The Burning Question - Chlorine & Dioxin

Written by Pat Costner
April 1997

Table of Contents

Figures

Foreword

In 1995, a new scientific study emerged in policy debates around the world concerning dioxin prevention strategies. The conclusions of the study, by H. G. Rigo et al. entitled "The Relationship Between Chlorine in Waste Streams and Dioxin Emissions From Waste Combustor Stacks," published by the American Society of Mechanical Engineers (ASME), are used to support the contention that there is no link between PVC or chlorine waste inputs to incinerators and the amount of dioxin output. This study is frequently cited by the chlorine industry as an authoritative rebuttal to cleaner material substitution policies.

Greenpeace decided to ask our Science Unit to review the ASME study for two reasons:

1. *The conclusions point in a different direction than most other published technical literature on the topic; and*
2. *Primary funding ($150,000 US) for the study was provided by the Vinyl Institute (VI), a trade association representing corporations that manufacture polyvinyl chloride plastic (PVC) and its chemical feedstocks.*

Our review shows that a surprisingly higher degree of correlation exists between chlorine input and dioxin stack emissions than is concluded by the ASME report. Over and above these discrepancies, the data and methodologies are inappropriate and/or unreliable for assessing the relationship between chlorine inputs and dioxi n outputs from incinerators.

Independent Investigation Needed

Our review raises serious questions about Rigo et al.'s methodology and the validity of the study's conclusions.

Greenpeace therefore calls upon the American Society of Mechanical Engineers and others to carry out a new review and an independent investigation into the Rigo study and its conclusions. An independent review should evaluate the statistical methodologies used, the appropriateness and reliability of using surrogates for chlorine inputs and dioxin outputs, the reliability of the data used, and limiting the analysis to air emissions of dioxin instead of total dioxin output.

We suggest that the following are some of the questions that should also be asked:

- Was the Rigo et al. study diligently and rigorously peer reviewed by scientists with no financial ties to the Vinyl Institute and its members?

- Is it possible that Rigo's perception of his client's expectations might have inappropriately biased the study's design and/or its reported conclusions?

- Did the American Society of Mechanical Engineers properly oversee the work and guarantee its integrity?

- To what extent has the Rigo et al. study and its conclusions affected policy decisions by government agencies and/or by private sector decision-makers?

How and Why the ASME Study was Commissioned

The Vinyl Institute needed a report to aggressively defend PVC during dioxin discussions in the USA. On September 6, 1994, one week prior to the scheduled release of the Draft Dioxin Reassessment Report by the United States Environmental Protection Agency (EPA), Robert Burnett, the Executive Director of VI, circulated an internal memorandum on crisis management to the members of his Executive Board. Attached to the memorandum was a plan entitled: "Crisis Communications Protocol for the Vinyl Institute" that had been prepared by a special VI working group.

Burnett, whose organization represents the American corporations that manufacture and market PVC, was expecting the worst. His group's "Crisis Communications Protocol" starts with a "Situation Analysis" that states:

> *"EPA will likely conclude that the incineration of chlorinated compounds is the single largest known contributor to dioxin."*

The "Situation Analysis" also asserts:

> *"Because of the aggressive tactics of Greenpeace and others pointing to PVC as a primary source of dioxin, we believe that PVC will be specifically mentioned [in the EPA report], and potentially slated for further regulation. This belief is supported by recent communications with EPA officials by Bob Burnett on behalf of the Vinyl Institute and members of the Vinyl Institute on behalf of their individual companies."*

As it turned out, in this instance, VI's concerns were not fully warranted. It appears Bob Burnett and his associates, in their "*communications with EPA officials*" had been more persuasive than they thought. Although EPA's report did contain much evidence that points towards the conclusions Burnett and his organization most feared, the Agency chose not to highlight PVC or other chlorinated compounds as primary sources of dioxin in its 1994 report release.

But VI understood that this issue was not going away. With the immediate crisis in hand, activity shifted to what the memorandum defined as VI's two "*long-term goals of crisis communication: To avoid deselection of PVC by major customers; and to prevent punitive regulation of PVC*."

The means to achieve this, as detailed in the memorandum, includes activities to:

> *"...aggressively defend the industry's credibility through the use of third party sources to debunk Greenpeace's — or even EPA's — misleading claims."*

This is where Rigo enters the picture. VI made a decision whose effect would be to nominate and encourage Rigo to serve in a role that might be described as "VI designated third party." As outlined in the Crisis Communication Protocol, the third party's assigned role is to debunk the conclusion "*that the incineration of chlorinated compounds is the single largest known contributor to dioxin*."

The way this was achieved is described in a memorandum dated August, 22, 1994 from Don Goodman, chairman of VI's Incineration Task Force. Membership in this small working group included representatives of Geon, Dow and Oxychem, three of the largest US producers of PVC and its feedstock chemicals. The Chlorine Chemistry Council of the Chemical Manufacturers Association (CCC) was also represented. The Goodman memo begins:

> *"The Vinyl Institute has created an Incineration Task Force in anticipation of adverse EPA actions regarding dioxins and furans. After the dioxin reassessment, we believe EPA will focus on dioxins from incineration, particularly the incineration of municipal waste (MSW), hospital waste (MW), and plant industrial waste (HWI & BIF) containing (high) levels of PVC and HCL."*

An academic named Dick Magee also served as a member of the Incineration Task Force. Magee was the author of a 1989 study for the Society of Plastics Industry that had found no link between PVC and dioxin emissions from municipal incinerators. Within VI, Magee had earned the title "Lead Contact" for incineration projects according to an August 1993 VI Status Report. He also served as an active member of ASME.

According to Goodman's memo:

> *"Dick Magee brought forward a proposal from the American Society of Mechanical Engineers (ASME) to hire Rigo & Rigo Associates, Inc. of Cleveland, Ohio. The purpose of ASME as the contractor is to provide unassailable objectivity to the study. The ASME oversight and review committee will bring independent reviewers (including EPA members) and high level peer reviewed documentation and reports."*

The memo goes on to state that the VI Incineration Task Force:

> *"interviewed Dr. H. Gregory (Greg) Rigo, principal of Rigo & Rigo Associates, Inc. by phone and found him to be extremely knowledgeable ...*

He is also user friendly (i.e. willing to set his priorities to our needs) and appears to be sympathetic to Plastics, Vinyl, PVC and Cl2."

In discussing the amount of money VI would need to pay Rigo and the ASME to perform the study, Goodman clearly implied in his memo that working group members were already assuming that Rigo's study, when completed, would reach conclusions in support of VI's objectives. The memo proposes a budget item to provide funds that could be used to allow Rigo to advocate on behalf of VI policy using his anticipated report as a basis. At this time, the study that would provide a basis for this report had not yet been designed nor had any work on it begun. As the memo states:

> "Since there are many unanswered questions regarding dioxins and since VI may want to use Greg Rigo as an expert witness or advocate to talk about the report, I am proposing an additional $20,000 as a contingency fund."

One can conclude from the above that there was some expectation that Rigo's study, on behalf of the ASME, would produce conclusions that would be useful to VI.

Often, chemical industry representatives refer to this study as a joint "*government/industry*" project. This is not altogether untrue.

A small portion of funds provided to the study (under $15,000 US) came from Environment Canada. In addition, some employees of the US EPA provided peer review. One US EPA employee, James Kilgroe, not only provided peer review, but also traveled to Amsterdam, the Netherlands and formally presented the ASME study and its findings to a meeting of the 16th International Symposium on Chlorinated Dioxins, PCBs and Related Compounds.

Did peer reviewers working for the US EPA diligently and rigorously do their work? Was Kilgroe authorized to present the ASME study at the Amsterdam scientific conference? In doing so, did Kilgroe convey to others present that the US EPA endorses the ASME study and its conclusions?

We would also like to know whether Environment Canada considers itself to be a sponsor of this study. (In our phone interviews, it seemed to downplay its involvement.) And if they do consider themselves a sponsor, did Environment Canada perform its own independent assessment of the validity of the study's methodology and the reliability of its reported conclusions?

Cleaner Materials Policies Challenged

Scientific integrity, however, is not the only question that potentially arises. Rigo et al.'s study and its conclusions have been widely and effectively used to influence public policy decisions by governments in several countries and also purchasing decisions within the private sector.

Chemical industry representatives cite ASME as proof that incineration of chlorinated compounds does not contribute to dioxin generation and release. A fact sheet distributed by the CCC entitled "Waste Combustors and Dioxin" cites Rigo et al. as its authority for the assertion that *"...the amount of chlorinated wastes burned in a combustor [incinerator] does not correlate to dioxin emissions from these facilities*."

The PVC industry, in particular, has used Rigo et al. to counter arguments put forward by advocates for public health and the environment who propose alternative cleaner materials policies to prevent dioxin generation at its source. Alternative materials policies stem from two circumstances: (1) dioxins are formed when materials containing carbon, hydrogen, oxygen and chlorine are subjected to elevated temperatures, such as those of waste combustors and accidental fires, as well as other reactive conditions; and (2) in most cases, chlorine is the limiting element for dioxin formation, since carbon, hydrogen, and oxygen are typically present in far greater abundance. With an alternative materials policy, the material that provides the chlorine for dioxin formation is replaced by an appropriate, chlorine-free material.

This is a practical way to prevent dioxin generation. As an example, PVC is the single largest use of global elemental chlorine, and its production is expanding. It is also known that dioxin is generated as a byproduct during its production, on a site specific basis, as well as via its use or disposal when burned. These are strong grounds for believing PVC is responsible for a substantial and growing proportion of global dioxin production and emissions. While cleaner substitutes exist for almost all uses of PVC, their adoption is heavily challenged by the chlorine industry.

At present, the most contentious issue around dioxin abatement strategies is on PVC and incineration. Chemical industry representatives strongly dispute the assertion that dioxin is generated by incinerators. As a result of the combustion of PVC plastic, chlorinated solvents and other chlorinated organic materials. To make this case, industry representatives generally cite Rigo et al. because much of the other technical literature on this topic points in the opposite direction.

Case Examples

Once an evaluation of the Rigo et al. study method and conclusions has been completed, it is important to review how this study's conclusions have been used in efforts to influence public policy. We conclude with a number of case examples from several regions of the world.

1) PVC and Hospital Waste in the USA

Kip Howlett, Managing Director of the CCC, sent a letter dated August 29, 1996 to Anthony Robbins, M.D., editor of Public Health Reports, the Journal of the US Public Health Service. The letter protests the Journal's publication of an article entitled:

"Hospitals and Plastics: Dioxin Prevention and Medical Waste Incineration." Howlett asserts:

> *"The author incorrectly states that 'Iatrogenic* dioxin pollution can be largely eliminated by replacing PVC products with alternative materials.' In a government/industry funded peer-reviewed study conducted under the auspices of the American Society of Mechanical Engineers, the findings regarding waste streams and incinerators were conclusive: 'The failure to find simultaneous increases in most cases and finding a few inverse relationships, indicates that whatever effect waste feed chlorine has on [dioxin] concentrations in combustor flue gases, it is smaller than the influence of the causative factors.'"*

Robbins also received a second letter of complaint from William Carroll of Occidental Chemical who challenged the competence of the authors and the judgment of the journal's editor. After quoting ASME, Carroll's letter continues:

> "Perhaps it would be of greater service to your readers to publish an article on medical waste incineration written by a technical expert in the field."

Later in 1996, the authors of the journal article introduced a resolution at the annual meeting of the American Public Health Association (APHA) restating the article's arguments and its recommendations to hospitals. Despite active lobbying from the CCC and other chemical industry interests against the APHA resolution, it was unanimously adopted. The resolution calls on health care facilities to explore ways to reduce or eliminate their use of PVC and adopt policies to encourage these practices.

2) PVC Packaging in Spain

Issues surrounding municipal incineration have been fiercely debated in Spain for many years. In 1995, in response to concerns about dioxin generation from incinerators, the Spanish government proposed a measure that would achieve a twenty percent reduction in PVC packaging within five years. Intense lobbying and a change in political parties led to the initiative being dropped. However, opposition parties tried to bring PVC reduction back to the political table. During this time the PVC industry initiated and has since intensified its campaign to promote PVC as an environmentally sound material.

Support for PVC is organized in Spain by the largest public relations firm in the world, Burson-Marsteller. Employees of this firm accompany the PVC industry in lobbying and public outreach work. They aggressively target communities who propose PVC reduction policies and particularly target journalists who write critically about PVC products and dioxin. An article opposing PVC or incineration is often followed by a phone call to the journal's owners complaining of bias and distorted facts. In response, APIA, the Spanish association of environmental journalists, awarded Burson-Marsteller its anti-environmental award for 1996.

One pro-PVC leaflet distributed by Burson-Marsteller is entitled "The Reality of PVC versus Greenpeace Accusations." This leaflet cites ASME, 1995 as its reference for the assertion: *"...the emissions of dioxins from municipal incinerators is independent of the presence of PVC in the waste*."

Another document distributed by Burson-Marsteller is an October, 1996 paper signed by the National Association of Electrochemistry (whose address is the same as that of Solvay, one of Spain's largest chlorine producers). This paper cites ASME to conclude:

> *" . . .there is no relation between production of dioxins in municipal waste incinerators and PVC content of waste. A recent study promoted by the American Society of Mechanical Engineers in the USA entitled, 'The Relationship Between Chlorine in Waste Streams and Dioxin Emissions from Waste Combustor Stacks' 6/1/95, confirms the conclusion indicated above. This study is based on the analysis of more than 1,700 samples from 155 incinerators."*

In 1997, in a public debate about packaging regulations in Spain, Solvay made a presentation entitled "What are the consequences of the packaging law for the PVC industry?" It concludes:

> *"...In-depth studies clearly show the fault of pseudo scientific claims of the radical environmental groups. In favour of PVC we can cite the recent study made by Dr. Rappe, the world's most prestigious expert on dioxin, as well as from the American Society of Mechanical Engineers, the Swedish Environmental Agency and the USA EPA. All of them categorically state that there is no relationship between PVC content in wastes and the formation of dioxin in the treatment plants that comply to the European Union Directive on Incineration."*

3) Global Negotiations on Persistent Organic Pollutants

As reported in Chemical Week, February 26, 1997:

> *"The international community aims to establish a legally binding treaty on persistent organic pollutants (POPs) by 2000. Detailed negotiations will begin early next year under the umbrella of the UN Environmental Program (UNEP) and the Intergovernmental Forum on Chemical Safety (IFCS)."*

The goal of such an international agreement will be to mandate action by governments to reduce and /or eliminate POPs. These are highly toxic substances that can travel long distances across international boundaries on air and water currents. Action will start with a short list that includes certain chlorinated pesticides such as DDT, chlordane and heptachlor, as well as dioxins and furans.

Chemical Week reports that while the chemical industry is not overly concerned with many of the issues that will be addressed during intergovernmental POPs negotiations,

> *"...the industry is keeping a close eye on regulation of dioxins and furans, which can be released during production, use and destruction of many chlorinated organic compounds. 'We want to make sure any regulation is based on sound science,' says Kip Howlett, executive director of the Chlorine Chemistry Council."*

When Howlett says "*sound science*," however, what he really means is "*Vinyl Institute science*."

During 1996, two meetings were held at which the scientific and technical framework for intergovernmental negotiations on POPs were debated and established. One took place in March in Canberra, Australia; the other in June in Manila, the Philippines. At both meetings, chemical industry representatives distributed copies of the Executive Summary of Rigo et al. together with explanatory materials. During the Canberra meeting, for example, VI distributed a press release stating:

> *"The world's vinyl plastic industry today shared with officials attending a United Nations conference here the results of tests in the United States, Europe, Japan and Australia underscoring the positive environmental performance of the vinyl production process and of vinyl products throughout their life cycle."*

Among the findings cited:

> "An exhaustive study by the American Society of Mechanical Engineers (ASME International) which analyzed 1,900 results from incinerator stack tests worldwide and concluded that there is no direct relationship between chlorine and dioxin in incineration."

Greenpeace representatives at the meetings argued that an effective global policy pointing toward dioxin elimination must incorporate measures that will encourage substitution of appropriate alternative materials for PVC and for other dioxin precursor materials. In preliminary negotiations, governments decided to consider both approaches for dioxin abatement: alternative materials policies and improved pollution control devices. Without a doubt, intense international debate will now take place.

4) PVC Waste Report in Sweden

In 1996 the Swedish government set up a Chemical Committee to review Swedish policies including a review of hazards from the PVC lifecycle. A government commission had declared that PVC had no place in a sustainable society and this led to calls for a phase-out implementation program. The Swedish Environmental Protection Agency was given the task of reviewing PVC waste management and in a 1996

government report entitled "Disposal of PVC Waste" that cites the ASME report, it concludes:

> *"A reduction in the PVC content of waste will not change the amount of emissions from dioxins in flue gases from waste incineration plants in Sweden."*

Using this and other submissions, the Chemical Committee is due to report to the Swedish government by June 1997.

5) PVC Building Materials in Australia

An Australian report entitled "The Environmental Aspects of the Use of PVC in Building Products" was commissioned by the Plastics and Chemicals Industries Association of Australia. It discusses the incineration of PVC waste and concludes:

> *"In a report published by the American Society of Mechanical Engineers (ASME, 1995) it was concluded from existing data that the dioxin concentrations in flue gas from MSW incinerators could not be correlated with fuel chlorine content. Any effect that chlorine had on the dioxin concentrations from commercial scale systems was masked by the effect of the air pollution control system temperature, ash chemistry, combustion conditions, measurement imprecision, and localized flow stratification."*

This has been used by the Australian PVC industry in an effort to weaken the Sydney 2000 Olympic Guidelines which incorporate the concept of ecologically sustainable development, including *"minimizing and ideally avoiding the use of chlorine based products (organochlorines) such as PCBs, PVC and chlorine bleached paper."*

6) The Barcelona Convention for the Mediterranean

In June 1995, the Barcelona Convention for the Protection of the Mediterranean Sea Against Pollution from Land-Based Sources, decided to eliminate by 2005 the greatest possible number of substances which are toxic, persistent and liable to bioaccumulate, in particular organohalogens. The following year, a Meeting of Experts was convened in Athens and agreed to binding regional action plans and programs to phase-out toxic, persistent and bioaccumulative inputs with measures and timetables for their implementation.

The protocol was signed by 14 countries bordering the Mediterranean: Albania, Croatia, Cyprus, France, Greece, Israel, Italy, Malta, Monaco, Morocco, Slovenia, Spain, Tunisia and Turkey. Then, in October 1996, at a conference to develop strategies for action, a UNEP background document was presented. It noted:

> *"Total disagreement to PVC phase-out as a strategy to reduce emissions of dioxins and furans to the environment was expressed by industry*

participants in the preparatory process towards the present Background Document...The hypothesis that there exists a relation between fuel chlorine content and combustor flue gas dioxins concentrations, including all the chlorinated dibenzo(p)dioxins and dibenzofuran isomers was not confirmed by ASME-controlled research and several other studies."

With the ASME report as the defense to take no action, the UNEP meeting resulted in a strangling debate. At issue was a dioxin elimination policy based on incineration design. The final draft document did not set any timelines or strategies towards achieving the decision to eliminate organohalogen inputs into the Mediterranean. The mandate given to this meeting did not result in timelines and specific elimination goals as requested by the prior Meeting of Experts in Athens.

Conclusion

As we have shown, the ASME report has been widely used to obstruct cleaner materials policies. Given the serious wildlife and human health dangers associated with dioxin exposure, Greenpeace calls upon ASME to carry out a new review and an independent investigation of the report's conclusions. In addition, governments should withdraw any use of the ASME report pending the outcome of the investigation.

Jack Weinberg, Team Leader, Greenpeace International Working Group on Persistent Organic Pollutants (POPs);

Lisa Finaldi, Coordinator, Greenpeace International Toxics Campaign

Executive Summary

In 1995, the American Society of Mechanical Engineers (ASME) published the report, "The Relationship Between Chlorine in Waste Streams and Dioxin Emissions From Waste Combustor Stacks," [a] which was prepared by H.G. Rigo, A.J. Chandler and W.S. Lanier. Funding was provided by The Vinyl Institute and the Chlorine Chemistry Council, with a minor contribution by Environment Canada.

Scope of the Report by Rigo et al.

The report by Rigo et al. addresses several aspects of the chlorine input/dioxin output issue. However, the quantitative relationship between chlorine input and dioxin output from combustors is the issue of greatest interest from public health and environmental perspectives. For that reason, this review focuses on those segments of the report that pertain to this issue.

The study by Rigo et al. does not evaluate the relationship between chlorine input and total dioxin output from combustors. That is, they do not examine the relationship between the quantity of chlorine fed into a combustor over a specific period of time and the quantity of dioxins that is released in stack gases, fly ash, and other residues during the same period.

Depending on the category of combustor, Rigo et al. compare dioxin concentrations in combustora gases to one or more of the following measures:

- Hydrogen chloride (HCl) concentrations in stack gases;
- Percent chlorine in feed; and
- For cement kilns only, chlorine feedrates normalized to daily production rates.

The relationships of these measures to the actual focus of concern — chlorine input and dioxin output — determine in large part the relevance of the report.

Greenpeace reviewed this report and concluded that Rigo et al. used inappropriate and/or unreliable surrogate measures for chlorine inputs and dioxin outputs from combustors. Consequently, the results of their statistical analyses do not provide a valid basis for assessing the relationship between chlorine input and the amount of dioxin generated and released by full-scale waste combustors.

It is not surprising that Rigo et al. conclude that the data examined show little correlation (or even negative correlations). It is surprising, however, that the statistical values calculated by Rigo et al. and presented in the appendices of their report do not appear to be consistent with their conclusions.

Inconsistencies in the Report by Rigo et al.

