



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY  
WASHINGTON, D.C. 20460

FILE

December 15, 1989

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Honorable William K. Reilly  
Administrator  
U.S. Environmental Protection Agency  
401 M Street, S.W.  
Washington, D.C. 20460

OFFICE OF  
THE ADMINISTRATOR

RE: OSW's Proposed Controls for  
Hazardous Waste Incinerators:  
Products of Incomplete Combustion

Dear Mr. Reilly:

The Science Advisory Board's Products of Incomplete Combustion Subcommittee has reviewed the Proposed Controls for Hazardous Waste Incinerators: Products of Incomplete Combustion (PICs) for the Office of Solid Waste. The Office of Solid Waste seeks to propose and promulgate rules which amend existing standards for boilers and industrial furnaces burning hazardous wastes fuels and for all hazardous waste incinerators. The Science Advisory Board was asked to address three questions:

1. Whether limiting carbon monoxide (CO) and total hydrocarbons (THC) is a reasonable approach to control emissions of PICs, given the current data base and statutory time constraints?
2. What is the feasibility of monitoring THC to determine to the aggregate emission rate of organic compounds?
3. Whether the proposed approach to assess the health risk from THC emissions is reasonable given the current data base and statutory time constraints?

To address these questions, the Subcommittee reviewed the documentation provided on PICs controls and held open meetings December 14 and 15, 1988, and January 26 and 27, 1989, in Washington, D.C. A final publicly announced meeting was held September 15, 1989 by conference call.

The Subcommittee also addressed: atmospheric dispersion simulation, selection of CO and THC concentration limits, selection of averaging methods and periods, alternate control approaches and research needs.

The proposal for controls was made even though OSW has not established that emission of PICs from hazardous waste incinerators currently pose a substantial risk. EPA's risk assessments indicate that emission of PICs at currently measured levels are not likely

to produce significant human health effects. However, since the current DRE standard applies only to designated POHCs, a 4-nines (99.99%) DRE does not preclude the possibility that emission of PICS could present significant human health risk

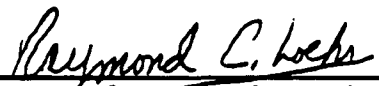
The Subcommittee findings and recommendations are found in the attached report. The Subcommittee would like to emphasize that, while the concept of using CO and/or THC concentrations to control incinerator operations is reasonable, their use to reduce the risk posed by the emission of PICS is based on policy rather than on science, because of limited data. In addition, there is a technical obstacle to the implementation of this concept if CO alone is controlled. When CO is high, THC (a surrogate for PICS) may be high or low; this lack of correlation at high concentrations of CO limits the usefulness of CO alone as an operational control for emission of PICS. Thus at high CO concentrations, a better measure of PICS is THC.

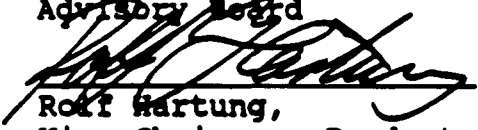
Due to the limitations of the emissions data and the large degree of uncertainty introduced by the various assumptions employed in the risk assessment methodology, the Subcommittee considers the methodology only sufficient to provide a risk-based check on the proposed THC emissions limit used when CO concentrations are high. Further, the Agency's evaluation of the emissions limit provides some evidence of adequate safety. However, the risk assessment is not sufficient for site-specific applications.

The SAB would like to compliment the Office of Solid Waste staff and that of the Atmospheric Research and Exposure Assessment Laboratory for their active and helpful participation in our review of the PICS issues.

The Science Advisory Board is pleased to have been invited to review this important issue and looks forward to a written response from EPA on the implementation of the Board's recommendations.

Sincerely,

  
Raymond C. Loehr, Chairman  
Executive Committee and  
Chairman, Products of  
Incomplete Combustion  
Subcommittee, Science  
Advisory Board

  
Rolf Hartung,  
Vice Chairman, Products of  
Incomplete Combustion  
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cc: D. Barnes, J. Berlow, D. Bussard, J. Cannon, J. Denit,  
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REPORT OF THE  
PRODUCTS OF INCOMPLETE COMBUSTION SUBCOMMITTEE  
SCIENCE ADVISORY BOARD  
U.S. ENVIRONMENTAL PROTECTION AGENCY  
REVIEW OF THE  
OFFICE OF SOLID WASTE  
PROPOSED CONTROLS FOR HAZARDOUS WASTE INCINERATORS:  
PRODUCTS OF INCOMPLETE COMBUSTION  
October 24, 1989

## ABSTRACT

The Products of Incomplete Combustion (PICs) Subcommittee of the EPA's Science Advisory Board reviewed the Office of Solid Waste's (OSW) proposal to control emissions of PICs from hazardous waste incinerators by instituting process controls based on CO and THC emission concentrations. Because compounds known to cause adverse human health effects have been detected at very low concentrations in PICs, it is prudent to take precautionary measures to control PICs. However, the linkages between emission concentration, exposure, and effects (health and environmental) were not documented.

The proposal for controls was made even though OSW has not established that emission of PICs from hazardous waste incinerators currently pose a substantial risk. EPA's risk assessments indicate that emission of PICs at currently measured levels are not likely to produce significant human health effects. However, since the current DRE standard applies only to designated POHCs, a 4-nines (99.99%) DRE does not preclude the possibility that emission of PICS could present significant human health risk.

