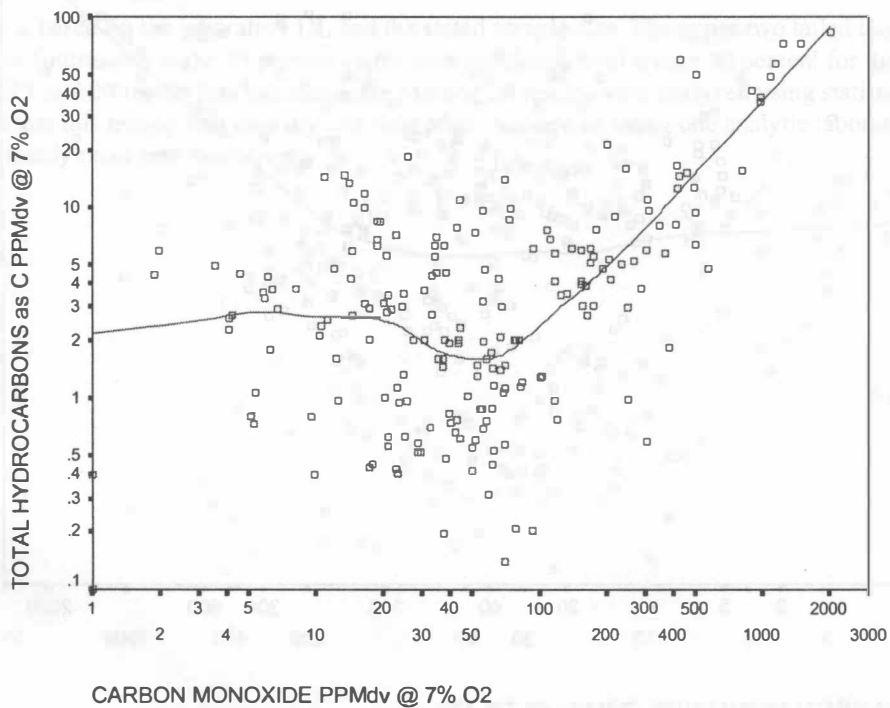


Figure 5. Scatter plot displaying the relationship between dioxins and total chlorobenzenes.