Municipal Waste Combustors
Rigo et al. conclusion: *"On a facility-by-facility basis, 17 [municipal waste combustion] facilities displayed no relationship — two increased and one decreased."*

Greenpeace review of statistical analyses by Rigo et al.: **At 15 of 22 municipal waste combustion facilities, dioxin concentrations in combustor gases increased at higher concentrations of hydrogen chloride in stack gases (an indicator of chlorine feedrate).[**b] The positive correlation coefficients calculated by Rigo et al. for these 15 facilities were statistically significant with greater than 95 percent confidence at five facilities, greater than 90 percent confidence at two facilities and less than 80 percent at the remaining eight. Among the seven facilities where Rigo et al. found negative correlations, none was statistically significant at the 95 percent confidence level; one reached a confidence level greater than 90 percent; and the remaining six were below 80 percent.

Medical Waste Incinerators
Rigo et al. conclusion: "Of the 17 medical waste incinerators with sufficient simultaneous data to explore the relationship, 14 showed no statistically significant trend, two increased and one decreased."

Greenpeace review of statistical analyses by Rigo et al.: **At 10 of 15 medical waste incinerators, dioxin concentrations in combustor gases increased at higher hydrogen chloride concentrations in stack gases.** The positive correlations found by Rigo et al. for the data from these 10 incinerators were statistically significant with greater than 95 percent confidence at two incinerators; greater than 90 percent confidence at one; greater than 80 percent confidence at two; and less than 80 percent at five. At the seven incinerators where negative correlations were found, statistical significance greater than 95 percent confidence was noted at one incinerator, while confidence levels were less than 80 percent at four. Statistical evaluations of data from the remaining two facilities were invalid: for one unit, hydrogen chloride concentrations were measured following treatment for removal of such acid gases; and, in the other, only two data pairs were presented.

Cement Kilns
Rigo et al. conclusion: *"Cement kiln chlorine feed rate has no discernible influence on the nature or quantity of PCDD/F [dioxins] emitted from the stacks of these facilities."*

Greenpeace analysis of data from Rigo et al.: **At 14 of 23 cement kilns, higher chlorine feed-rates were accompanied by increased dioxin concentrations in combustor gases.** Rigo et al. presented no statistical values for individual cement kilns in their report. Instead, they based their conclusion on a scatter plot of the aggregated data from the kilns, in which dioxin concentrations are plotted against chlorine feedrates normalized to daily clinker output. No clinker output data are included in their report. Statistical analyses of chlorine feedrates and dioxin concentrations given for individual kilns in their

report show that increasing chlorine feedrates were accompanied by greater dioxin concentrations in gas streams. Positive correlations were statistically significant with greater than 95 percent confidence at three kilns; greater than 80 percent confidence at two kilns; and less than 80 percent confidence at nine. Of the nine kilns where dioxin concentrations decreased at higher chlorine feedrates, no negative correlation was statistically significant at a 95 percent confidence level. At two kilns, negative correlations were statistically significant with greater than 80 percent confidence, while confidence levels were less than 80 percent at the remaining seven.

Hazardous Waste Incinerators
Rigo et al. conclusion: *"The available data indicate that, depending on the hazardous waste incinerator, changing chlorine concentration can have no observable effect (20 facilities); increase PCDD/F concentrations (4 facilities); or decrease PCDD/F concentrations (4 facilities)."*

Greenpeace analysis of data from Rigo et al.: **No conclusions can be drawn from these data about the relationship between chlorine input and dioxin concentrations in stack gases of hazardous waste incinerators.** Rigo et al. did not calculate statistical values for individual hazardous waste incinerators from data describing chlorine input and dioxin output from the stack. They compared percent chlorine in feed and dioxin concentrations in stack gases. This comparison would have been valid if the waste feedrates and stack gas flowrates had been held constant during the trial burns and other tests that were the sources of these data. However, reports describing these efforts show that both waste feedrates and stack gas flowrates were not constant, but fluctuated over substantial ranges.

Boilers and Industrial Furnaces
Rigo et al. conclusions: Two contradictory conclusions were presented: *(1) "There is too little hazardous waste fired boiler data to reach firm conclusions," and (2) "Chlorine feed concentration is inversely related to PCDD/F concentrations at the stack for this very limited data set."*

Greenpeace analysis of data from Rigo et al.: **No conclusions can be drawn from these data about the relationship between chlorine input and dioxin concentrations in stack gases of boilers and industrial furnaces**. Rigo et al. present no statistical analyses for individual boilers and industrial furnaces. Their second conclusion is apparently based on a scatter plot of percent chlorine in feed versus dioxin values from the three combustors for which these data were available. However, a comparison of these two measures is valid only when waste feedrates and stack gas flowrates are held constant, which was not shown to be the case for these combustors. As a result, their first conclusion is the more accurate of the two.

Biomass Combustors
Rigo et al conclusions: Two contradictory conclusions are presented in the report: *(1) "Given the variation in PCDD/F concentrations over the range of chlorine feed concentrations and stack HCl concentrations, there is too little data to draw any*

definitive conclusions," and (2) "There does not appear to be any relationship between chlorine in the waste feed to biomass fired furnaces and PCDD/F concentrations."

Greenpeace analysis of data from Rigo et al.: **No conclusions can be drawn from these data about the relationship between chlorine input and dioxin concentrations in stack gases of biomass combustors**. Rigo et al. present no statistical values for individual biomass combustors in their report. Instead, they apparently rely on two scatter plots: (1) an aggregation of dioxin concentrations in combustor gases versus percent chlorine in feed for three combustors, and (2) an aggregation of dioxin concentrations in combustor gases versus hydrogen chloride concentrations in combustor gases from three facilities with five combustors. No conclusions can be drawn from their first scatter plot, since there are no data describing waste feedrates and stack gas flowrates and no evidence that these variables were held constant. Data from the five combustors in their second aggregate plot were insufficient to allow statistical evaluation: four combustors had only one data pair each, while the remaining combustor had only two data pairs. As a result, no conclusions can be drawn from these data.

Limitations of Design and Execution of Study by Rigo et al.
The following factors must be taken into account in relation to the evaluation by Rigo et al.of the relationship between selected measures used as indicators of chlorine input and dioxin concentrations in combustor gases:

- **The study by Rigo et al. does not answer the question, "Does chlorine input influence dioxin output from combustors?"**

  Rigo et al. offer no evidence that dioxin concentrations in air emissions correlate with the total dioxin outputs of the full-scale combustors in their study. Indeed, such a correlation would be unexpected: while air pollution control devices capture dioxins from stack gases and deposit them in other combustor residues, some of these devices also enhance the formation of dioxins. As a result, the quantity of dioxins released in stack gases is, as suggested by one study, relatively independent of total dioxin output. In other words, even if statistical analyses of data describing chlorine input and dioxin stack emissions from full-scale combustors are carried out rigorously with appropriate, accurate measures, the results of such analyses cannot be presumed to reflect the relationship between chlorine input and total dioxin output.

- Rigo et al. compared two measures — those used as indicators of chlorine input and dioxin concentrations in combustor gases — that are either inappropriate for comparison or have margins of error too great to support rigorous statistical evaluation.

  Chlorine Input: Of the two indicators of chlorine input used by Rigo et al., one measure — the percent of chlorine in waste feed — is insufficient unless waste feedrates are held constant, which was not shown to be the case for the combustors in this study. The other measure — the concentration of hydrogen chloride in stack

gases — is not a reliable indicator of chlorine input and has margins of error too high to support rigorous statistical evaluation.

Dioxin Output: Rigo et al. obtained their data describing dioxin concentrations in combustor gases from sources in several countries with no common method for sampling and analysis of such gases. Moreover, the data were taken from archival records of early studies as well as reports from relatively current trial burns and other tests. Even contemporary data obtained by a single sampling method and analyzed by a single laboratory are known to have margins of error as high as +/- 30 percent. Consequently, the data relied on by Rigo et al. can be expected to have even higher margins of error.

- **Rigo et al. defined and then tested a hypothesis of limited value by applying statistical methods of questionable suitability to measures that not only appear to be inappropriate but also have levels of uncertainty so high as to render them unsuitable for rigorous statistical analysis**.

Notes

a The title of their report and much of the language in its text suggest that Rigo et al. compared various chlorine-related measures to dioxins in stack emissions. However, when evaluating some combustors, they pooled data describing dioxin concentrations in stack gases with data from other sampling locations in the process train, e.g., boiler outlets, secondary combustion chamber outlets, etc.

b Differences between the total number of facilities addressed in the conclusions by Rigo et al. and those cited by Greenpeace are fully explained for this and the other combustor categories in the body of the review.

Introduction

Dioxin [a] generation occurs during combustion or other reactions when both organic matter and an available chlorine source are present. Much evidence suggests that the global dioxin burden stems primarily from the life-cycle [b] of chlorine-containing synthetic organic materials (e.g., polyvinyl chloride (PVC) plastic, chlorinated solvents, chlorinated pesticides, chlorine-based bleaching agents, etc.). For this reason, the elimination of dioxin generation at the source can best be achieved, in many cases, by substituting chlorine-free alternative materials. Indeed, many technically feasible and economically competitive cleaner products and processes already exist. In waste combustion systems, chlorine is the limiting element for dioxin formation. This suggests that the total dioxin outputc from these systems can be reduced and/or eliminated through a materials policy that curbs chlorine input, as pointed out by an advisory group for the U.K. Department of the Environment: [1]

> *"One of the more obvious primary ways of minimizing TOMPS [toxic organic micropollutants, e.g., dioxins] in incinerators and in other thermal processes is to try to avoid (or reduce) TOMPS, their precursors or fundamental species (such as chlorine or bromine) being included in the feedstock."*

Materials policies have already been incorporated into some dioxin abatement efforts:

- A 1996 report from the Intergovernmental Forum on Chemical Safety (IFCS) concluded that it was appropriate and important to consider materials policies in developing strategies to minimize and/or eliminate releases of both the polychlorinated and polybrominated dioxins and furans; [2]
- The Governing Council of the United Nations Environmental Programme adopted the recommendations of the IFCS report on Feb. 7, 1997, as part of the process of achieving a global, legally binding agreement to eliminate or reduce persistent organic pollutants in the global environment; [3]
- On November 22, 1996, the American Public Health Association adopted a resolution urging health care facilities and suppliers to reduce or eliminate their use of PVC and other chlorinated plastics that are currently disposed of in medical waste incinerators; [4]
- The Central Pollution Control Board of India ruled in July 1996 that polyvinyl chloride (PVC) can no longer be burned in medical waste incinerators; [5]
- In 1994, the International Joint Commission (IJC) between the U.S. and Canada recommended that *"...the Parties ... alter production processes and feedstock chemicals so that dioxin, furan and hexachlorobenzene no longer result as byproducts" and "... develop timetables to sunset the use of chlorine and chlorine-containing compounds as industrial feedstocks and that the means of reducing or eliminating other uses be examined."* [6] *This followed the IJC's 1992 conclusion: "We know that when chlorine is used as a feedstock in a manufacturing process, one cannot necessarily predict or control which chlorinated organics will result and in*

what quantity. Accordingly, the Commission concludes that the use of chlorine and its compounds should be avoided in the manufacturing process;" [7] and

- In 1992, the German Federal Government enacted a prohibition against using chlorinated and brominated compounds as petrol additives to reduce dioxin release via car exhausts. [8]

Scientific support for such materials policies is found among the many studies in which dioxin output from incinerators and other combustors has been shown to increase as chlorine input is elevated. In a smaller number of studies, no relationship has been found between chlorine input and dioxin output.

One of the more recent and widely-publicized studies from the latter category and the subject of this review is "The Relationship Between Chlorine in Waste Streams and Dioxin Emissions from Waste Combustor Stacks," by H. Gregor Rigo, A. John Chandler and W. Steven Lanier. This report is sometimes referred to as the ASME report or the Rigo report.

Primary funding for the report of some $150,000 came from the Vinyl Institute, which selected the American Society of Mechanical Engineers as contractor to "*provide unassailable objectivity to the study."* [9] Nonetheless, there appear to be striking discrepancies between the authors' conclusions and the statistical findings presented in their report.

Over and above the obvious discrepancies, it seems that Rigo et al. chose to test a hypothesis of limited value by applying a statistical method of questionable suitability to measures that not only appear to be inappropriate but also have levels of uncertainty so high as to render them unsuitable for rigorous statistical analysis. This review addresses these and other aspects of the report by Rigo et al.

Notes

a The terms "dioxin" and "dioxins" include all of the polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs).
b The term "life-cycle" includes extraction of raw materials, their processing into the usable or salable product, the use of that product, recycling (if any) of the discarded product, accidental or deliberate combustion (e.g., building fires), treatment for disposal (if any) of the discarded product (e.g., incineration), and the return into the environment of the discarded product and/or the residues of its treatment.
c Total dioxin output includes the quantity of dioxins released in stack gases as well as that released in fly ash, bottom ash, and other residues, such as scrubber water, filtercake from scrubber water treatment, etc..

1 Air Pollution Abatement Review Group, "Report on the Abatement of Toxic Organic Micropollutants (TOMPS) from Stationary Sources 1995," Prepared at the request of Air Quality Division, Department of the Environment, AEA Technology, National Technology Centre, Abingdon, Oxfordshire, UK, 1995.
2 Intergovernmental Forum on Chemical Safety, "IFCS Ad Hoc Working Group on Persistent Organic Pollutants Meeting: Final Report," Geneva: IFCS Secretariat, c/o World Health Organization, 21-22 June 1996.
3 United Nations Environmental Programme, "International Action to Protect Human Health and the Environment Through Measures Which Will Reduce and/or Eliminate Emissions and Discharges of Persistent Organic Pollutants, Including the Development of an International, Legally-Binding Instrument,"

Decision Taken By Nineteenth Session of the UNEP Governing Council, Nairobi, 7 February, 1997, Geneva: United Nations Environmental Programme, February 1997.
4 American Public Health Association, Resolution Adopted at the 124th Annual Meeting, New York City, New York, 20 November 1996.
5 Central Pollution Control Board, Ministry of Environment and Forests, Government of India, "Environmental Standards and Guidelines for Management of Hazardous Waste," New Delhi, India, 12 July 1996.
6 International Joint Commission, "Seventh Biennial Report on Great Lakes Water Quality," ISBN 1-895085-74-8, Washington, D.C.: International Joint Commission, 1994.
7 International Joint Commission, "Sixth Biennial Report on Great Lakes Water Quality," ISBN 1-895085-36-5, Washington, D.C.: International Joint Commission, 1992.
8 Schulz, D., PCDD/PCDF - German policy and measures to protect man and the environment, Chemosphere 27 (1-3): 501- 507 (1993).
9 Goodman, D., "Incineration Task Force," August 22, 1994.

Chapter 1: Scope of the ASME Report

The ASME report addresses several aspects of the chlorine input/dioxin output issue. However, the quantitative relationship between chlorine input and dioxin output from full-scale combustors is the issue of greatest interest from public health and environmental perspectives. For that reason, this review focuses on those segments of the ASME report that pertain to this issue. The study by Rigo et al. does not evaluate the relationship between chlorine input and total dioxin output from combustors. i.e., they do not examine the relationship between the quantity of chlorine fed into a combustor over a specific period of time and the quantity of dioxins that is released in stack gases, fly ash, and other residues during the same period.

Depending on the category of combustor, Rigo et al. compare dioxin concentrations in combustor [a] gases to one or more of the following chlorine-related measures:

- Hydrogen chloride (HCI) concentrations in stack gases;
- Percent chlorine in feed; and
- For cement kilns, chlorine feedrates normalized to daily clinker [b] production.

The relationships of these measures to the actual measures of concern, chlorine input and dioxin output, determine in large part the relevance of the ASME report.

Dioxin Output

According to its title, the study by Rigo et al. compares chlorine in waste streams to dioxin stack emissions. The selection of dioxins in stack emissions rather than total dioxin output for this comparison brings into question the methodology, findings and conclusions of their study.

Dioxin Stack Emissions

Dioxin stack emissions [c] are only one, commonly small, portion of a full-scale combustor's dioxin output. For example, a study of eleven European municipal waste combustors found that stack emissions accounted for less than 12 percent of dioxin output. The major share was distributed among fly ash, bottom ash, and other residues. [1] Dioxin stack emissions have been characterized as *"nearly independent of the PCDD/F concentrations in the raw gas."* [2] This suggests that dioxin stack emissions correlate poorly, if at all, to total dioxin output.

It is well known that both the magnitude of the dioxin output and its pattern of distribution among combustor residues is influenced by numerous factors. For example, depending on the materials from which they are constructed, wet scrubbers can either reduce or increase dioxins in stack emissions and alter the PCDD/F profile, while adding to the dioxin load in scrubber water and subsequent treatment residues, such as filter cake. [3] Other methods that reduce dioxin stack emissions may increase total dioxin output, as has been observed with carbon injection. [4]

In summary, an evaluation of the relationship between chlorine input and dioxin stack emissions from full-scale combustors, such as this study by Rigo et al., provides little if any insight into the relationship between chlorine input and total dioxin output.

Dioxin Concentrations in Stack Gases

Dioxin concentrations in stack gases may be determined using a number of sampling and analytical protocols which, in some cases, have been further modified. Most of these methods have changed considerably during the period of time between the oldest (1984) and the most recent (1994) data in the ASME report's database, as alluded to by the authors: [5]

> Rigo et al.: *"Reports from the mid-1980's do not reflect the level of detail found in PCDD/F tests conducted in the 1990's ..."*

Even with modern procedures applied by a single laboratory to replicate samples from a single combustor over a fixed time period, dioxin measurements may have relatively high margins of error, as acknowledged by Rigo et al.: [6]

> *"TNO (1994) reports that the total PCDD/F concentration uncertainty is +/- 30% for raw data. Extending the analysis to include the effect of diluent correction (Hamil and Thomas, 1976) raises the uncertainty to +/- 35%."*

Other studies have found replicate measurements of dioxins in combustor emissions to vary by as much as three orders of magnitude. [7]

Rigo et al. aggregated dioxin measurements taken at the stack with those taken at other sites, such as boiler outlets, secondary combustion chamber outlets, etc. Due to differences in temperature and other factors that affect both formation and capture rates, dioxin concentrations in samples from these various sites commonly span a very wide range. As a result, the overall uncertainties of the dioxin measurements used in the study by Rigo et al. can be expected to be even greater than those for stack concentrations only.

Given the great uncertainties and poor precision of dioxin measurements, which are discussed in more detail in Section 11, small numbers of single-measurement values for dioxin concentrations in combustor emissions, such as those relied upon in many cases by Rigo et al., cannot be expected to meet stringent criteria necessary for statistical analysis.

Chlorine Input

Rigo et al. frequently employ language indicating that they used chlorine input in their evaluations. However, no direct measures of chlorine input were used in their analyses of municipal solid waste combustors, medical waste incinerators, hazardous waste incinerators, boilers and industrial furnaces, or biomass combustors. In their analysis of

cement kilns, Rigo et al. compared dioxin concentrations in stack gases with chlorine feedrates that were normalized relative to clinker production rates, which they did not disclose.

Chlorine Input to Municipal Solid Waste Combustors and Medical Waste Incinerators

For municipal solid waste combustors and medical waste incinerators , Rigo et al. compared dioxin concentrations in gas streams to a surrogate based on output chemistry. The use of this surrogate, hydrogen chloride (HCl) concentrations in stack gases, is predicated on the assumption that "*all the chlorine in the waste is converted to HCl or Cl2 and not tied-up in the residue*." [8] This assumption is contradicted by numerous studies, as discussed in greater detail in Section 10.2. For example, the efficiency with which the chlorine in materials fed into a combustor is converted into HCl may vary according to the chemical nature of the chlorine, [9] the design of the incinerator, [10] and other factors.

It is also important to note that the measurements of HCl taken during testing of the combustors in the ASME study differed greatly from sampling emissions for dioxin content in the length of time required for sampling. I.e., these two measures were not truly synchronous. This is evident from the description of sampling procedures given by Rigo et al.: [11]

> "*The uncontrolled HCl data comes from a single 1 hour test conducted during the 6 hour PCDD/F sampling period. This is typical of much of the available data since the sampling times for HCl and PCDD/F determinations are different."*

Some HCl data may result from even briefer sampling times, for instance near-instantaneous determinations with continuous emissions monitors, while sampling for dioxin analyses sometimes requires considerably more than 6 hours. For example, in Germany, stack samples for dioxin determinations may be collected over a period of 16 hours. [12] Particularly with highly heterogeneous wastes, such as municipal and medical wastes, there is little basis for assuming that one HCl measurement made over a brief period is representative of HCl concentrations during the 4-16 hours throughout which a stack sample is collected for dioxin analysis.

There are also several different methods and modifications of these methods that are used for measuring HCl in stack gases. These can give widely disparate results, as described by USEPA [13] and acknowledged by Rigo et al. [14] (See Section 10.3 for a more detailed discussion of the limitations of analytical methods for HCl).

Even in carefully controlled experiments at one full-scale combustor, the margin of error of HCl measurements was +/- 28 percent. [15] In short, HCl concentrations in stack gases are not highly reliable or accurate indicators of chlorine input to full-scale municipal waste combustors and medical waste incinerators.

Chlorine Input to Hazardous Waste Incinerators and Boilers and Industrial Furnaces

The ASME report's database includes chlorine feedrates for hazardous waste incinerators and boilers and industrial furnaces. However, Rigo et al. did not assess the relationship between chlorine feedrates and dioxin emission rates. They compared percent chlorine in feed and dioxin concentrations in stack gases. Percent chlorine in feed simply describes the composition of the feed material and, in the absence of feedrates, tells little about the actual quantity of chlorine that is fed into a combustor. Consequently, it is an appropriate surrogate for chlorine input only when assessing data from one combustor with a constant waste feedrate or when used in combination with data describing waste feedrates.

As the report's database shows, chlorine feedrates to the combustors in this study were seldom constant, even though percent chlorine in feed often was. In other words, percent chlorine in feed cannot be regarded as a reliable, accurate surrogate measure of chlorine input to the full-scale hazardous waste incinerators, boilers and industrial furnaces, and other combustors evaluated by Rigo et al.

Notes

a The title of their report and much of the language in its text suggest that Rigo et al. compared various chlorine-related measures to dioxins in stack emissions. However, when evaluating some combustors, they pooled data describing dioxin concentrations in stack gases with data from other sampling locations in the process train, e.g., boiler outlets, secondary combustion chamber outlets, etc.
b “Clinker” is the material that is collected from the cement kiln and ground into cement.
c In this review, the term “emissions” is used to refer only to stack emissions, e.g., the quantity of dioxins released from a combustor’s stack. (See also footnote “a”).

1 Huang, H., and Beukens, A. On the mechanisms of dioxin formation in combustion processes. Chemosphere 31 (9): 4099-4117 (1995).
2 Kreisz, S., Hunsinger, H., and Vogg, H. Wet scrubbers - a potential PCDD/F Source? Chemosphere 32 (1): 73-78 (1996).
3 Ibid.
4 Lamb, C., Rollins Environmental, Houston, Texas. Comments offered at EPA Dioxin Workshop on Formation Processes and Sources, Chevy Chase, Maryland, November 18-20, 1996.
5 Rigo et al., p. 2-14.
6 Rigo et al., p. 2-51.
7 Air Pollution Abatement Review Group, “Report on the Abatement of Toxic Organic Micropollutants (TOMPS) from Stationary Sources 1995,” Prepared at the request of Air Quality Division, Department of the Environment, AEA Technology, National Technology Centre, Abingdon, Oxfordshire, UK, 1995.
8 Rigo et al., p. 3-2.
9 Sonnenberg, L., and Nichols, K. Emissions of hydrochloric acid, PCDD and PCDF from the combustion of chlorine-containing kraft pulp mill bleach plant waste. Chemosphere 31 (10): 4207-4223 (1995).
10 Kanters, M.J., Van Nispen, R., Louw, R., and Mulder, P. Chlorine input and chlorophenol emission in the lab-scale combustion of municipal solid waste. Environ. Sci. Technol. 30(7): 2121-2126 (1996).
11 Rigo et al., p. 2-48.
12 Funcke, W., and Linneman, H. Sampling of polychlorinated dibenzofurans (PCDF) and dibenzo(p)dioxins in emissions from combustion facilities using an adsorption method. Chemosphere 24 (11): 1563-1572 (1992).
13 Johnston, L. “Stack Sampling Methods for Halogens and Halogen Acids,” PB96-184452, Research Triangle Park, NC: U.S. Environmental Protection Agency, 1996.

14 Rigo et al., p. 4-12.
15 Lenoir, D., Kaune, A., Hutzinger, O., Mutzenich, G., and Horch, K. Influence of operating parameters and fuel type on PCDD/F emissions from a fluidized bed incinerator. Chemosphere 23 (8-10): 1491-1500 (1991).

Chapter 2: Statistical Analysis

The validity of any statistical analysis depends on many factors including the relevancy of the data, sample size, and sample quality. If the data are not sound measures or are of poor quality, the utility of the resulting analyses will be greatly decreased or eliminated entirely.

Rigo et al. evaluated the relationship of measures related to chlorine input and dioxin concentrations in combustor gases primarily in two ways: (1) simple correlation analysis and (2) multivariate analysis. Each approach has certain limitations. Further, their use was based on the unsupported assumption that the combustors in their study were operating in a state of thermodynamic equilibrium during sampling and analysis.

Correlation analysis is useful when performed on two variables that have a linear relationship. However, if their relationship is exponential, as was suggested for chlorine input and dioxin output by De Fre and Rymen (1989) [1], these variables will necessarily show a reduced correlation due to model misspecification — use of the wrong model. On the other hand, in multiple comparisons such as those in the ASME study, some correlations will occur simply as a matter of chance.

Rigo et al. carried out multivariate analyses on data from several of the municipal waste combustors in their study and the aggregated data from municipal waste combustors, medical waste combustors, hazardous waste incinerators and cement kilns. One important factor governing the usefulness of such analyses is the state of knowledge of the reaction mechanism or mechanisms of dioxin formation. If reaction mechanisms are not sufficiently understood to allow adequate mathematical modeling, multivariate analysis can, like correlation analysis, have misleading results: [2]

> *"...[T]he statistical efficiency of multivariate models comes at a price, which is the assumption that a given mathematical form describes the relation of study variables. ... If the model is incorrect, however, the improved efficiency may be negated by an intolerable degree of bias; furthermore, the bias will not be detected without special efforts, and the caution that such efforts characterize can easily be eroded by the seductive appeal of a neat, efficient-looking model."*

Much has been learned about dioxin formation during combustion. However, much remains to be learned. In particular, little is known about competing and/or complementary formation pathways and their interactions within the complex, constantly-fluctuating environment of a full-scale incinerator.

Correlation analyses are the only statistical evaluations presented by Rigo et al. for all of the individual municipal waste combustors, medical waste incinerators and hazardous waste incinerators in their study. Consequently, this review focuses primarily on the statistical values obtained by this method, which served as the basis of their facility-specific conclusions.

Basic Elements of Statistical Analysis

When small numbers of samples are used to characterize a large population, they must be carefully randomized in order to be meaningful. The randomization should be applied both to the combustors representing the population of combustors as well as to the data collected from each individual combustor. Correlation coefficients calculated on relatively small samples are often unreliable since they are subject to considerable chance fluctuations, [3] and are less likely to yield statistically significant results.

The study by Rigo et al. was designed to test the "...hypothesis that fuel chlorine content and combustor flue gas PCDD/F concentrations are related..." [4] In an analysis such as this, statisticians always define two hypotheses: the alternative hypothesis and the null hypothesis. In this case, the alternative hypothesis is the premise described above by Rigo et al. The unstated null hypothesis is that fuel chlorine content has no effect on dioxin concentrations in combustor flue gas.

It is important to note that the alternate hypothesis defined by Rigo et al. suffers from two serious flaws: (1) those portions of the total dioxin output that are distributed to ash and other residues are not considered; and (2) comparisons of fuel chlorine content and dioxin concentrations in stack gases are meaningful only under certain conditions – constant waste feedrates and stack gas flowrates – which did not exist at many of the facilities when the data used by Rigo et al. were collected. The more meaningful alternate hypothesis, which was not tested by Rigo et al., is the hypothesis that chlorine input and total dioxin output are related.

The null hypothesis is actually the hypothesis that is tested in statistical analysis. [a] If the results of analysis lead to the rejection of the null hypothesis, then the alternate hypothesis is accepted. A key decision made by statisticians in designing a statistical study is choosing the confidence level – the critical probability level at which the null hypothesis will be rejected.

In other words, in their statistical analyses, Rigo et al. were actually testing the premise that the mass of chlorine input to combustors has no relationship to the quantity of dioxins emitted in stack gases. Rigo et al. chose their criteria for rejecting this null hypothesis as follows: [5]

> *"Statistically significant findings had to exceed the 95% confidence level and be found in two or more similar test programs to attribute probable causality to the relationship. Finding the same behavior in the majority of experiments where it should appear is needed to confirm probable causality."*

By selecting a stringent confidence level, greater than 95 percent (>95 percent), Rigo et al. reduced the likelihood of "false positive" errors [b] – concluding that there is no

relationship between chlorine input and dioxin emissions when, in fact it does exist. It appears, therefore, that the data may have been collated and analyzed with a pre-determined outcome in mind.

Sample Size and Quality

Rigo et al. describe their database as containing over 1,900 test results from 169 combustion facilities in seven categories: municipal waste combustors, medical waste incinerators, hazardous waste incinerators, boilers and industrial furnaces, cement kilns, biomass combustors, and laboratory-, bench- and pilot-scale combustors. [6]

Rigo et al. offer no evidence that the combustors in their database were randomly selected from the wide array of combustors for which relevant data are available. Indeed, as documented in the sections of this review that are devoted to each of the six full-scale combustor categories, Rigo et al. also omitted some of the combustors in their database from their analyses. In other words, the sample of combustors selected by Rigo et al. for statistical analysis may contain significant bias.

The validity of any statistical analysis also depends on the quantity of data available. Whether sufficient data exist for each combustor to lend sufficient power to the analyses by Rigo et al. is questionable. As discussed in the sections devoted to each combustor categories, the answer to this question is "No." Furthermore, numerous inconsistencies are apparent from which data were used in the facility-specific statistical analyses.

Notes

a *"We evaluate the null hypothesis by assuming it is true and test the reasonableness of this assumption by calculating the probability of getting the results if chance alone is operating. If the obtained probability turns out to be equal or less than a critical probability level called the alpha (a) level, we reject the null hypothesis. Rejecting the null hypothesis allows us, then to accept indirectly the alternative hypothesis since, if the experiment is done properly, it is the only other possible explanation."* from Pagano, R.R., "Understanding Statistics in the Behavioral Sciences," Second Edition, St. Paul, MN: West Publishing Company, 1986.
b In decision theory, this is known as a "Type I Error," a conclusion that an important relationship exists when there is actually none. A "Type II Error" is a conclusion that an important relationship does not exist when it actually does. From Freund, J., "Modern Elementary Statistics," Fourth Edition, Englewood Cliffs, NJ: Prentice-Hall, Inc., 1973.

1 De Fre, R., and Rymen, T. PCDD and PCDF formation from hydrocarbon combustion in the presence of hydrogen chloride. Chemosphere 19: 331-336 (1989).
2 Rothman, "Modern Epidemiology," Boston, Massachusetts: Little, Brown and Company, 1986, pp. 306-307.
3 Freund, J.E., "Modern Elementary Statistics," 4th Edition, ISBN 0-13-593475-3, Englewood Cliffs, NJ: Prentice-Hall, Inc., 1973.
4 Rigo et al. p. 1.
5 Rigo et al., p. 1-7.
6 Rigo et al., p. v.

Chapter 3: Confounding Factors

Rigo et al. identified a number of factors that may have confounded the results of other studies in which chlorine input and dioxin emissions exhibited positive relationships. In some cases they noted the potential influence of such factors when their analyses of the data from these studies corroborated the original findings. However, Rigo et al. gave little or no consideration to these same factors when drawing conclusions from their facility-specific analyses.

For example, Rigo et al. discuss outliers and their influences on statistical outcomes, and they sometimes identified and set aside outliers in their critiques of other studies with positive outcomes. In their own study, however, they used all data points in their statistical calculations.

Many of the confounding factors are quite general, such as *"...no ash catalyst chemistries (copper and iron), no mass balances, incomplete data ...."* [1] Others can be grouped into the two general categories below.

Design and Operating Conditions

In the ASME report, numerous factors related to the design and operation of combustion facilities are identified as influencing emission data, e.g., *"... flue gas temperature, intentional experimental changes, salt versus organochloride spiking, design differences..."* [2]*; " ... flue gas moisture ..."* [3]*; "...different types of waste combustors and APCS [air pollution control systems]..."* [4]*; "... time to reach stabilization ... from a minimum of three hours to more than eight hours from a cold start... "* [5]*, also described as "... lag in system response ..."* [6] and *"... facility ... and start-up condition effects ...".* [7]

Another interesting factor discussed by Rigo et al. is the *"fly wheel effect,"* [8], in which the release of dioxins following the input of chlorine containing materials is delayed and protracted. They caution that "*failure to provide adequate stabilization time between conditions calls into question identification of the cause of any change in PCDD/F concentrations. ..."*.[9]

Rigo et al. acknowledge that "*different facilities behave in dissimilar manners"* [10] and that changes in the "*underlying waste stream"* [11], and waste characteristics, such as "*sludge burning*" [12], influence the results of input/emissions data. They also note that *"[s]tack chlorine level changes and PCDD concentration changes are both induced by the APCS,"* confounding results for some combustors. [13] For example, they observed that " *... stack concentrations vary between units with no APCS and those with advanced APCS."*

While evaluating the results of several studies in which a positive correlation between chlorine input and dioxin output was found, they drew particular attention to the importance of timing. For example, they observed in one case that *"... PCDD/F*

concentrations may not have reached steady state levels for the intended operating condition and confounded data may be being analyzed." [14] In another they noted as follows:

> Rigo et al.: *"Runs conducted first thing in the morning after operating the furnace overnight on normal MSW would have had a different amount of cross-contamination than a test conducted shortly after a change in condition."* [15]

Sample Collection and Analysis

Rigo et al. also identified confounding factors related to sample collection and analysis. For example, in their critiques of other studies, they made frequent references to the significance of *"sampling location,"* [16] alluding to differences in *"... tests performed at different locations (i.e., boiler outlet, stack, etc.)".* [17] In one of their critiques, they cautioned as follows:

> Rigo et al. "*Sample location and sampling conditions are potentially important confounding variables ...."* [18]

In another, they explicitly *noted "...the influence of sampling location on PCDD/F concentrations ..."* [19]. For example, they commented as follows:

> Rigo et al.: *"In the case of furnace outlet data, interpretation must recognize that PCDD/F test methods have not been validated at this location. High temperature sampling could result in catalytic destruction of PCDD/F ...";* [20]

In evaluating other studies, the authors of the ASME report also acknowledged confounding factors related to sample analysis. For example, they noted *"... limitations in the sampling and analysis techniques at low concentrations ..."* [21] and referred several times to *"... laboratory ... effects ..."* [22], e.g., *"... low laboratory recoveries ...".* [23] In their assessment of another study, they noted as follows:

> Rigo et al.: *"The most obvious difference identified between tests at a given facility was attributed to analytical laboratory difference."* [24]

In particular, Rigo et al. also acknowledged problems encountered when assessing low dioxin concentrations, drawing attention to *"...the U.S. practice of reporting Below Quantitation Limits [BQL] and BDL results as zeros rather than as best estimates and the detection limit."* [25] They identified difficulties caused by *"...between laboratory differences or numerous low and BDL [below detection limit] concentrations in the samples"* [26] and *"different numbers of below detection limit [BDL] results".* [27]

Another confounding factor identified by Rigo et al. in their evaluations of other studies were sampling train contamination, as follows:

> Rigo et al: *"Significantly different results, either in terms of the signature or the quantity of material, in any triplicate during a particular test series could result from either the lack of equilibration time before testing started or from sampling train contamination."* [28]
>
> Rigo et al.: *"Great care is exercised when recovering and cleaning Method 23 sampling trains, yet USEPA reported in the method evaluation (MRI, 1990) that trains should not be switched between clean and dirty locations due to possible hysteresis effects."* [29]

It is difficult to see the rationale for the use of such data to investigate correlations between chlorine input and dioxin output from full-scale combustors. As discussed below, others have concluded that such efforts are too simplistic for the complexities of interactive, multiple pathways of formation of micropollutants such as dioxin that are taking place within the constantly fluctuating environment of full-scale combustion systems.

Limitations of Data from Full-Scale Combustors

As mentioned earlier, Rigo et al. relied on data obtained during trial burns, compliance tests and other similar projects that were, in most cases, carried out for some purpose other than exploring the relationship between chlorine input and dioxin emissions. Many regard the acquisition from full-scale combustors of data that is sufficiently reliable for such comparisons to be difficult, if not impossible, even when tests are designed and carried out for that specific purpose. For example, the Danish Ministry of the Environment offered the following observations about other studies that have explored the relationship of chlorine input to combustors and dioxin output: [30]

> *"Reports are released which conclude that there is no correlation between the dioxin formation and the PVC content in the waste and reports are released which conclude that there is a correlation. It seems most likely that in the test design and running of the tests, there are many difficulties in keeping all relevant parameters constant (e.g., combustion conditions) and one variable only (e.g., chlorine content)."*

Cains and Dyke (1994), researchers in the United Kingdom are similarly critical of attempts to define the relationship of chlorine input and dioxin output by comparing data obtained from full-scale waste combustors: [31]

> *"Generally, the global comparisons in this work have not identified clear causal effects. ... This is hardly surprising, given that each plant is designed to work under a specific set of conditions with specific types of feedstock."*

Other leading European researchers, such as Fangmark et al. (1991) have pointed out the difficulties of acquiring useful data from directed experiments with full-scale combustors: [32]

> *"...[M]ajor drawbacks with full scale studies are that it is difficult to control operating parameters such as temperatures, CO concentrations, and fuel composition which collectively make it impossible to perform experiments that are fully comparable."*

Commenting on the U.S. Environmental Protection Agency Waste Incineration Research Program in 1996, the Agency's Science Advisory Board was both blunt and succinct on the topic of full-scale combustor data, as follows: [33]

> *"In fact, the variability in full-scale performance is unlikely to result in any meaningful data at all."*

As discussed earlier, evidence of any discernible trend from statistical evaluations of the data in the ASME database must be regarded as most unexpected.

Notes

1 Rigo et al., p. 2
2 Rigo et al., p. 3.
3 Rigo et al., p. 2-48
4 Rigo et al., p. 1-4.
5 Rigo et al., p. 2-21.
6 Rigo et al., p. 2-30.
7 Rigo et al., p. 2-40.
8 Rigo et al., p. 2-32.
9 Rigo et al., p. 2-55.
10 Rigo et al., p. 2-38.
11 Rigo et al., p. 2-46.
12 Rigo et al., p. 2-38.
13 Rigo et al., p. 3-12.
14 Rigo et al., p. 2-40.
15 Rigo et al., p. 2-54.
16 Rigo et al., p. 3.
17 Rigo et al., p. 6.
18 Rigo et al., p. 2-8.
19 Rigo et al., p. 2-42
20 Rigo et al., p. 2-8.
21 Rigo et al., p. 2-28.
22 Rigo et al., p. 2-40.
23 Rigo et al., p. 2-50.
24 Rigo et al., p. 2-36.
25 Rigo et al., p. 2-36.
26 Rigo et al., p. 2-40.
27 Rigo et al., p. 6.
28 Rigo et al., p. 2-31.
29 Rigo et al., pp. 2-31 to p. 2-32.

30 Moller, S., Larsen, J., Jelnes, J.E., Faergemann, H., Ottosen, L.M., and Knudsen, F.E., "Environmental Aspects of PVC," Environmental Project No. 313, Denmark: Ministry of the Environment, Danish Environmental Protection Agency, 1995.
31 Cains, P.W., and Dyke, P., Chlorinated dibenzodioxin and dibenzofuran emissions from waste combustion plants in the U.K. Chemosphere 28 (12): 2109-2119 (1994).
32 Fangmark, I., Marklund, S., Rappe, C., Stromberg, B., and Berge, N. Use of a synthetic refuse in a pilot combustion system for optimizing dioxin emission, Part II. Chemosphere 23 (8-10): 1233-1242 (1991).
33 U.S. Environmental Protection Agency Science Advisory Board, "Review of the Waste Incineration Research Program," Draft. Washington, D.C., 1 May 1996.

Chapter 4: Municipal Waste Combustors

Rigo et al. began their discussion of this category by stating, *"Data from the 63 MWC facilities in the database were used in this portion of the study."* [1] Later in their report, the number of facilitiesa relied on for their quantitative evaluation is reported as 27 facilities that have 38 individual combustors. [2] In yet another section, the number is given as 26 facilities that have 31 combustors. [3] Finally, in their summary findings for municipal waste combustors, Rigo et al. refer to 20 facilities with no indication of their identities or the number of combustors at these facilities. [4] These inconsistencies need to be addressed.

Analyses by Rigo et al.

For municipal waste combustors, Rigo et al. assumed hydrogen chloride (HCl) concentrations in stack gases to be reliable indicators of chlorine feedrates. According to Rigo et al., their statistical analyses of the relationship between the stack gas concentrations of HCl and dioxin led to the following conclusion: [5]

> Rigo et al.: *"On a facility-by-facility basis, 17 [municipal waste combustion] facilities displayed no relationship — two increased and one decreased."*

This conclusion can be compared to the statistical values calculated by Rigo et al. which were excerpted from Appendix D-1 of their report and listed in Table 4-1. These values and their associated confidence levels can be summarized as follows:

> On a facility-by-facility basis, a positive relationship between HCl and dioxin concentrations was found at 15 of 22 municipal waste combustion facilities. This positive correlation was statistically significant at confidence levels >95 percent at five facilities; >90 percent at two facilities; and <80 percent at the remaining eight facilities. Among the facilities exhibiting a negative correlation, this relationship was statistically significant at a confidence level> 90 percent at one facility, while the remaining six had confidence levels <80 percent.

Table 4-1 Municipal Waste Combustors

Statistical Data from Rigo et al.

Positive Correlation at >95% Confidence Level

RRID	*Facility*	*n*	*R*	*p*
153	Detroit	6	0.94794	0.0040
191	Helsingor	8	0.79663	0.0180
44	Lancaster (3 Combustors*)	18	0.50202	0.0338
51	Pittsfield (Vicon) (3 Sampling Sites**)	38	0.46688	0.0031
19	Refa (2 Test Periods**)	30	0.36768	0.0456

Positive Correlation at >90% Confidence Level

RRID	*Facility*	*n*	*R*	*p*
188	Kara	15	0.47298	0.0750
189	Reno Syd (2 Test Periods)	33	0.31156	0.0776

Positive Correlation at Confidence Levels <80%

RRID	*Facility*	*n*	*R*	*p*
156	Hartford (2 Sampling Sites)	26	0.02270	0.9123
71	Horsholm (SO2 Reagent)	26	0.25478	0.2091
150	MERC (2 Sampling Sites)	8	0.12076	0.7758
92	Quebec	13	0.10524	0.7322
145	Quebec SS (3 Sampling Sites)	35	0.01812	0.9177
171	Roosendaal	3	0.89936	0.2881
196	Thyra	7	0.16151	0.7294
89	Wurtzburg (3 Sampling Sites)	30	0.14258	0.4523

Negative Correlation at >90% Confidence Level

RRID	*Facility*	*n*	*R*	*p*
100	Albertslun	11	-0.53511	0.0898

Negative Correlation at Confidence Levels <80%

RRID	*Facility*	*n*	*R*	*p*
217	Amager	8	-0.49805	0.2091
197	Brondby	14	-0.24906	0.3905
168	Oswego (3 Sampling Sites)	21	-0.25401	0.2665
175	PRRI	7	-0.03593	0.9390
187	Reno Nord (3 Test Periods)	37	-0.21551	0.2089
80	Westchester (3 Sampling Sites)	37	-0.0560	0.7420

No Regression Results Presented by Rigo et al.