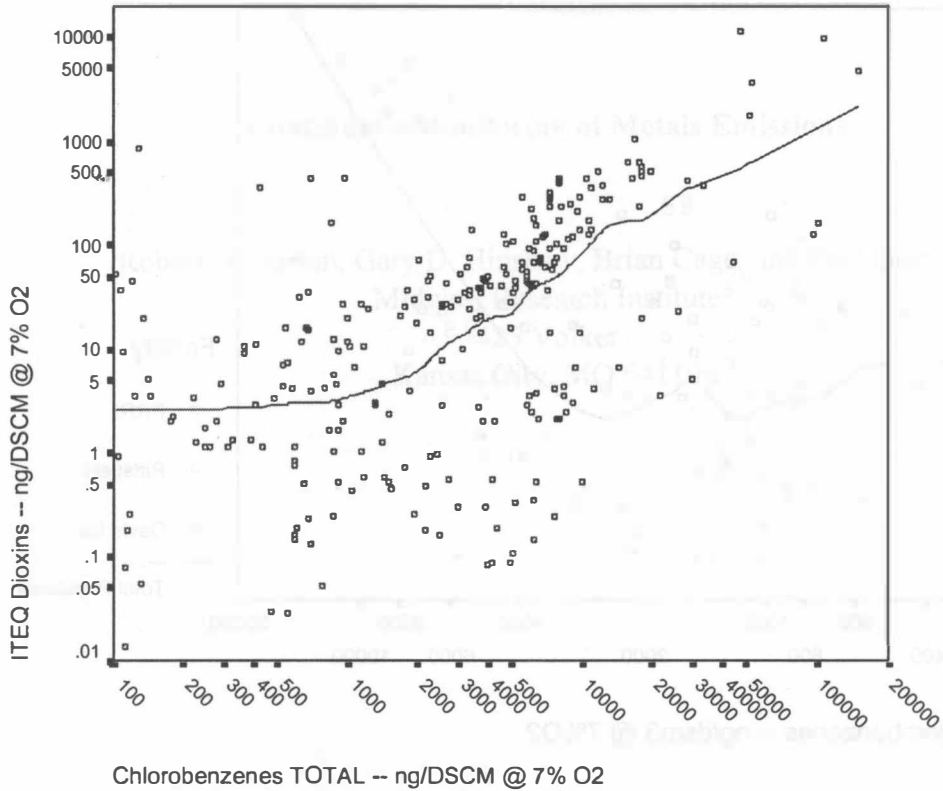


Figure 6. Scatter plot displaying the relationship between dioxins and total chlorobenzenes for three simultaneously measured facilities.

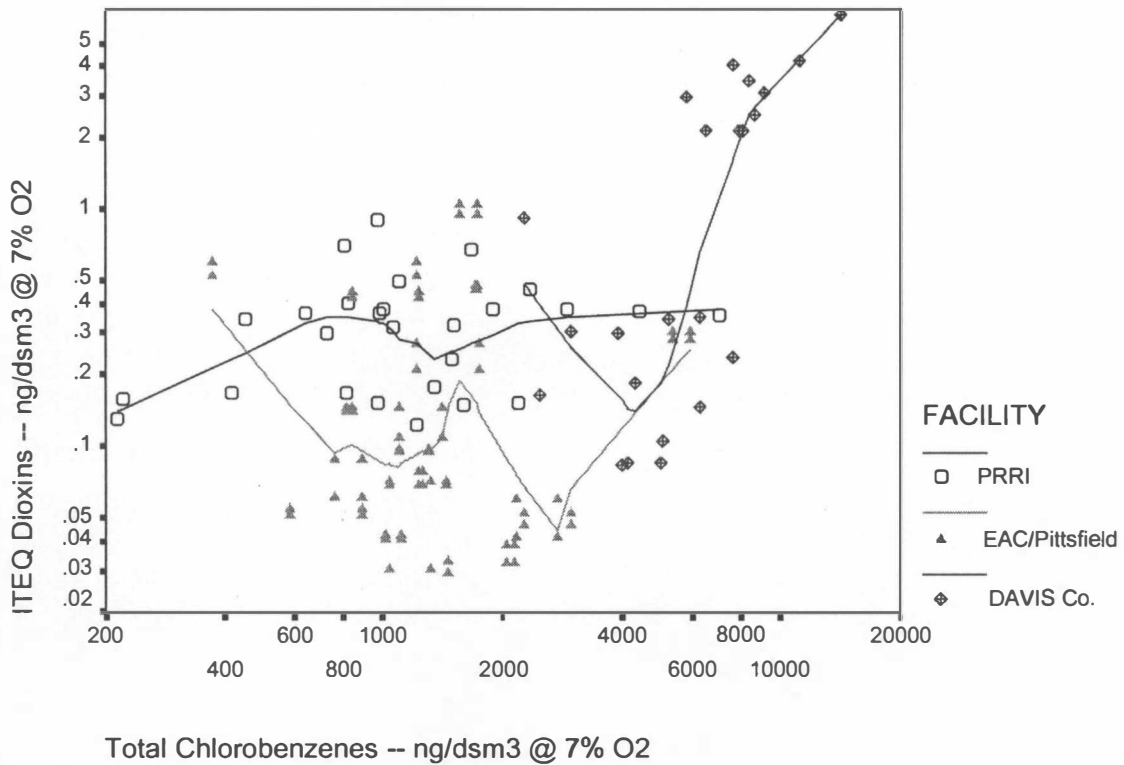


Figure 7. Scatter plot displaying the relationship between dioxins and total chlorobenzenes for three simultaneously measured facilities treating the data as a single group.