RRID	*Facility*	*n*	*R*	*p*
202	Arhus Nord			
94	AVR			
116	Leeuwarden			
91	PEI			
169	Sioux Center			
176	Zaanstad			

No Simultaneous Measures of HCI and Dioxins in Database

RRID	*Facility*	*n*	*R*	*p*
179	AVI			
95	Gevudo			

* Rigo et al. combined data from three separate combustors at this facility.

**Dioxin data were collected not only from the stack but other locations as well and these data were aggregated for analysis by Rigo et al.
***Dioxin and HCI data were collected during tests separated by periods of time ranging from weeks to years.

As illustrated in Figure 4-1, the statistical values from the ASME report clearly show the predominance of positive correlation. In contrast, Rigo et al. presented the aggregated data in a scatter plot, reproduced as Figure 4-2, in which no relationship is discernible.

As noted above, Rigo et al. included 20 facilities in their conclusion for this combustor category. [6] In contrast, a review of Appendix D-1 of the ASME report indicates that they carried out statistical evaluations of data from 22 municipal waste combustion facilities. Moreover, their database in Appendix C-1 contains the requisite HCl and dioxin data for 28 facilities. This suggests that, of 28 facilities included in their database, one quarter were excluded from the final evaluation. No acknowledgment or explanation was given for these omissions.

Data were handled in such a way that any relationship between HCl and dioxin is unlikely to have been discernible. As mentioned earlier, Rigo et al. commingled data from three separate combustors and performed a statistical analysis of these aggregated data, rather than analyzing each individual combustor. For four facilities, they commingled data from two test series, which were conducted as much as a year apart.

Rigo et al. acknowledged and discussed *"...the influence of sampling location on PCDD/F [dioxin] concentrations."* [7] Nonetheless, at 11 MWC facilities, they compared HCl concentrations with mixtures of dioxin measurements that included not only samples taken at the stack but also those taken at other points in the system, e.g., the boiler outlet, secondary combustion chamber outlet, etc.

This aggregation of data across implicit barriers obviously obscured the relationship between HCl and dioxin. For example, when Rigo et al. commingled dioxin measurements taken at the stack with those taken at the boiler outlet at one municipal waste combustor, their comparison of these aggregated data with HCl concentrations showed only a very weak positive correlation coefficient of negligible significance, as shown in Figure 4-3. However, when data from these two sampling sites were analyzed separately, HCl and dioxin concentrations showed a very strong positive correlation with high confidence at each sampling site, as illustrated in Figures 4-4 and 4-5.

Greenpeace Analyses of Raw Data from Rigo et al.

As described earlier, the ASME database contains data identified as simultaneous measures of HCl and dioxin concentrations in the stack gases of 28 municipal waste combustion facilities. Following the same general approach as that by Rigo et al., correlation coefficients and p-values were calculated using the logarithms of these variables. [b] As shown by the results listed in Table 4-2, these analyses by Greenpeace corroborated, with a few exceptions, the statistical values presented by Rigo et al.

At 20 of the 28 facilities, HCl and dioxin concentrations showed a positive correlation, as shown in Figure 4-6. In other words, at some 70 percent of the municipal waste combustion facilities in the ASME database, dioxin concentrations increased with rising HCl concentrations. This positive trend was statistically significant at five facilities with >95 percent confidence; >90 percent confidence at three; and <80 percent confidence at twelve. Data from eight facilities exhibited a negative correlation which was statistically significant at one facility with >95 percent confidence; one facility, >90 percent confidence; and <80 percent at five.

Evidence of any dominant trend, whether positive or negative, from data so diverse in origins as that from these 28 facilities is entirely unexpected. These data were produced by a mixture of constantly evolving sampling and analysis methods, coming as they do from facilities in five different countries with no common method [8] during a period when sampling and analysis methods were undergoing considerable change. As discussed in greater detail in Sections 10 and 11, these and related factors can be expected to yield data that vary greatly in their precision and accuracy and, consequently, their comparability.

As indicated in Table 4-3, these evaluations of the relationship of HCl and dioxin concentrations in stack gases of municipal waste combustors are based on a very small, non-random sample of these combustors. The 28 facilities for which the ASME database contains both HCl and dioxin data represent only 1.1 percent of the 2,583 MWCs operating in 13 of the industrialized nations. [9]

In their report, Rigo et al. also discussed having aggregated and analyzed HCl and dioxin data from ten of the Danish MWC facilities, which constituted the largest block of MWC facilities in their assessment. They reported a "*weak [positive] relationship ... that confirms the original findings."*10

Their statistical values cannot be corroborated since they did not present their analysis. However, their finding of a weak positive relationship between HCl and dioxin was confirmed by reanalysis of the aggregated data. The reanalysis also showed that, although the positive correlation is weak ($r = 0.1485$), it is statistically significant with a very high degree of confidence, e.g., >95 percent.

In summary, despite many factors that can be expected to obscure any dominant trend in the relationship of HCl and dioxin concentrations in stack gases, both the analysis by Rigo et al. and the analysis by Greenpeace reveal that increasing HCl concentrations were accompanied by rising dioxin concentrations at two-thirds or more of the municipal waste combustion facilities assessed.

Table 4-2 Municipal Waste Combustors

Statistical Values by Greenpeace

Positive Correlation at >95% Confidence Level

RRID	*Facility*	*n*	*R*	*p*
153	Detroi	6	0.947957	0.00191
191	Helsingor	8	0.811371	0.011441
44	Lancaster (1991 & 1992) (3 Units)	18	0.503409	0.03235
51	Pitssfield (Vicon)(3 Sampling Sites)	38	0.46717	0.003055
195	Refa (1987 & 1999)	30	0.370425	0.043584

Positive Correlation at >90% Confidence Level

RRID	*Facility*	*n*	*R*	*p*
202	Arhus Nord	4	0.794256	0.161631
188	Kara	15	0.489098	0.062741
189	Reno Syd (2 Test Periods)	33	0.300072	0.089451

Positive Correlation at Confidence Levels <80%

RRID	*Facility*	*n*	*R*	*p*
94	AVR	3	0.334092	0.75688
156	Hartford (2 Sampling Sites)	26	0.023061	0.910929
71	Horsholm (with and without SO2 rgnt)	26	0.25486	0.20845
150	MERC (2 Sampling Sites)	8	0.121534	0.772949
175	PRRI	7	0.025651	0.956109
145	Quebec SS (3 Sampling Sites)	35	0.017494	0.92053
187	Reno Nord (3 Test Periods)	37	0.203884	0.225907
171	Roosendaal	3	0.899432	0.175847
169	Sioux Center	9	0.0189	0.961337
196	Thyra	7	0.212119	0.644636
89	Wurtzburg (3 Sampling Sites)	30	0.14213	0.45351
176	Zaanstad	6	0.148469	0.776057

Negative Correlation at >95% Confidence Level

RRID	*Facility*	*n*	*R*	*p*
116	Leeuwarden	3	-0.978437	0.041788

Negative Correlation at >90% Confidence Level

RRID	*Facility*	*n*	*R*	*p*
100	Albertslund	11	-0.541314	0.082247

Negative Correlation at Confidence Levels <80%

RRID	*Facility*	*n*	*R*	*p*
217	Amager	8	-0.493309	0.207375
197	Brondby	14	-0.272172	0.345058
168	Oswego (3 Sampling Sites)	21	-0.254012	0.265824
91	PEI (2 Sampling Sites)	21	-0.145204	0.529623
92	Quebec	13	-0.10532	0.735896
80	Westchester (3 Sampling Sites)	37	-0.056064	0.741664

No Simultaneous Measures of HCI and Dioxins in Rigo Database

RRID	*Facility*	*n*	*R*	*p*
179	AVI			
95	Gevudo			

Table 4-3 Municipal Waste Combustors in ASME Report

Location	*Facilities*	*Combustors*	*Percent of Nation's MWCS10*
Denmark	11	11	22%
United States	8	10	<5%
Canada	4	4	23%
Netherlands	4	4	27%
Germany	1	1	2%

Notes

a Rigo et al. use the terms "facility" and "facilities" to mean a site or sites at which there are one or more combustors. In a search of Appendix C-1 of the ASME report, only one municipal waste combustion facility was found to be the site of more than one combustor with the requisite HCl and dioxin data. Rather than evaluating each of the three combustors at this site, Rigo et al. aggregated the data and calculated a single correlation coefficient and other statistical values.
b Rigo et al. carried out their statistical evaluations using the logarithms of HCl concentrations and dioxin concentrations, converted to picomoles per dry standard cubic meter. The analyses by Greenpeace were carried out using the logarithms of HCl concentrations and dioxin concentrations, expressed as nanograms per dry standard cubic meter. Comparisons of the two methods of expressing dioxin concentrations showed no significant difference.

1 Rigo et al., p. 4.
2 Rigo et al., Table 2.3-1, pp. 2-10 to 2-13.
3 Rigo et al. Rigo et al., p. 2-9.
4 Rigo et al., p. 2-63.
5 Rigo et al., p. 2-66.
6 Rigo et al., p. 2-63.
7 Rigo et al., p. 2-42.
8 Liem, A.K.D., and van Zorge, J.A. Dioxins and related compounds: Status and regulatory aspects. Environ. Sci. & Pollut. Res. 2 (1): 46-56 (1995).
9 Ibid.
10 Ibid.

Chapter 5: Medical Waste Incinerators

Two of the medical waste incinerators in the quantitative assessment by Rigo et al. were located in Denmark, while the remainder were in the U.S. The data from these incinerators were collected during tests carried out between 1986 and 1993. It is also important to note that, according to the ASME database, most but not all of the U.S.-based medical waste incinerators were burning both medical waste and municipal solid waste while the emission data were obtained.

Analyses by Rigo et al.

Again using HCl as a surrogate for chlorine feedrate, Rigo et al. assessed the relationship between HCl and dioxin concentrations in gas streams of medical waste incinerators and concluded as follows: [1]

> Rigo et al.: *"Of the 17 plants [medical waste incinerators] with sufficient simultaneous data to explore the relationship, 14 showed no statistically significant trend, two increased and one decreased."*

In Table 3.4-1 of their report, Rigo et al. listed 19 medical waste incineration facilities with one combustor each. [2] In Figure 3.5-4, a scatter plot of HCl versus dioxin concentrations, they listed 24 facilities. Included among these are six incinerators for which no uncontrolled HCl data are presented in their database; one which has only two data pairs, which are too few for statistical analysis; and one which is not listed in their database.

Rigo et al. presented statistical analyses for only 18 medical waste incinerators in Appendix D-2 of their report. [3] However, complete analysis should be possible for only 15 of these, since there are no suitable HCl data in the ASME report's database for two units and there are only two data pairs for the third. [4] In their statistical analyses of the data from five medical waste incinerators, Rigo et al. calculated correlation coefficients using dioxin data that consisted of the commingled values obtained at both the stack and at other sampling locations.

According to statistical values excerpted from the ASME report and presented in Table 5-1, Rigo et al. actually found that increasing HCl concentrations were associated with higher dioxin concentrations at two-thirds of the medical waste incinerators in their study. The results of their analyses and associated confidence levels are illustrated in Figure 5-1 and summarized as follows:

> Concentrations of HCl and dioxin exhibited a positive correlation at 10 of 15 medical waste incinerators. Among these, confidence levels were >95 percent at two facilities, >90 percent at one, >80 percent at two, and <80 percent at five. At the remaining five medical waste incinerators, HCl and dioxin showed a negative correlation with >95 percent confidence at one facility and <80 percent confidence at four facilities.

The predominance of positive correlations that was found in the facility-specific analyses by Rigo et al. is readily visible in Figure 5-1. It is interesting to compare this depiction of Rigo et al.'s statistical values with the graphical presentations of medical waste incinerator data given in their report and shown here in Figures 5-2 and 5-3.

Table 5-1 Medical Waste Incinerators

Statistical Data from Rigo et al.

Positive Correlation at >95% Confidence Level

RRID	*Facility*	*n*	*R*	*P*
84	AMI Central	9	0.97287	0.0000
203	Frederikssund	6	0.96237	0.0021

Positive Correlation at >90% Confidence Level

RRID	*Facility*	*n*	*R*	*p*
214	Borgess (2 Sampling Sites)	11	0.55923	0.0737

Positive Correlation at >80% Confidence Level

RRID	*Facility*	*n*	*R*	*p*
190	Kaiser (2 Sampling Sites)	4	0.89140	0.1086
207	Lenoir	9	0.55092	0.1242

Positive Correlation at Confidence Levels <80%

RRID	*Facility*	*n*	*R*	*p*
208	Cape Fear	9	0.41341	0.2687
132	Cedars Sinai (2 Sampling Sites)	5	0.42033	0.4810
198	St. Bernardines	3	0.74254	0.4672
199	Sutter	3	0.47290	0.6864
211	U. of Michigan (2 Sampling Sites)	6	0.30728	0.5536

Negative Correlation at >95% Confidence Level

RRID	*Facility*	*n*	*R*	*p*
213	Morristown (2 Sampling Sites) (Hg Rgnt)	12	-0.86203	0.0003

Negative Correlation at >80% Confidence Level

RRID	*Facility*	*n*	*R*	*p*

Negative Correlation at Confidence Levels <80%

RRID	*Facility*	*n*	*R*	*p*
193	Huldovre	6	-0.14038	0.7908
46	Rochester	3	-0.86035	0.3405

206	Stanford	6	-0.06997	0.8952
205	USC Medical	3	-0.2137	0.8629

Miscellaneous Facilities

RRID	*Facility*	*n*	*R*	*p*
385	Clean Harbors [1]			
123	Humber [2]			
126	Jordan Hospital [3]			
197	St. Agnes [4]			

1 No linear regression was presented for this facility.
2 The database contains no uncontrolled HCl data for this facility.
3 Rigo et al. performed a linear regression on the data from this facility. However, their database contains no uncontrolled HCl data for this facility.
4 This facility had only 2 datapoints, which are not sufficient to determine a valid correlation coefficient.

Greenpeace Analyses of Raw Data from Rigo et al.

As noted above, the assessment of medical waste incinerators presented in the ASME report suffers from numerous inconsistencies. However, using the same general procedures followed by Rigo et al., Greenpeace calculated the correlation coefficients for HCl and dioxin concentrations listed in Table 5-2. These statistical values, which are also illustrated in Figure 5-4, can be summarized as follows:

> Increasing HCl concentrations were associated with elevated dioxin concentrations at 11 of 16 medical waste incinerators. The positive correlations of these variables were statistically significant as follows: two incinerators, >95 percent confidence; one, >90 percent confidence; two, >80 percent confidence; and six, <80 percent confidence. HCl and dioxin were found to correlate negatively at five facilities. The correlations were statistically significant at a confidence level of >95 percent at one incinerator and <80 percent at the remaining four.

Statistical analyses by both Rigo et al. and Greenpeace show that dioxin concentrations rose with increasing HCl concentrations at two-thirds of the medical waste incinerators. As expected from data of diverse quality, confidence levels for the correlations were generally low. However, the levels of confidence achieved also support the predominance of positive correlations.

Table 5-2 Medical Waste Incinerators

Greenpeace Analysis of Raw Data

Positive Correlation at >95% Confidence Level

RRID	*Facility*	*n*	*R*	*p*
84	AMI Central	9	0.97486	2.8E-06
203	Frederikssund	6	0.962124	0.000882

Positive Correlation at >90% Confidence Level

RRID	Facility	n	R	p
215	Borgess (2 Sampling Sites)	11	0.552641	0.074707

Positive Correlation at >80% Confidence Level

RRID	*Facility*	*n*	*R*	*p*
190	Kaiser (2 Sampling Sites)	4	0.895964	0.06495
207	Lenoir	9	0.551837	0.118102

Positive Correlation at Confidence Levels <80%

RRID	*Facility*	*n*	*R*	*p*
208	Cape Fear	9	0.399071	0.282772
132	Cedars Sinai (2 Sampling Sites)	5	0.417155	0.471115
198	St. Bernardines	3	0.778409	0.340729
206	Stanford (2 Sampling Sites)	6	0.053518	0.918807
199	Sutter	3	0.450886	0.663621
211	U. of Michigan (2 Sampling Sites)	6	0.320412	0.528754

Negative Correlation at >95% Confidence Level

RRID	*Facility*	*n*	*R*	*p*
213	Morristown (2 Sampling Sites) (w/ and w/out Hg Rgnt)	12	0.870075	0.000165

Negative Correlation at Confidence Levels <80%

RRID	*Facility*	*n*	*R*	*p*
385	Clean Harbors	3	-0.88543	0.197057
192	Huldovre	6	0.172904	0.739825
46	Rochester	3	0.872636	0.215877
205	USC Medical	3	0.255359	0.816416

Miscellaneous Facilities

RRID	*Facilities*	*n*	*R*	*p*
126	Jordan Hospital*			
123	Humber*			
197	St. Agnes**			

* The database contains no uncontrolled HCl data for this facility.
** This facility had only two datapoints, which are not sufficient for a valid linear regression.

Notes

1 Rigo et al., p. 3-22.
2 Rigo et al., p. 3-7 to 3-9.
3 Rigo et al., Appendix D-2.
4 Rigo et al., Appendix C-2.

Chapter 6: Hazardous Waste Incinerators

Other than one Canadian facility, all hazardous waste incinerators for which locations were disclosed were at U.S.-based facilities. The data were obtained at most of these units between 1986 and 1994. However, test dates were not given in all cases.

Comparisons of Percent Chlorine in Feed and Dioxin Concentration in Stack Gases

For their assessment of hazardous waste incinerators, Rigo et al. evaluated the relationship of percent chlorine in feed to dioxin concentrations in stack gasesa. Based on statistical analyses of these data for each unit, they reached the following conclusions:

> Rigo et al.: *"A variable relationship was found; 18 of 28 [hazardous waste incineration] units with simultaneous PCDD/F and chlorine characterization information display no statistically significant relationship. Five facilities show an increase in PCDD/F concentrations with increased chlorine in the feed and five facilities show a decrease."* [1]

> Rigo et al.: *"The available data indicate that, depending on the plant [hazardous waste incinerator], changing chlorine concentration can have no observable effect (20 facilities); increase PCDD/F concentrations (4 facilities); or decrease PCDD/F concentrations (4 facilities)."* [2]

These two conclusions, while moderately inconsistent, are not surprising, given the nature of the variables compared. Percent chlorine in feed is the quantity of chlorine in a given amount of feed. In itself, this measure reveals little about the rate at which chlorine is fed into an incinerator. The latter measure, chlorine feedrate, is obtained by multiplying percent chlorine in feed and waste feedrate. Similarly, the dioxin concentration in stack gas must be multiplied by the stack gas flowrate to determine the dioxin emission rate.

Comparison of these two measures — percent chlorine in feed and dioxin concentration in stack gas — is meaningful only when waste feedrates and stack gas flowrates are held constant. If waste feedrate increases, chlorine feedrate will also increase, even though the percent chlorine in feed may remain the same. Similarly, if stack gas flowrate increases, dioxin emissions increase even though dioxin concentration may not change.

Appendix C-3 of the ASME report contains both percent chlorine in feed and chlorine feedrates for many of the same hazardous waste incinerators. For the overwhelming majority of these units, chlorine feedrates were varied during emissions testing, sometimes by more than six-fold during a single test series.

No stack gas flowrates are given by Rigo et al. However, according to the trial burn report for one of the incinerators in the ASME database, stack gas flowrates fluctuated by +/- 17 percent in tests carried out at the same waste feedrate. During all six tests of this

trial burn, both the waste feedrates and stack gas flowrates varied, in an unrelated fashion, by +/- 16 percent. [3]

It is interesting to note that the conclusions presented by Rigo et al. are not supported by the raw data in Appendix C-3 of their report or by the statistical values presented in Appendix D-3. The raw data describe percent chlorine in feed and dioxin concentrations in gases for 26 hazardous waste incinerators [b], rather than the 28 cited in the conclusions. Of these 26 units, Rigo et al. present statistical values for 18 incinerators which are listed in Table 6-1 and illustrated in Figure 6-1. It is also interesting to compare Figure 6-1 with Figures 6-2 and 6-3, which are scatter plots of hazardous waste incinerator data taken from the ASME report.

Table 6-2 and Figure 6-4 present the results of the Greenpeace analysis of the 26 hazardous waste incinerators for which percent chlorine in feed and dioxin concentrations were given in Appendix C-3. With some notable exceptions, the resulting values corroborate the majority of those obtained by Rigo et al. as well as expand the number of facilities assessed.

Table 6-1 Hazardous Waste Incinerators

Statistical Data from Rigo et al.

(Note: Percent chlorine in feed, which was one of the variables used in calculating these values, is not a valid surrogate for chlorine feedrate, as discussed earlier. Consequently, these data are useless for assessing the relationship between chlorine input and dioxin emissions.)

Positive Correlation at >95% Confidence Level

RRID	*Facility*	*n*	*R*	*p*
220	Aptus, Utah	9	0.71318	0.0310
215	3M	8	0.90081	0.0023
263	*Occidental	10	0.73119	0.0163
271	Rollins, Baton Rouge	3	0.99955	0.0191

Positive Correlation at >80% Confidence Level

RRID	*Facility*	*n*	*R*	*p*
227	CWM, Chicago	4	0.84229	0.1577

Positive Correlation at Confidence Levels <80%

RRID	*Facility*	*n*	*R*	*p*
270	DOD, Rocky Mtn.	3	0.94941	0.2034
246	*Eastman-Kodak, NY	8	0.12276	0.7721
254	GE, Pittsfield	5	0.07828	0.9004
274	Ross, Ohio	3	0.76966	0.4408

Negative Correlation at >95% Confidence Level

RRID	*Facility*	*n*	*R*	*p*
219	*Aptus, Kansas	14	-0.78443	0.0009
399	Confidential B	6	-0.82516	0.0432
388	*CWM, Texas	9	-0.66592	0.0502
283	*WTI, Ohio	22	-0.58711	0.0041

Negative Correlation at >80% Confidence Level

RRID	*Facility*	*n*	*R*	*p*
273	*Rollins, Deer Park	5	-0.68146	0.2052

Negative Correlation at Confidence Levels <80%

RRID	*Facility*	*n*	*R*	*p*
230	Chevron, Richmond	6	-0.3213	0.9518
231	*Ciba, Baton Rouge	3	-0.36347	0.7632
268	Pfizer	3	-0.86516	0.3344
282	Vulcan, KS	5	-0.13712	0.8260

Miscellaneous Facilities

RRID	*Facility*	*n*	*R*	*p*
224	BROS Lagoon**			
398	Confidential A**			
400	Confidential C**			
396	Dow, Canada A**			
238	Dow Midland**			
239	Dow, Plaquemine***			
252	GE, Waterford**			
382	New Bedford**			
389	Waste Tech, LA**			

*Data were collected during two or more tests that were conducted at different times and aggregated for analysis.
**No linear regression is presented for this facility.
***The database contains no data describing percent chlorine in feed for these facilities.

Comparisons of Chlorine Feedrate and Dioxin Concentration

As noted earlier, chlorine feedrates for some of the hazardous waste incinerators can also be found in the ASME database. The relationship of these feedrates with dioxin concentrations were evaluated using the same general procedure as that used by Rigo et al. in their comparisons of percent chlorine in feed and dioxin concentrations. As shown by the results, which are presented in Table 6-3 and illustrated in Figure 6-5, correlations between chlorine feedrate and dioxin concentrations in stack gases were positive at slightly more than half of the hazardous waste incinerators. The results of these analyses can be summarized as follows:

> The ASME database contains both chlorine feedrate and dioxin concentrations in stack gases for 24 hazardous waste incinerators. Among 11 of these units, chlorine feedrates and dioxin concentrations exhibited statistically significant positive correlations as follows: three units, >95 percent confidence; three units, >80 percent; and five units, 95 percent confidence, two incinerators; and It should be noted that the relationship between chlorine input and dioxin concentrations cannot be accurately evaluated by using chlorine feedrate in the comparison unless stack gas flowrates are held constant. Otherwise, chlorine feedrate, which is normally expressed as mass per unit of time (e.g., kilograms per hour) must be compared to the dioxin emission rate, which is obtained when dioxin concentration is multiplied by stack gas flowrate.

Dioxin emission rates of the hazardous waste incinerators in the ASME study cannot be calculated, since stack gas flowrates are not presented in the database. As a consequence, the above conclusion can only be regarded as indicative, within the limits of the fluctuations of stack gas flowrates during each test series at each incinerator, of a predominantly positive relationship between chlorine feedrates and dioxin emission rates.

It must be pointed out again that these results were obtained by following the practice of Rigo et al. of aggregating data that were collected during two or more separate test series carried out at the same facility. The correlation coefficients of the aggregated data are, as expected, often quite different from the correlation coefficients of the data for each individual test series. This is illustrated in Figure 6-6 by comparing coefficients from aggregated data (denoted by the facility identification numbers, 219, 231 and 246) with those of the individual test series (e.g., 219-86 and 219-90). The disparities shown in this figure attest to the errors that can be introduced by aggregation of data in this way.

Figure 6-7 allows a comparison of Rigo et al.'s correlation coefficients for percent chlorine in feed and dioxin concentration with the correlation coefficients for chlorine feedrate and dioxin concentration for all of those hazardous waste incinerators for which the ASME database contained such data. The results are, as expected, often strikingly different. This further emphasizes the unsuitability of percent chlorine in feed as a surrogate for chlorine feedrate.

In summary, the statistical analyses carried out by Rigo et al. on percent chlorine in feed and dioxin concentrations in stack gases of hazardous waste incinerators are inappropriate for assessment of the relationship between chlorine input and dioxin emissions from hazardous waste incinerators. Greenpeace analyses of chlorine feedrates and dioxin concentrations in stack gases show a slight predominance of positive correlations. This finding suggests, in turn, that there may be a slight predominance of positive correlations between chlorine feedrate and rates of dioxin emissions, which cannot be confirmed in the absence of stack gas flowrates.

Table 6-2 Hazardous Waste Incinerators

Reanalysis of Percent Chlorine in Feed vs PCDD/Fs

Positive Correlation at >95% Confidence Level

RRID	*Facility*	*n*	*R*	*p*
220	Aptus, Utah	9	0.714934	0.026852
388	*CWM,Texas (1990, 92, 92, & 94 Tests)	26	0.801854	6.9E-07
215	3M	8	0.905036	0.001236
263	*Occidental (1986 & 1987 Tests)	13	0.641864	0.016769
271	Rollins, Baton Rouge	3	0.9976609	0.004766

Positive Correlation at >80% Confidence Level

RRID	*Facility*	*n*	*R*	*p*
227	CWM, Chicago	4	0.825204	0.130728

Positive Correlation at Confidence Levels <80%

RRID	*Facility*	*n*	*R*	*p*
238	Dow Midland	4	0.473916	0.501946
246	*Eastman-Kodak, NY (1986 & 1992 Tests)	8	0.090549	0.830118
251	GE, Pittsfield	5	0.058321	0.924271
382	New Bedford	3	0.44227	0.670754
389	Waste Tech., LA	3	0.418208	0.690437

Negative Correlation at >95% Confidence Level

RRID	*Facility*	*n*	*R*	*p*
219	*Aptus, Kansas (1986 & 90 Tests)	18	-0.797293	6.1E-05
399	Confidential B	6	-0.844738	0.025185
273	*Rollins, Deer Park (1987 & 88 Tests)	8	-0.945824	0.000188
283	*WTI, Ohio (2 Test Series)	22	-0.581595	0.00433

Negative Correlation at >80% Confidence Level

RRID	Facility	n	R	P
231	*Ciba, Baton Rouge (1988 & 93 Tests)	6	-0.695238	0.11085

Negative Correlation at Confidence Levels <80%

RRID	*Facility*	*n*	*R*	*p*
224	BROS Lagoon	9	-0.97784	0.801462
230	Chevron, Richmond	6	-0.09995	0.848688
398	Confidential A	5	-0.58294	0.281863
252	*GE Waterford (2 Test Series)	6	-0.609542	0.184712
268	Pfizer	3	-0.905326	0.166715
282	Vulcan, KS	6	-0.05324	0.919227

Facilities With Zero Correlation

RRID	*Facility*	*n*	*R*	*p*
400	Confidential C (% chlorine is constant;dioxins vary)	3	0	0.002171
270	DOD, Rocky Mtn. (% chlorine varies; dioxins are constant)	3	0	
396	Dow, Canada A (% chlorine is constant; dioxins vary)	4	0	2E-06
274	Ross, Ohio (% chlorine is constant; dioxins vary)	3	0	0.299378

No Simultaneous Measures of Percent Chlorine and Dioxins

RRID	*Facility*	*n*	*R*	*p*
239	Dow, Plaquemine			

* Data were collected during two or more tests that were conducted at different times, as noted, and aggregated for analysis, following the practice of Rigo et al.

Table 6-3 Hazardous Waste Incinerators

Chlorine Feedrate vs. Dioxin Concentration in Stack Emissions, Raw Data from Rigo et al.

Positive Correlation at >95% Confidence Level

RRID	*Facility*	*n*	*R*	*p*
388	*CWM, Texas (1990, 92, 92, 94)	26	0.72026	3E-05
215	3M	8	0.841397	0.006596
283	*WTI, Ohio (2 Test Periods)	22	0.805939	4.8E-06

Positive Correlation at >80% Confidence Level

RRID	*Facility*	*n*	*R*	*p*
227	CWM - Chicago	4	0.890719	0.069498
263	*Occidental (1986 & 1987)	13	0.457497	0.113657
271	Rollins, Baton Rouge	3	0.971409	0.054862

Positive Correlation at <80% Confidence Level

RRID	*Facility*	*n*	*R*	*p*
238	Dow Midland	4	0.700321	0.259405
251	GE - Pittsfield	5	0.072897	0.905367
274	Ross	3	0.785959	0.331496
282	Vulcan	6	0.407514	0.413014
389	Waste Tech	3	0.910654	0.158355

Negative Correlation at >95% Confidence Level

RRID	*Facility*	*n*	*R*	*p*
246	*Eastman (1986 & 1992)	8	-0.741909	0.030183
273	*Rollins, Deer Park (1987 & 1988)	8	-0.73496	0.032711

Negative Correlation at <80% Confidence Level

RRID	*Facility*	*n*	*R*	*p*
219	*Aptus, KS (1986 &1990)	18	-0.110946	0.660843
220	Aptus, UT	9	-0.411031	0.26708
224	Bros Lagoon	9	-0.28777	0.449556
230	Chevron	6	-0.126055	0.80951
231	*Ciba (1988 & 1993)	6	-0.571932	0.221973
252	*GE - Waterford (1991 & 1992)	6	-0.541819	0.253718
268	Pfizer	3	-0.821056	0.286945

Facilities With Zero Correlation

RRID	*Facility*	*n*	*R*	*p*
400	Confidential C	3	7.7E-15	0.002171
270	DOD	3	ERR	0.53241
396	Dow Canada A	4	0	0.000743
392	New Bedford	3	5E-16	0.051768

Facilities With No Chlorine Feedrate Data

RRID	*Facility*	*n*	*R*	*p*
398	Confidential A - No Cl Feedrate			
399	Confidential B - No Cl Feedrate			

* Data were collected from these facilities during two or more tests that were conducted at different times, as noted, and aggregated for analysis, following the practice of Rigo et al.

Notes

a Unlike other combustor categories, all dioxin concentrations for hazardous waste incinerators were measured at the stack.
b Twenty-two of 26 hazardous waste incinerators are located in the U.S.; one, in Canada; and three, undisclosed. Ten of the U.S. facilities are listed by the U.S. Environmental Protection Agency as commercial hazardous waste incinerators, of which the Agency lists a total of 37. The remaining U.S.-based units evaluated by Rigo et al. include incinerators at Superfund sites and proprietary, on-site combustors owned and operated by particular industries for their own waste streams.

1 Rigo et al., pp. 7 and 8.
2 Rigo et al., p. 4-20.
3 Radian Corporation, "Trial Burn Test Report, Aptus Incineration Facility, Coffeyville, Kansas," Herndon, Virginia: Radian Corporation, December 1991.

Chapter 7: Boilers and Industrial Furnaces

Rigo et al. compared percent chlorine in feed, rather than chlorine feedrate, to dioxin concentrations in gas streams in their assessment of boilers and industrial furnaces. Rather than facility-specific statistical analyses, they prepared an aggregate scatter plot of percent chlorine in feed versus dioxin concentrations for these combustors, which apparently served as the basis for the following contradictory conclusions: [1]

> Rigo et al.: *"There is too little hazardous waste fired boiler data to reach firm conclusions."*
>
> Rigo et al.: *"Chlorine feed concentration is inversely related to PCDD/F concentrations at the stack for this very limited data set."*

Although Rigo et al. noted that their "database includes PCDD/F data for five boilers," [2] they did not make clear the fact that only three of these units have both dioxin and chlorine-related measures. [3] Percent chlorine in feed data are provided for all three units. However, at each unit, all dioxin concentrations were measured at the same percent chlorine in feed. This can also be seen in the scatter plot prepared by Rigo et al. [4]

With no variation in percent chlorine in feed, it is impossible to determine whether or not dioxin concentrations change when percent chlorine in feed changes, even if such a comparison were valid. (As discussed earlier, percent chlorine in feed is a valid surrogate for chlorine feedrate only when considering an individual combustor for which both the waste feedrate and stack gas flowrates are held constant.)

Chlorine feedrate data are also provided for one unit. However, the feedrate was held constant for all dioxin determinations. Consequently, these data cannot be used for determining the relationship of chlorine input and dioxin concentrations in stack gases.

In summary, the data in the ASME report are not useful for evaluating the relationship between chlorine input to boilers and industrial furnaces and dioxin concentrations in stack gases.

Notes

1 Rigo et al., p. 4-36.
2 Rigo et al., p. 4-21.
3 Rigo et al., Appendix C-4.
4 Rigo et al., p. 4-25.

Chapter 8: Cement Kilns

All of the facilities are located in the U.S. and their emission data were obtained during the period of 1992-1994. According to the ASME database, most of these cement kilns were burning both hazardous waste and commercial solid waste during testing, while at least one was co-firing municipal solid waste. It is not clear that the chlorine content of these co-fired materials were reflected in the data describing chlorine feedrate and percent chlorine in feed.

Analyses by Rigo et al.

Rigo et al. do not present facility-specific or combustor-specific statistical analyses for the cement kilns in their study, all of which were sited in the U.S. Instead, they offer a scatter plot of the aggregated data from the kilns, showing dioxin concentrations at chlorine feedrates normalized to daily clinker outputs. The aggregate scatter plot lists 20 facilities, several of which have multiple kilns. [1] However, their database contains no chlorine feedrate data for the kilns at six of the 20 facilities included in the plot. Since no clinker output data are included in their report, the following conclusion cannot be corroborated: [2]

> Rigo et al.: *"Cement kiln chlorine feed rate has no discernible influence on the nature or quantity of PCDD/F emitted from the stacks of these facilities."*

Greenpeace Analysis of Raw Data from Rigo et al.

Statistical analyses of the chlorine feedrates and related dioxin concentrations given in Appendix C-5 of the ASME report show that increasing chlorine feedrates were accompanied by increasing dioxin concentrations at 14 of 23 cement kilns, as listed in Table 8-1 and illustrated in Figure 8-1. The conclusion that can be drawn from these analyses is as follows:

> Fourteen of 23 cement kilns exhibited positive correlations between chlorine feedrate and dioxin concentrations in gas streams. At three kilns, this positive relationship was statistically significant with >95 percent confidence; at two, >80 percent confidence; and, at the remaining nine, <80 percent confidence. Of the nine kilns that evidenced negative correlations, two showed statistical significant at >80 percent confidence levels while the remaining seven had confidence levels of <80 percent.

As discussed earlier, these comparisons of chlorine feedrates and dioxin concentrations in gas streams are useful for evaluating the relationship of chlorine feedrates and dioxin emission rates only to the extent that stack gas flowrates were held constant during individual test series at the individual kilns. In the absence of substantiating flowrate data, they can only be regarded as suggestive.

In summary, due to insufficient data, the conclusion presented by Rigo et al. on the relationship between chlorine feedrates normalized to daily clinker output and dioxin concentrations in gas streams from cement kilns cannot be corroborated. However, statistical analyses of chlorine feedrates and dioxin concentrations taken from the ASME database show that dioxin concentrations increased with increasing chlorine feedrates at 60 percent of the cement kilns evaluated. This suggests that increases in chlorine feedrates were generally accompanied by increased dioxin emission rates.

Table 8-1 Cement Kilns

Chlorine Feedrate vs. Dioxin Concentrations in Gas Streams, Raw Data from Rigo et al.

Positive Correlation at >95% Confidence Level

RRID	*Facility*	*n*	*R*	*p*
316	*Chanute(Unit 1)(1992, 93 & 94)	15	0.707855	0.002824
47	Holly Hill(Unit 1)	6	0.95665	0.001226
47	Holly Hill(Unit 2)	5	0.991629	0.000185

Positive Correlation at >80% Confidence Level

RRID	*Facility*	*n*	*R*	*p*
200	*Freedonia(Unit 1)(1992 & 93)	11	0.495825	0.117518
312	Knoxville	6	0.655411	0.143161

Positive Correlation at <80% Confidence Level

RRID	*Facility*	*n*	*R*	*p*
201	Alpina (Unit 5)	3	0.737013	0.389377
294	Bath (Unit 2)	3	0.282297	0.796286
311	Fairborn (Unit 1)(All Sampling Sites)	9	0.08463	0.793218
62	Foreman (Unit 2)	6	0.437149	0.375646
200	Fredonia (Unit 2)(1993)	3	0.115437	0.918101
313	Kosmosdale	3	0.85032	0.247521
64	Logansport	4	0.216318	0.774545
317	Louisville (Unit 1)	5	0.391289	0.502313
317	Louisville (Unit 2)	4	0.687096	0.273453

Negative Correlation at >80% Confidence Level

RRID	*Facility*	*n*	*R*	*p*
293	Artesia	3	-0.953992	0.086199
302	Essroc (All Sampling Sites)	9	-0.53949	0.12848

Negative Correlation at <80% Confidence Level

RRID	*Facility*	*n*	*R*	*p*
294	Bath (Unit 1)	3	-0.806321	0.305989
316	*Chanute (Unit 2) (1992 & 94)	14	-0.088857	0.762193
49	Clarksville	6	-0.497279	0.303534
62	Foreman (Unit 1)	4	-0.612941	0.352777
62	Foreman (Unit 3)	3	-0.67011	0.46192
304	Wampum (Unit 3)	5	-0.331552	0.5756
304	Wampum (Unit 12)	3	-0.752886	0.371101

* Data were collected at two or more tests, as noted, and, following the practice of Rigo et al., these data were aggregated for analysis.

Notes

1 Rigo et al., p. 4-34.
2 Rigo et al., p. 4-36.

Chapter 9: Biomass Combustors

Rigo et al. list nine biomass combustors in Table 5.3-1 of their report. [1] However, their database includes eight units; five of these are accompanied by data describing dioxin concentrations and one or more of the following chlorine-related measures: HCl emissions, percent chlorine in feed and chlorine feedrate. [2] Although not listed as such in the database, one of the five (RRID 144) is apparently a facility with two combustors. [3]

These five biomass combustion facilities are located as follows: Canada, two; United Kingdom, one facility with two combustors; Netherlands, one; and United States, one. For their emissions data, the time of origin ranged from 1987 to 1994, with no date given for one facility.

Rigo et al. do not present facility-specific or combustor-specific statistical analyses for the biomass combustors. Instead, they provide two scatter plots: one with dioxin concentrations versus percent chlorine in feed for three facilities with one combustor each, and one with dioxin concentrations versus uncontrolled HCl concentrations for three facilities with a total of five combustors. These two aggregate scatter plots led to two contradictory conclusions: [4]

> Rigo et al.*: "Given the variation in PCDD/F concentrations over the range of chlorine feed concentrations and stack HCl concentrations, there is too little data to draw any definitive conclusions."*
>
> Rigo et al.: *"There does not appear to be any relationship between chlorine in the waste fed to biomass fired furnaces and PCDD/F concentrations."*

As described earlier, the comparison of percent chlorine in feed with dioxin concentration in stack gas is meaningful only under certain circumstances — constant feedrate and stack flowrate. As a consequence, little if anything can be concluded about the relationship between chlorine input and dioxin emissions at the three biomass combustors for which Rigo et al. used percent chlorine in feed as a surrogate for chlorine input.

Rigo et al. used HCl concentration as a surrogate for chlorine input for two biomass combustion facilities having a total of five individual combustors. However, for each of these combustors, there were insufficient data in the ASME report's database for determining the relationship between HCl and dioxin concentrations: four of the combustors had only one data pair — one HCl value associated with one dioxin value — and the fifth unit had only two data pairs.

In summary, the data presented by Rigo et al. are insufficient to allow evaluation of the relationship between chlorine input and dioxin emissions from biomass combustors.

Notes

1 Rigo et al., p. 5-5.
2 Rigo et al., Appendix C-7.
3 Rigo et al., p. 5-10 (Figure 5.4-1).
4 Rigo et al., p. 5-11.

Chapter 10: Hydrogen Chloride Concentrations in Stack Gases as Indicators of Chlorine Input

For their evaluation of the relationship of chlorine input and dioxin emissions from municipal waste combustors and medical waste incinerators, Rigo et al. compared hydrogen chloride (HCl) concentrations in stack gases and dioxin concentrations measured at the stack and other locations. As discussed below, HCl concentrations in stack gases of full-scale combustors are not reliable indicators of chlorine input. Moreover, the methods used for sampling and analysis of HCl in combustor gases are subject to considerable imprecision and bias.

Municipal and medical wastes are quite heterogeneous so that chlorine content can vary widely within a relatively brief period. Likewise, both waste feedrates and, consequently, chlorine feedrates as well as stack gas flowrates also can fluctuate over wide ranges. As a result, to ensure their comparability, stack gases samples for HCl and dioxin analyses must be collected over the same period of time.

Non-Synchronicity of HC1 and Dioxin Data

At several points in their report, Rigo et al. describe their HCl and dioxin data as being simultaneous. However, based on their description of sampling procedures, these data were not actually collected over the same time period: [1]

> Rigo et al.: *"The uncontrolled HCl data comes from a single 1 hour test conducted during the 6 hour PCDD/F sampling period. This is typical of much of the available data since the sampling times for HCl and PCDD/F determinations are different."*

In some cases, the dioxin sampling period may exceed the four to six hour period required by many methods. For example, according to Funcke et al. (1993), the duration of stack sampling for dioxins "*has to be between 6 to 16 hours*." [2]

Since gas flowrates at the stack differ considerably from those at sampling points upstream in a combustion system, direct comparisons of HCl concentrations at the stack with dioxin concentrations taken at other points will necessarily lead to erroneous conclusions. Neither the necessary flowrate data nor acknowledgment of this issue are given in the ASME report.

Conversion of Chlorine in Wastes to Hydrogen Chloride Emissions

Rigo et al. used HCl concentration in stack gases as a surrogate for chlorine input based on the assumption that essentially 100 percent of all forms of chlorine in combusted materials is converted into HCl and deposition in ashes is insignificant:

> Rigo et al.: *" ... the input chlorine level is usually inferred from uncontrolled flue gas HCl concentration data on the assumption that little chlorine is tied up by the ash. Some limited North American studies containing both HCl data and MSW [municipal solid waste] chlorine content verify the reasonableness of the stoichiometric release assumption...."* [3]
>
> Rigo et al.: *"The HCl data provide a direct indication of the waste feed chlorine content for MWI [medical waste incinerator] facilities without acid gas control equipment if all the chlorine in the waste is converted to HCl or Cl2 and not tied-up in the residue."* [4]

This assumption is not, however, supported by other studies. For example, in developing a method to estimate the HCl emission potential of wastes destined for incineration, the United States Environmental Protection Agency (USEPA) found HCl formation to depend strongly on the chemical form of the chlorine. While organically-bound chlorine was "essentially completely converted to HCl," conversion of inorganic chlorides, such as sodium chloride, proceeded considerably less efficiently (e.g., 30 to 50 percent conversion), varying according to other factors, such as moisture content. [5]

Researchers for the United States Department of Energy found that "measured offgas HCl concentrations ranged from 63% to 1% of the theoretical HCl emissions." They postulated that the remaining chlorine that was not emitted as HCl went into the formation of chlorinated metal compounds. [6]

In their recent study, Kanters et al. (1996) found a substantial fraction of chlorine sequestered in ash and conversion of chlorine to HCl that was non-stoichiometric, varying, in the case of sodium chloride, with incinerator operating conditions, as follows: [7]

> *"Origin of Hydrochloric Acid. Organic and inorganic chloride are equally abundant in regular MSW, and the HCl emission versus chloride remaining in the ash was found to be about 80/20. Ashes are usually alkaline in nature and therefore are capable of retaining the HCl through salt formation. However, at least a part of the original inorganic chloride is emitted as HCl. ... in the most realistic experiment, with the addition of aqueous NaCl to compostables and using humidified air, a HCl emission of 50-60% of the NaCl intake was observed; ca. 25% of the Cl remained in the ash. The remainder has probably been deposited on the wall. ... The degree of conversion of NaCl to HCl varies with the operating conditions and the design of the incinerator."*

Sonnenberg and Nichols (1995) found, in tests at a full-scale incinerator burning bleach plant solids from a kraft pulp mill, that only 5 percent of total chlorine in the waste was emitted as HCl. This was regarded as consistent with earlier studies showing that most

organic chlorine is trapped as sodium chloride when the materials burned contain a molar excess of sodium over chlorine. [8]

In summary, during high temperature combustion, the conversion of both organic chlorine and inorganic chlorine into HCl varies with the design and operating conditions of the combustor and waste feed characteristics. In general, conversion of organic chlorine seems to be more efficient and less variable than that of inorganic chlorine. As a consequence, HCl concentrations in stack gases are not reliable surrogates for chlorine feedrates in statistical evaluations of full-scale combustors.

Accuracy and Precision of Hydrogen Chloride Measurements

In addition to the limitations of HCl as an indicator of waste chlorine content, HCl analyses also suffer from a notable lack of precision. Even in a closely controlled study carried out on the same combustor, using the same sampling and analytical procedures, HCl measurements exhibited a standard deviation of +/- 28 percent. [9]

There is no internationally accepted protocol for HCl sampling and analysis. Indeed, most countries have no national protocols. For instance, in the absence of a national protocol, USEPA has issued recommendations advising those carrying out HCl sampling and analysis to avoid using certain resin traps to collect samples for HCl analysis due to potential contamination of the resin and/or retention of HCl on the resin. [10]

In a recent USEPA-sponsored survey of methods of sampling and analyzing for HCl, Johnston (1996) described in detail the vulnerabilities and problems encountered with two USEPA methods as well as two proposed methods. For example, two methods were confirmed to have a variable, negative bias at low concentrations, which seemed to correlate better with gas stream moisture content than with HCl concentration. The presence of alkaline particulate matter in gas streams was also identified as a source of negative bias, which varied with the composition of the particulates. A positive bias was noted when ammonium chloride was present in stack gases. [11]

In simultaneous tests of a USEPA method and a confirmed instrumental method for monitoring HCl emissions from cement, the USEPA method produced results that "ranged from being low by a factor of 2 to extremely low by a factor of 30." Laboratory spiking studies with this method found it to yield results that were low by factors of three to five. [12]

The imprecise nature of HCl measurements are well illustrated by the ASME report itself. For example, while burning "normal solid waste feed" in the Horsholm incinerator, with no extra chlorine input and no sulfur dioxide reagent, the highest HCl concentration was 1.5 times greater than the lowest measure. With no extra chlorine and addition of a sulfur dioxide reagent at a constant rate, HCl concentrations varied by as much as tenfold. [13] At the Sioux Center municipal waste incinerator, HCl concentrations varied from 71.7 to 240.8 ppm while wastes that were reported as containing zero percent chlorine were burned. [14]

In their discussion of cement kilns, Rigo et al. found that, in simultaneous analyses, USEPA Method 26 indicated HCl concentrations of 35-40 ppm (while a FTIR** analyzer reported no HCl). This led the authors of the ASME report to conclude as follows: [15]

> Rigo et al.: "*Hence, reported HCl concentrations are suspect*."

In summary, the methods used for sampling and analysis of HCl in stack gases of full-scale combustors do not have the accuracy and precision sufficient to yield meaningful results in statistical evaluations such as those carried out by Rigo et al.

Notes

1 Rigo et al., p. 2-48.
2 Funcke, W., Linneman, H., and Philipp, C. Long-term sampling method for polychlorinated dibenzofurans (PCDFs) and dibenzo(p)dioxins (PCDDs) in flue gas of combustion facilities. Chemosphere 26 (12): 2097-2101 (1993)
3 Rigo et al., p. 2-3.
4 Rigo et al, p. 3-2.
5 Peterson, M.R., Albritton, J.R., and Jayanty, R.K.M. Laboratory Method to Estimate Hydrogen Chloride Emission Potential Before Incineration of a Waste.
EPA/600/S3-90/054. Research Triangle Park, NC: USEPA, August 1990.
6 Burns, D.B., "Final Report Consolidated Incineration Facility Metals Partitioning Test (U)," WSRC-TR-93-623, Aiken, SC: U.S. Department of Energy, Savannah River Technology Center, August 31, 1993.
7 Kanters, M.J., Van Nispen, R., Louw, R., and Mulder, P. Chlorine input and chlorophenol emission in the lab-scale combustion of municipal solid waste. Environ. Sci. Technol. 30 (7): 21121-2126 (1996)
8 Sonnenberg, L., and Nichols, K. Emissions of hydrochloric acid, PCDD and PCDF from the combustion of chlorine-containing kraft pulp mill bleach plant waste. Chemosphere 31 (10): 4207-4223 (1995).
9 Lenoir, D., Kaune, A., Hutzinger, O., Mutzenich, G., and Horch, K. Influence of operating parameters and fuel type on PCDD/F emissions from a fluidized bed incinerator. Chemosphere 23 (8-10): 1491-1500 (1991).
10 U.S. Environmental Protection Agency, "Hazardous Waste Incineration Measurement Guidance Manual: Volume III of the Hazardous Waste Incineration Guidance Series," EPA/625/6-89/021, Washington, D.C.: U.S. Environmental Protection Agency, June 1989.
11 Ibid.
12 Ibid.
13 Rigo et al., Appendix C-1.
14 Ibid.
15 Rigo et al., p. 4-24.

Chapter 11: Quality and Comparability of Dioxin Data

Some of the data relied on by Rigo et al. originated as long ago as 1983, while others were collected as recently as 1994. During this period of time, there were marked improvements in the methods used for sampling and analyzing dioxins in combustor gases.

In 1984, the USEPA method was directed toward only one of the dioxins - 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) - and had a detection limit of 1 to 5 micrograms per cubic meter with a stack gas sample of 5 cubic meters. [1] With the methods used today, all dioxins are measured in stack gases and reported (expressed as equivalents of 2,3,7,8-TCDD) at concentrations more than a thousand times lower.

As existing methods of sampling and analysis were modified and new methods developed during 1983-1994, the quality of the dioxin data obtained also changed. As a consequence, the dioxin data evaluated by Rigo et al. are quite diverse in quality.

While Rigo et al. rather subtly acknowledge that methods of sampling and analysis have changed over time, they do not address the impacts of such changes on the quality and, thus, the comparability of the data in the ASME database. They do, however, discount differences in sampling and analysis methods that are more geographic in nature, as follows: [2]

> Rigo et al.: *"The data used in this project came from around the world. While North American sampling and analytical methods at any point in time are essentially the same, European techniques are slightly different. These data have been included, however, in this study because several researchers have compared the various methods and showed little difference in total concentrations..."*

This assessment by Rigo et al. contrasts rather starkly with the findings of other scientists. In their review, Liem and van Zorge (1995) reported that there are still no validated European standards for sampling and measuring dioxins in exhaust gases from stationary sources, pointing out the uncertainty of dioxin values and their limited comparability as follows: [3]

> *"Several interlaboratory comparison studies have shown that analytical results may differ substantially (e.g., WHO, 1989 and 1991). ...Therefore, it should be taken into account that the numerous data used to estimate dioxin emissions ...are only of limited comparability. ...The analytical uncertainty will influence largely the comparisons between the estimated dioxin emissions for the several countries."*

Johnke and Stelzner (1992) have identified several factors that limit the comparability of data from German municipal waste combustors. As shown below, these factors are equally germane to the study by Rigo et al: [4]

> *"The measurements were carried out from 1985 to 1990. ...The comparability of the measurement data was a question that arose especial [sic] in the overall evaluation of the measurement programme, since the sampling equipment and analytical methods used for the measurements differed. This was due to the following reasons:*
>
> - *The great length of time over which the programme extended, during which numerous improvements to the measurement technology were made.*
> - *The large number of measurement institutes and analytical laboratories participating. ... The uncertainties resulting from the use of differing sampling equipment and analytical methods cannot be assessed precisely. ... A sensible approach therefore seems to be to carry out an evaluation that takes all measurement data into account in a differentiated manner."*

Recent studies in the U.K. have found a margin of error of 50 percent for dioxin emission data. [5] However, authors of an ECETOC technical report remarked that, in sampling and analysis of combustor gases for dioxins, "...the results from different laboratories may differ by as much as one order of magnitude, particularly at low levels." They also described a report by Marklund (1990) of parallel sampling by five different sampling techniques and analyses by two different laboratories in which dioxin concentrations differed by as much as 2.7 times for different sampling procedures and 1.8 times for the same procedure. [6]

In their comparative study of five different techniques for sampling flue gases for dioxins, Marklund et al. (1992) found as follows: [7]

> *"Most countries have their own sampling methods and sampling protocols for PCDDs and PCDFs in flue gases, and most also have their own analytical procedures. ... Comparable results were obtained with all sampling procedures when the results were NOT compensated for incomplete sampling recoveries and the recoveries for the pre-sampling spikes were highly erratic."* [Emphasis in original]

Rigo et al. recognized the relatively high margin of error of contemporary data as follows: [8]

> Rigo et al.: *"TNO (1994) reports that the total PCDD/F [dioxin] concentration uncertainty is +/- 30% for raw data. Extending the analysis to include the effect of diluent correction (Hamil and Thomas, 1976) raises the uncertainty to +/- 35%."*

Nonetheless, in their conclusions, Rigo et al. made no mention of the severity of the limitations imposed on comparisons of data having margins of error as large as those encountered in their database.

Factors Affecting Data Quality

In a particularly interesting finding, the European Standards body CEN reported that agreement between methods depends strongly on the type of combustor tested. Where dioxins occurred primarily in the gas phase, different methods showed generally good agreement. In contrast, results differed by three orders of magnitude when the majority of the dioxins were bound to particles. [9] In other words, the distribution of dioxins between the gas phase and particles is an important factor in both the accuracy and the variability of data.

The difficulties presented in quantifying particle-bound dioxins are illustrated by the study by Fangmark (1990) in which the polyurethane foam plugs used in some methods were shown to have poor capture of small particulates (< 2 microns). Fangmark (1990) noted as follows: [10]

> *"The small particle fraction must therefore be included in the flue gas sample in order to obtain true values and not underestimate the concentrations of PCDDs and PCDFs."*

Similarly, Hunsinger et al. (1996) found that other filter materials that are also used in some methods had a great influence on the dioxin concentrations obtained: *"...at high temperatures (240° C) PCDD/F concentrations were found to be much smaller for the quartz filter compared to the PTFE filter."* [11]

Commenting on the difficulties of sampling combustor stacks, Janssens et al. (1992) noted *"...the possibility of serious artifacts occurring in situ during the sampling of the hot effluent."* Comparing sample collection with analysis, they concluded, "Much larger errors can be made during the sample collection in the stacks of incinerators." [12] Funcke et al. (1992) warned that *"...possible non-homogeneities in the flue gas channel have to be taken into consideration*" in a comparison of different sampling methods used in Germany. [13]

Other very important, but seldom-reported issues affecting data quality are deviations from the approved procedures during the application of stack sampling and analysis methods. In 1995, U.K. reviewers reported that departures from written protocols and accepted practices are common: [14]

> *"... [F]ew UK sampling teams claim to follow Method 23 in detail. ... [I]t has become clear that much UK sampling work has been carried out without the analysis of blank samples, with incompletely cleaned apparatus and with unsuitable sampling positions leading to the use of*

flexible hoses which have been shown to retain significant quantities of TOMPS [toxic organic micropollutants, including dioxin]."

In their evaluation of two Swedish stack sampling methods, Fangmark et al. (1990) observed, *"It is not unusual to accept a lower degree of precision during sampling compared to the analytical precision, though weaknesses in sampling methodology and sampling strategy could spoil the relevance of many results."* [15]

Limitations of USEPA Method 23

USEPA Method 23 has gained favor in many countries. For example, this method has been described as *"the favoured approach in the UK because of the commercial availability of the apparatus, the versatility of the equipment for measuring other pollutants such as heavy metals or particles and the lack of customer acceptance of other methods."* [16]

Wide acceptance notwithstanding, Method 23 has numerous shortcomings. Some are less serious, external issues that can be resolved by external measures. For example, the complexity of the sampling train makes it difficult to assemble and to operate correctly, leading operating personnel to deviate from approved procedures. [17]

Others, such as those that are intrinsic to the method, are less easily resolved. When USEPA scientists assessed the predecessor to Method 23, Modified Method 5 (MM5), they measured the recovery of dioxin congeners that were introduced through both static and dynamic spiking. For dynamic spiking, isotopic dioxin congeners were injected into the front end of a sampling train while combustor stack gases were sampled. [18]

With a lab-scale combustor, MM5 had recoveries of dynamically spiked congeners ranging from 50 to 99 percent. However, at the full-scale incinerator, *"recovery of the dynamic spikes had an overall average of 21% and were moderately variable."*

During this same study, USEPA also pursued methods for improving spike recoveries and, thus, the overall accuracy and precision of the method. For example, the overall recovery of dynamically spiked isotopic dioxin congeners was increased to 26 percent by extracting sample filters with benzene rather than the dichloromethane specified in the method.

Considerably greater improvements were noted when the back-half glassware of the MM5 sampling train was coated with a thin layer of a special grease. At the full-scale incinerator, rinsing the coated back-half glassware with toluene resulted in recoveries ranging from 62.9 to 107 percent, although precision was relatively poor.

When USEPA officially replaced MM5 with Method 23 in 1991, the Agency did not incorporate the changes that had led to markedly higher recoveries during dynamic spiking, albeit with poor precision. [19] Since the only substantive difference between MM5 and Method 23 is the substitution of toluene for dichloromethane during extraction,

the overall recovery of Method 23 can be expected to be at or near the 26 percent achieved with MM5.

Takeshita et al. (1995) recently identified three *"controversial problems in the application of XAD-2 resin as an adsorbent for the sampling of PCDD/F in flue gas"* in USEPA Method 23: [20]

- *"One of the most important problems is the efficiency in trapping PCDD/F, especially in gaseous form."* The limited adsorbency of the XAD-2 resin requires a backup system downstream from the resin column.

- Method 23 specifies that a condenser is placed immediately upstream from the resin column: *"...[W]ater condensed by the cooler may cover the XAD-2 resin nonuniformly, occasionally resulting in partial routing of flue gas in the column. Under such a condition, flue gas introduced into the system would preferentially pass through the dry XAD-2 resin, avoiding the wet area with higher air resistance, resulting in incomplete trapping of PCDD/F in the flue gas."*

- *"Since the XAD-2 resin after sampling may be moist, this would disturb the extraction of PCDD/F from the resin by nonpolar solvents. In addition, the XAD-2 resin generally contains several monomers of the resin raw materials ... that would be simultaneously extracted in the separation of PCDD/F, and they may disturb the analysis of PCDD/F by gas chromatography/low resolution mass spectrometry."*

Another recent study involving USEPA Modified Method 5 (also known as Method 23) raises the possibility that dioxin concentrations measured using this method may vary according to the concentrations of HCl in stack gases. Tan and Liem (1996) reported that higher HCl in stack gases resulted in lower recoveries of certain semi-volatiles by desorbing them from the XAD-2 resin during sampling. At low HCl concentrations, such as those commonly found after acid gas scrubbers, recovery efficiencies for all chlorophenols averaged 95 percent. At higher HCl levels, recovery of less chlorinated species, such as 4-chlorophenol, was as low as 16 percent. More highly chlorinated species were less affected, with pentachlorophenol recoveries as high as 89 percent. [21]

The quantification of dioxins in combustor gases, as has been made obvious by the preceding discussion, is quite accurately and succinctly described by Unsworth et al. (1995) as follows: [22]

> *"There are no standard repeatability or reproducibility values available for dioxin concentration in flue gases — significant potential sources of error occur in both the sampling and analysis procedures."*

Given these constraints, it seems unlikely that any relationships would arise from the statistical analyses employed. Although these issues are raised by Rigo et al., they are not sufficiently addressed as contributing factors to poor correlations with regard to their own analyses and interpretations.

With this extent of uncertainty in mind, it is quite surprising that a preponderance of positive relationships between chlorine input and dioxin stack emissions was evident among the statistical values calculated by Rigo et al. for individual full-scale municipal waste, medical waste and hazardous waste combustors as well as by the values calculated by Greenpeace for cement kilns. Perhaps these findings are indicative of stronger underlying trends linking chlorine input with dioxin concentrations in stack emissions, at least in certain types of combustors. In any event, these findings appear to heighten the probability that evaluation of more appropriate, accurate data (e.g., dioxin concentrations in other combustor residues, production rates of the residues, stack gas flowrates, waste feedrates or chlorine feedrates, etc.) would have found chlorine input to correlate positively with total dioxin output from the full-scale combustors in this study.

Notes

1 Harris, J.C., Larsen, D.J., Rechsteiner, C.E., and Thrun, K.E., "Sampling and Analysis Methods for Hazardous Waste Combustion," EPA-600/884-002, Washington, D.C.: U.S. Environmental Protection Agency, February 1984.
2 Rigo et al., p. A-1.
3 Liem, A.K.Djien, Job. A. van Zorge. Dioxins and Related Compounds: Status and Regulatory Aspects. Environ. Sci. and Pollut. Res. 2(1): 46-56 (1995).
4 Johnke, B., and Stelzner, E., "Results of the German dioxin measurement programme at MSW incinerators," Waste Management & Research 10: 345-355 (1992).
5 Air Pollution Abatement Review Group, "Report on the Abatement of Toxic Organic Micropollutants (TOMPS) from Stationary Sources 1995," Prepared at the request of Air Quality Division, Department of the Environment, AEA Technology, National Technology Centre, Abingdon, Oxfordshire, UK, 1995.
6 ECETOC, "Technical Report No. 49: Exposure of Man to Dioxins: A Perspective on Industrial Waste Incineration," Second Edition, Brussels, September 1992.
7Marklund, S., Soderstrom, G., Ljung, K., Rappe, C., Kraft, M., Hagenmaier, H. Parallel sampling for dioxins using various sampling techniques at a Swedish municipal solid waste incinerator. Waste Manage. & Research 10: 21-36 (1992)
8Rigo et al., p. 2-51.
9 Air Pollution Abatement Review Group, "Report on the Abatement of Toxic Organic Micropollutants (TOMPS) from Stationary Sources 1995," Prepared at the request of Air Quality Division, Department of the Environment, AEA Technology, National Technology Centre, Abingdon, Oxfordshire, UK, 1995.
10 Fangmark, I., Wikstrom, L-E, Marklund, S., Rappe, C., "Studies on sampling methods for PCDDs and PCDFs in stack emissions," Chemosphere 20 (10-12): 1333-1340 (1990).
11 Hunsinger, H., Kreisz, S., and Vogg, H. Experiences gained from the sampling of chlorine aromatics in the raw gas of waste incineration plants - conclusions with regard to dedusting technology. Chemosphere 32 (1): 109-118 (1996)
12 Janssens, J.J., Daelmans, F.F. and Schepens, P.J.C. Sampling incinerator effluents for PCDDs and PCDFs: A critical evaluation of existing sampling procedures. Chemosphere 25 (710): 1323-1332 (1992)
13 Funcke, W., and Linneman, H. Sampling of polychlorinated dibenzofurans (PCDF) and dibenzo(p)dioxins in emissions from combustion facilities using an adsorption method. Chemosphere 24(11): 1563-1572 (1992)
14 Air Pollution Abatement Review Group, "Report on the Abatement of Toxic Organic Micropollutants (TOMPS) from Stationary Sources 1995," Prepared at the request of Air Quality Division, Department of the Environment, AEA Technology, National Technology Centre, Abingdon, Oxfordshire, UK, 1995.
15 Fangmark, I., Wikstrom, L-E, Marklund, S., Rappe, C., "Studies on sampling methods for PCDDs and PCDFs in stack emissions," Chemosphere 20 (10-12): 1333-1340 (1990).
16 Air Pollution Abatement Review Group, "Report on the Abatement of Toxic Organic Micropollutants (TOMPS) from Stationary Sources 1995," Prepared at the request of Air Quality Division, Department of the Environment, AEA Technology, National Technology Centre, Abingdon, Oxfordshire, UK, 1995.

17 Air Pollution Abatement Review Group, “Report on the Abatement of Toxic Organic Micropollutants (TOMPS) from Stationary Sources 1995,” Prepared at the request of Air Quality Division, Department of the Environment, AEA Technology, National Technology Centre, Abingdon, Oxfordshire, UK, 1995.
18 Coates, J.T., “Validation of Emission Test Method for PCDDs and PCDFs,” EPA/600/3-90/007, U.S. Environmental Protection Agency, Research Triangle Park, NC, March 1990.
19 United States Environmental Protection Agency, “Standards of Performance for New Stationary Sources; Addition of Methods for Measurement of Polychlorinated Dibenzo-p-Dioxins, Polychlorinated Dibenzofurans, and Hydrogen Chloride Emissions From Stationary Sources,” Federal Register, Vol. 56, No. 30, Wednesday, February 13, 1991, pp. 5758-5775.
20 Takeshita, R., Akimoto, Y., and Nito, S. Effective sampling system for polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans in flue gas from municipal solid incinerators. Environ. Sci. Technol. 29(5): 1186-1194 (1995).
21 Tan, L.K. and Liem, A.J. Effect of hydrochloric acid on sampling and analysis of semivolatile organic compounds in incineration flue gas. 1. Chlorophenols. Environ. Sci. Technol. 30(3): 1053-1060, 1996.
22 Unsworth, J.F., Felix, A., Broadbent, C.P., and Adkins, N.J. Dioxin issues in the thermal oxidative processing of mercury contaminated wastes. TransIChemE, Vol.73, Part B, pp.123-31. May 1995.

Figures

Figure 4-1: Municipal Waste Combustors

Correlation of HCI and Dioxin Concentrations as calculated by Rigo et al.

Confidence levels are based on coefficients and p-values from Rigo et al. Those that are 80% and higher are as noted.

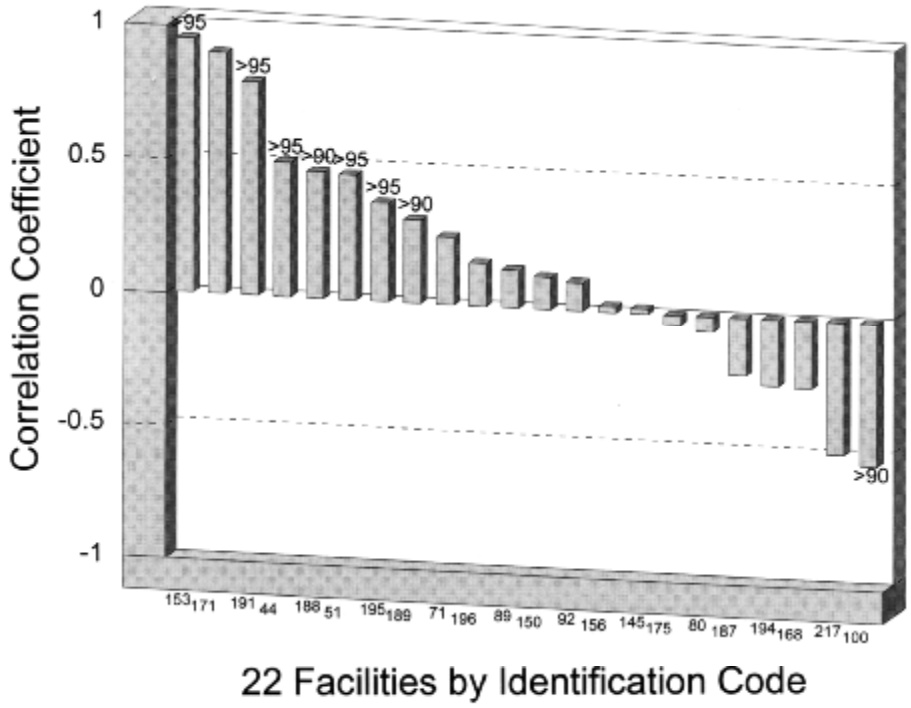


Figure 4-2: Municipal Waste Combustors

Scatter Plot from Rigo et al.

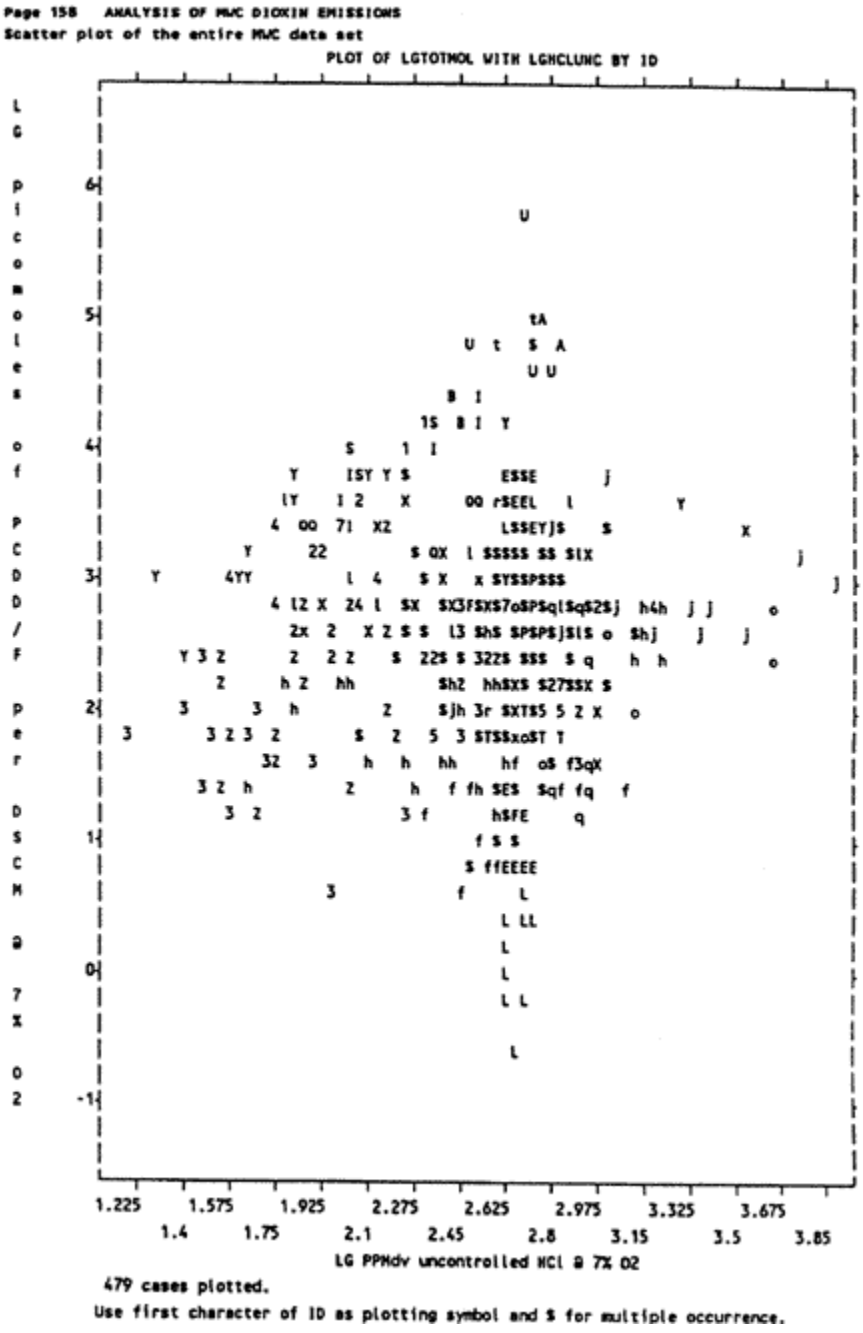
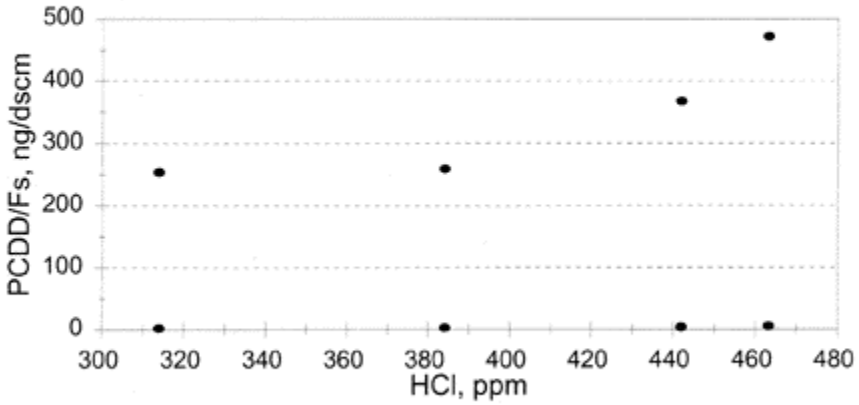


Figure 4-3: Municipal Waste Combustors

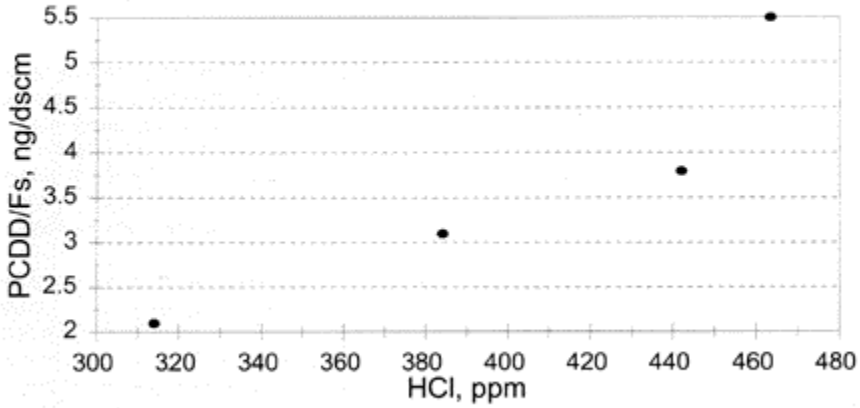
Merc Aggregate Data.
RRID 150 MERC (1988) All Sample Locations.



Statistical Values from Rigo et al.:
Correlation Coefficient, r= 0.12076, p- value= 0.7758

Figure 4-4: Municipal Waste Combustors

Merc Stack Data. RRID 150 MERC (1988).
Sample Location - Stack 1



Statistical Values from Reanalysis:
Correlation Coefficient, r = 0.961182, p- value = 0.016028

Figure 4-5: Municipal Waste Combustors

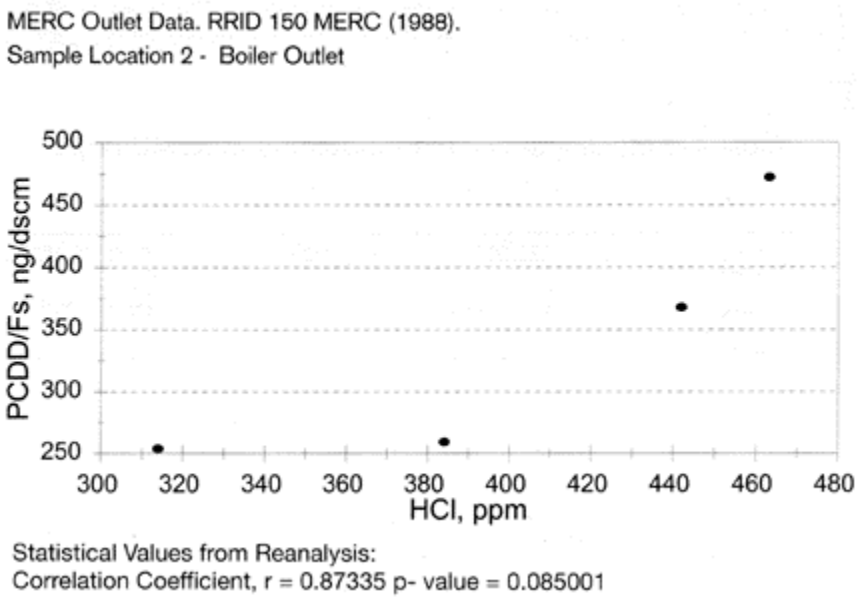


Figure 4-6: Municipal Waste Combustors

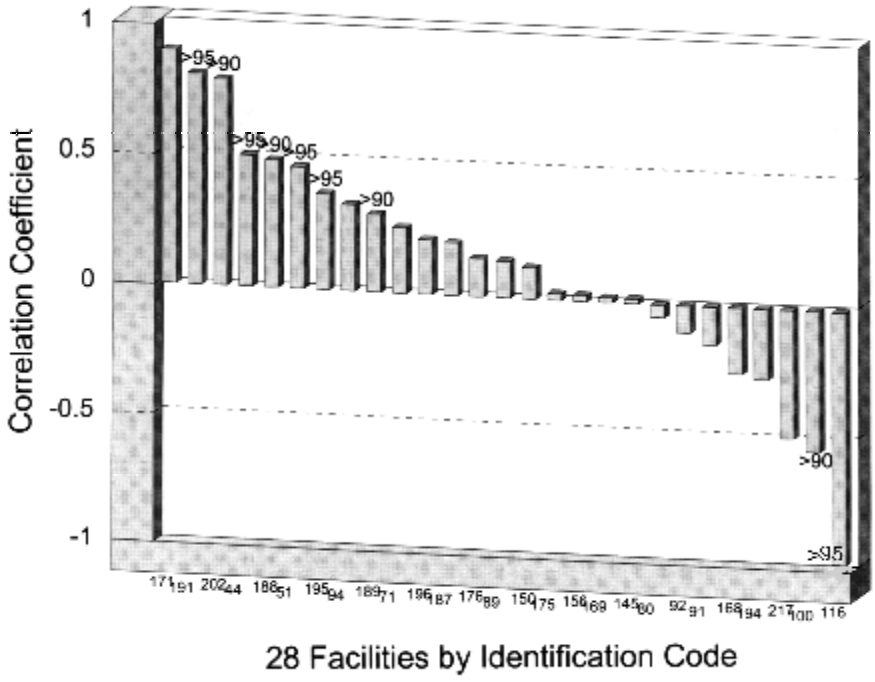


Figure 5-1: Medical Waste Incinerators

Statistical Values by Rigo et al.

Correlation of HCI and Dioxin Concentrations, as calculated by Rigo et al.

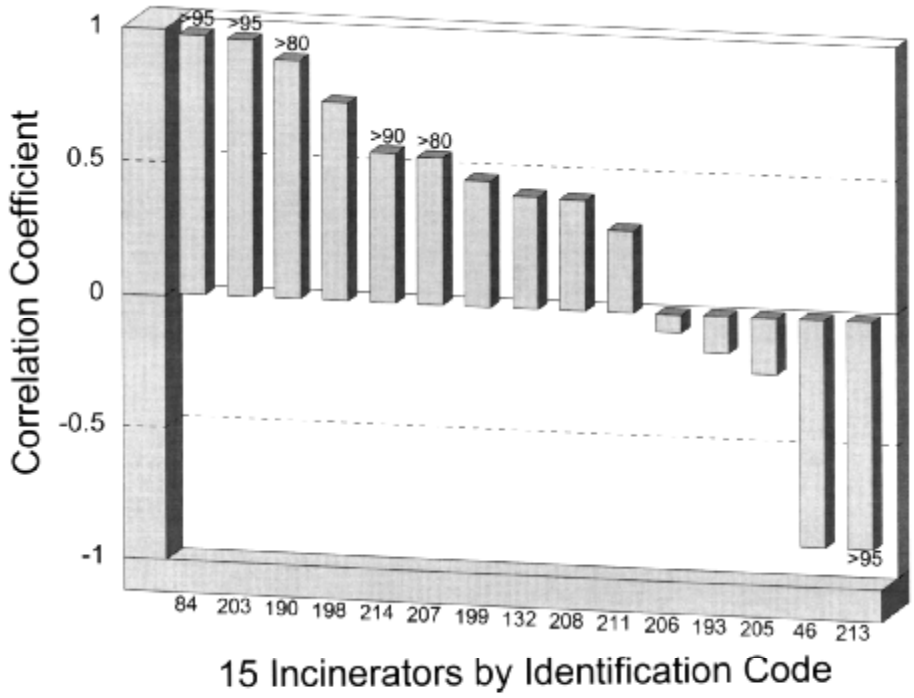


Figure 5-2: Medical Waste Incinerators

Scatter Plot by Rigo et al.

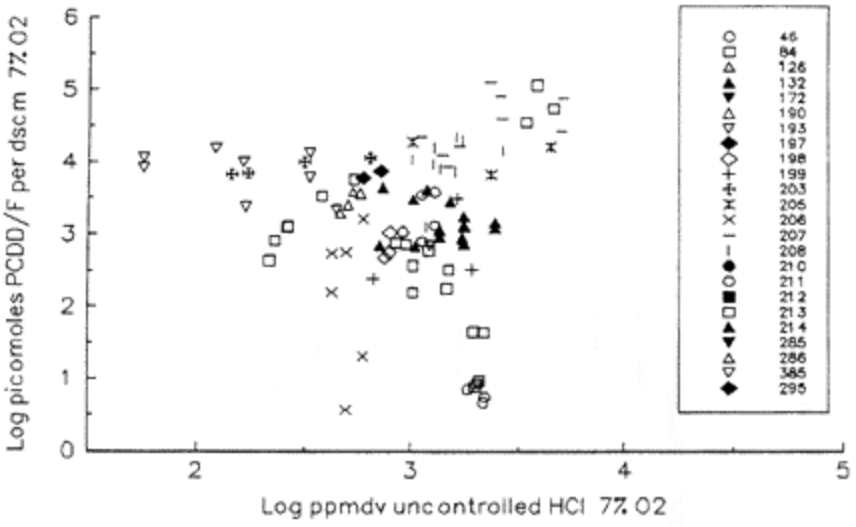
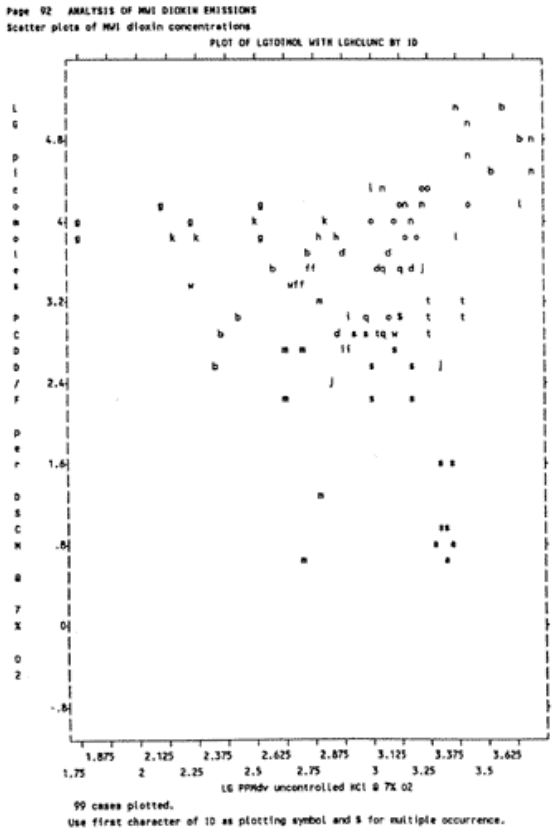


Figure 5-3: Medical Waste Incinerators



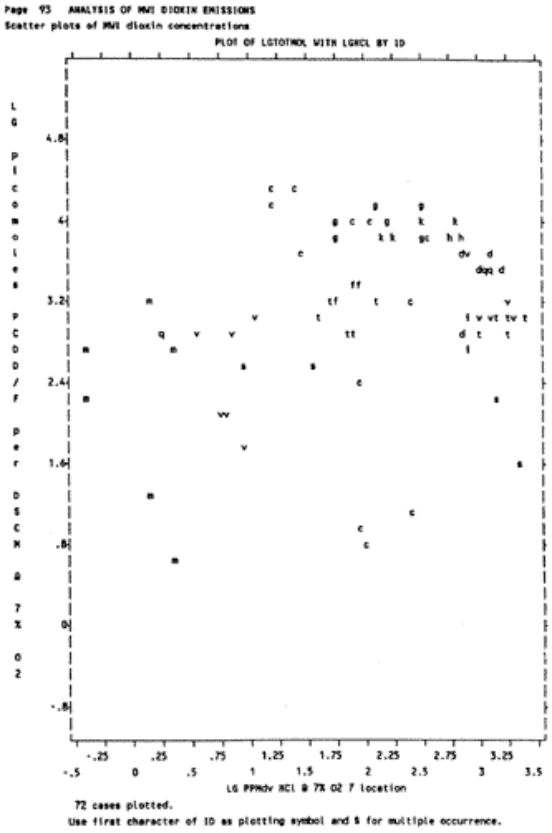


Figure 5-4: Medical Waste Incinerators

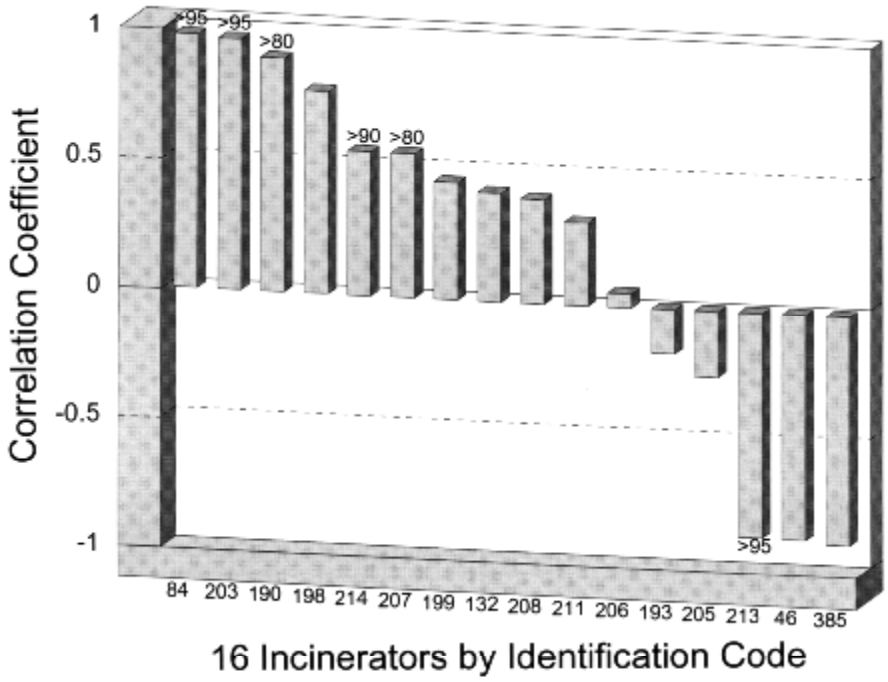


Figure 6-1 Hazardous Waste Incinerators

Correlation of Percent Chlorine in Feed and Dioxin, as Calculated by Rigo et al.

Note: The data in this graph are not useful for assessing the relationship between chlorine input and dioxin emissions.

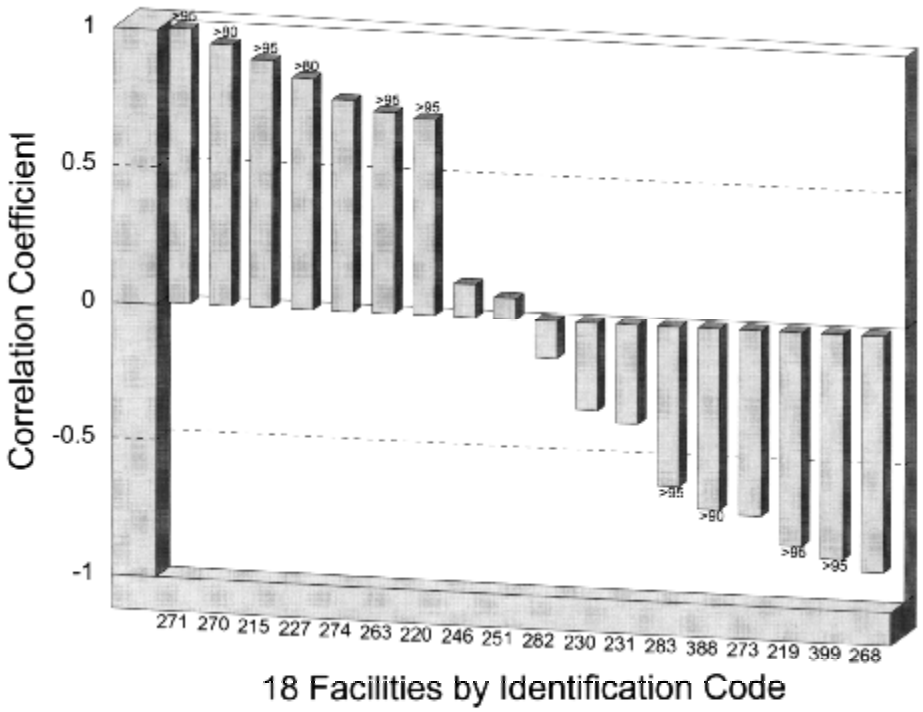
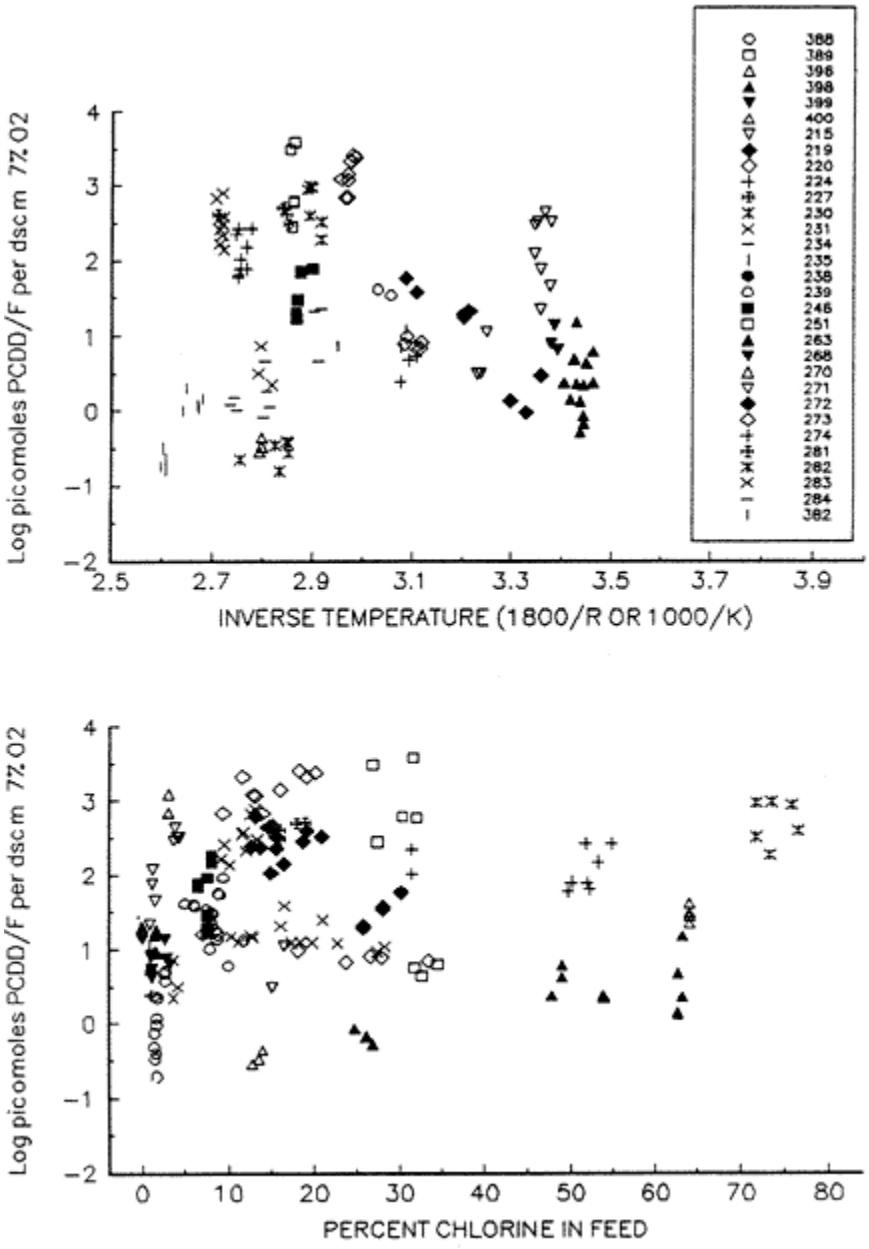


Figure 6-2 Hazardous Waste Incinerators

Scatter Plot by Rigo et al.



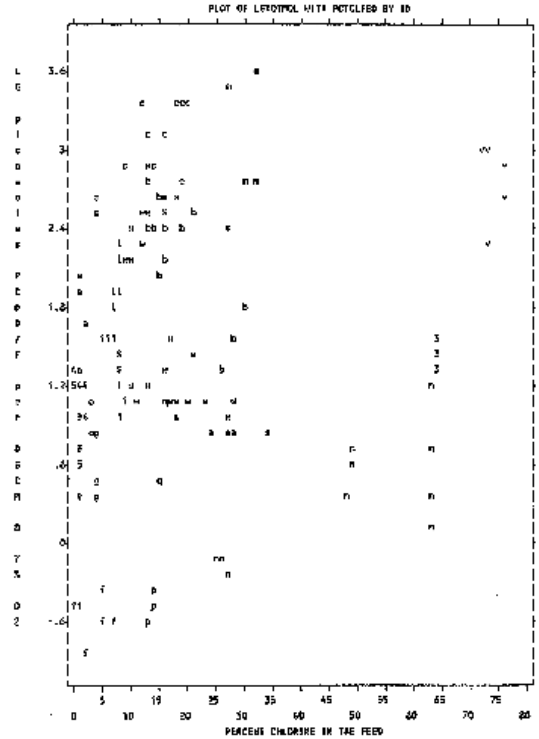
Scatter plot showing the lack of relationship between moles of PCDD/F and either temperature or percent chlorine feed of HWI.

Figure 6-3 Hazardous Waste Incinerators

Scatter Plot by Rigo et al.

All NAT Bioassay Data Treated as a Single Group

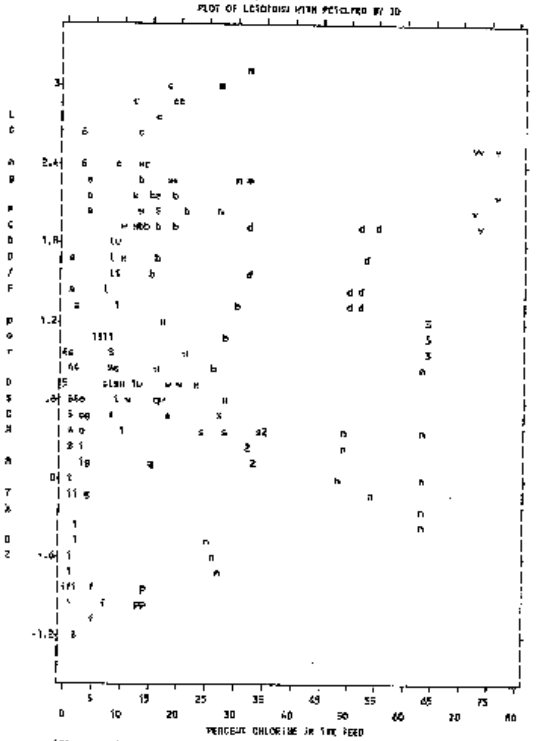
PLOT OF LEPTOPHOS WITH PCTCLFED BY ID



133 cases plotted.
Use first character of ID as plotting symbol and * for multiple occurrences.

All NAT Bioassay Data Treated as a Single Group

PLOT OF LEPTOPHOS WITH PCTCLFED BY ID



181 cases plotted.
Use first character of ID as plotting symbol and * for multiple occurrences.

Figure 6-4 Hazardous Waste Incinerators

Correlation of Percent Chlorine in Feed and Dioxin Concentrations. - Greenpeace

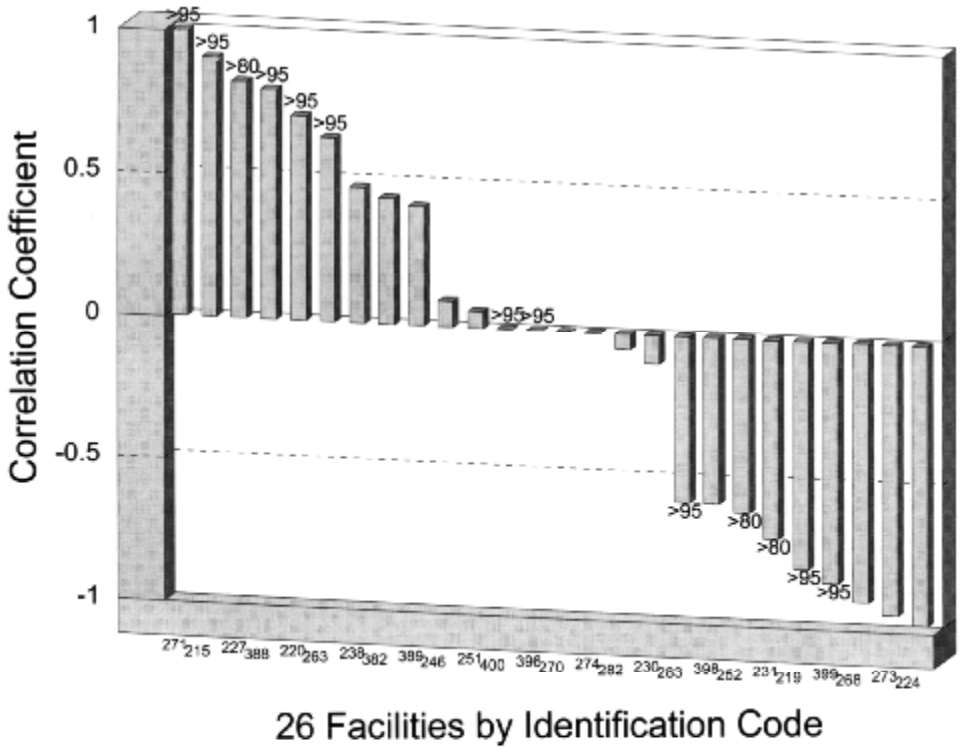


Figure 6-5 Hazardous Waste Incinerators

Chlorine Feedrate vs. Dioxin Concentrations - Greenpeace Analysis

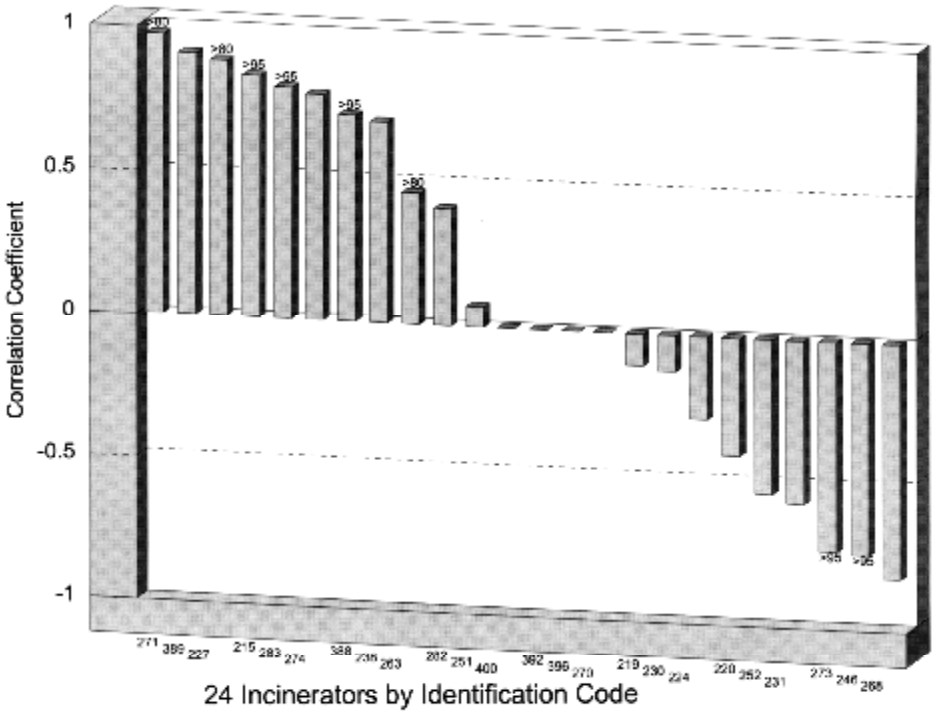


Figure 6-6 Hazardous Waste Incinerators

Effects of Aggregating Data Sets. Chlorine Feedrates vs. PCDD/Fs.

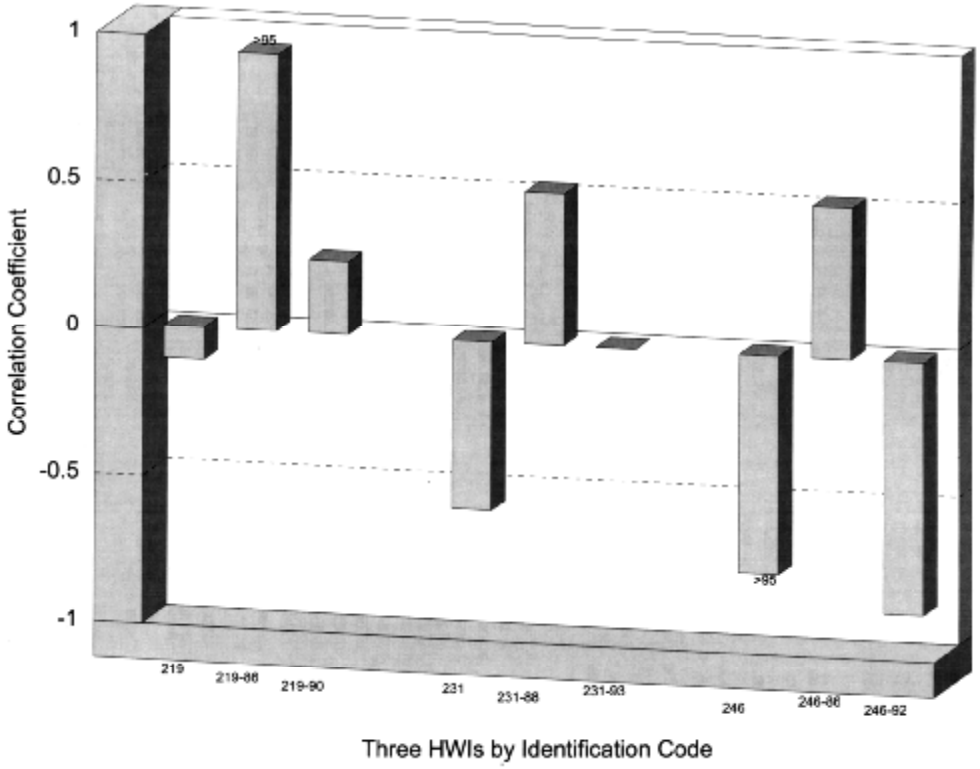


Figure 6-7 Hazardous Waste Incinerators

Comparison of Correlation Coefficients for Chlorine Feedrate vs. PCDD/Fs and Percent Chlorine in Feed vs. PCDD/Fs.

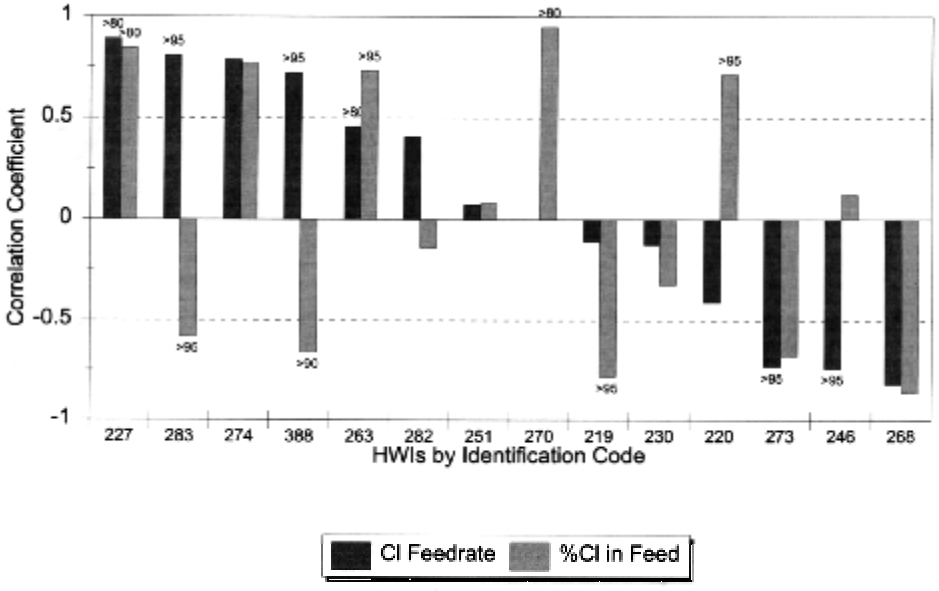
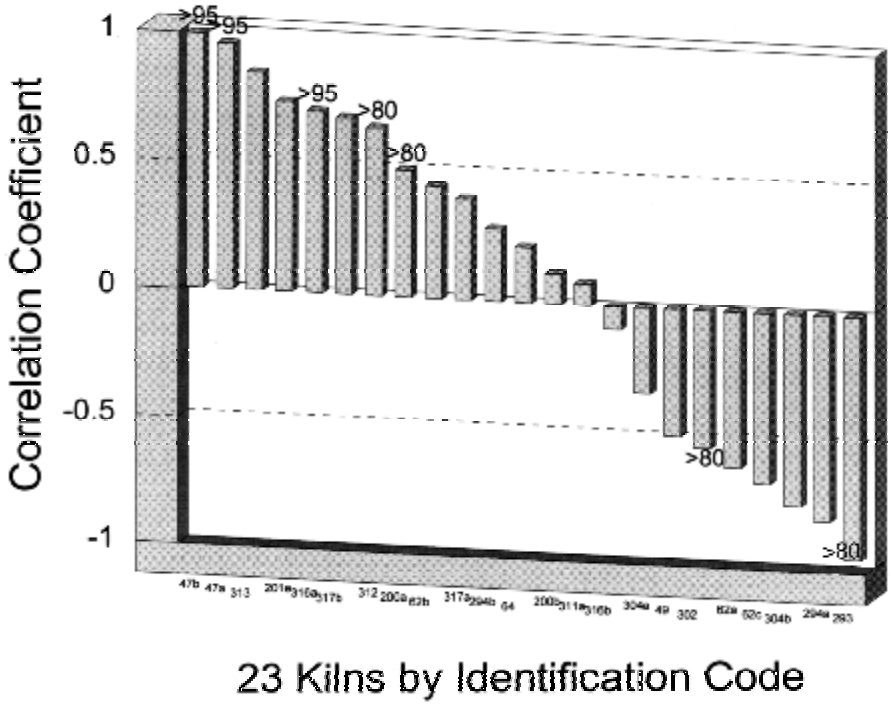


Figure 8-1 Cement Kilns

Relationship of Chlorine Feedrate and Dioxin Concentrations. Greenpeace Analysis of Data from ASME Database.



Acknowledgements

Thanks to the Following Contributors:

Editorial Assistance: Charlie Cray, Lisa Finaldi, Rick Hind, Paul Johnston, Kathy O'Keefe, Beverley Thorpe, Bill Walsh, Jack Weinberg

Production Assistance: Robert King, Jay Townsend

Special Thanks to: Barry Commoner, CBNS, Queens College, Flushing, New York, USA; Paul Connett, St. Lawrence University, Canton, New York, USA; David Santillo, Greenpeace International Science Unit, Exeter University, Exeter, Devon, U.K.; and Tom Webster, Boston University School of Public Health, Boston, Massachusetts, USA, for reviewing the draft of the report.

In addition, thanks are due to Tom Hotard and J. Pat Valentik for their assistance with statistical matters and to Jack Weinberg, Lisa Finaldi, Beverley Thorpe for their advice and encouragement.

This document was funded by Greenpeace International.