The concept of using CO and/or THC as guidance for incinerator operational control is reasonable. The concentration limits for CO and THC, the averaging methods, and the averaging periods EPA chose were selected on the basis of informed judgments using the best available data.

Continuous emissions monitoring for THC with a cold system appears to be practical for routine operations. Because incinerators may emit more PICs when upset from changes in waste quantity or composition that can result from abrupt waste feed shutoff, a poorly implemented automatic shutdown strategy has the potential to create more pollution than it stops.

The Subcommittee found the data base characterizing PICs in emissions would not allow a correlation to be established with CO or THC levels for various combustion devices and/or conditions. The sparseness of data introduces large uncertainties into EPA's risk assessment. This uncertainty limits the usefulness of one approach proposed by OSW to control THC emissions--using site-specific quantitative risk assessment to establish acceptable THC emission rates. Despite the limitations of the risk assessment methodology, however, the Subcommittee considers the methodology sufficient to provide a risk-based check on an alternative proposal by OSW--limiting THC concentrations to levels representative of good operating practice.

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## 1. EXECUTIVE SUMMARY

At the request of the Office of Solid Waste (OSW), the Science Advisory Board's Products of Incomplete Combustion (PIC) Subcommittee reviewed the approach OSW proposed in June 1988 for the control emission of PICs. The Subcommittee was charged to address the following three questions:

1. Whether limiting carbon monoxide (CO) and total hydrocarbons (THC) is a reasonable approach to control emission of PICs, given the current data base and statutory time constraints,
2. What is the feasibility of monitoring THC to determine the aggregate emission rate of organic compounds?
3. Whether the proposed approach to assess the health risk from THC emissions is reasonable given the current data base and statutory time constraints?

The Subcommittee also addressed: atmospheric dispersion simulation, selection of CO and THC concentration limits, selection of averaging method and period, alternate control approaches, and research needs.

The Subcommittee's task was to review the documents provided, to provide advice on the technical and scientific adequacy of the indicated approaches, and to suggest how to improve the approaches. The task was not to provide on-going continuing oversight of the EPA effort as it may have evolved since the Subcommittee meetings.

Agency staff were present at the Subcommittee meetings, participated in the discussions and heard the comments of the Subcommittee members. In addition, Agency staff were provided with drafts of this report as it was being prepared. This report has been compiled from information obtained and discussions held at the Subcommittee meetings (including the publicly announced conference call meeting of September 15), from written comments submitted by the Subcommittee members and from comments supplied from the members as they reviewed earlier drafts of this report.

The data base on PICs is sparse particularly for full-scale incinerators. (Note: In this report the terms "PICs" and "THC" refer to emissions of residual organic compounds and include toxic compounds such as chlorinated dioxins and benzene as well as non-chronically toxic compounds such as ethane and methane.) Those emissions which have been characterized have shown that individual PICs are present over a wide range of concentrations. Likewise, the potential toxicities of the PICs differ over a wide spectrum of concentrations. Under good combustion conditions, the concentrations of individual measured PICs have been found to be

relatively low in relation to the known toxic concentrations. The correlation of CO, THC, or other parameters with combustion efficiency and PICs emission concentration is weak for some conditions and for some combustion devices. The relationship between THC and emission of PICs below levels of public health concern for hazardous waste incinerators indicates that at low CO concentrations (less than 100 ppm) THC emissions are low (less than 20 ppm). At higher CO concentrations, THC may or may not be high.

Compounds known to cause adverse health effects are among the PICs detected in the ppb and ppt range in actual incinerator emissions. One risk assessment, based on measured emission levels and employing conservative assumptions, suggests that PICs do not pose a significant health risk.(2,7) This risk assessment, however, considered only organic compounds in the emissions that were actually identified and quantified (for example, these ranged from 1% to 60% of the total organic emissions at a specific site), and was limited to the direct inhalation route. Environmental risks and human health risks resulting from indirect routes of exposure have not been assessed.

Plant upsets can increase emission of PICs. Therefore, any proposed controls should minimize unnecessary waste feed shutoffs which may result in upsets; otherwise, the controls may cause more pollution than they prevent. OSW's approach can result in automatic shutdowns and plants may be upset by sudden changes in the amount or composition of waste or auxiliary fuel burned. Parameters used for control must relate to actual emission of PICs and be practical as well if they are to be of use. Oxygen monitoring, frequent periodic testing for THC and other factors discussed in the report may be additional guides for operational controls. The appropriate control parameter and level may vary by class of combustion device.

Because the available database on CO and organic emissions shows CO does not correlate well with THC at high CO concentrations, reliance on controlling CO alone would have serious limitations.

While EPA's risk assessment approach in this case follows previously accepted methodologies, the Subcommittee believes that it lacks both the precision and accuracy needed to be useful in a site-specific regulatory context. Given the assumptions and uncertainties, it is the judgment of the Subcommittee that it is not possible to calculate total THC risks reliably and that at present the method is not suitable for setting site-specific limits based upon THC levels alone.

Due to the limitations of the emissions data and the large degree of uncertainty introduced by the various assumptions employed in the risk assessment methodology, the Subcommittee

considers the methodology only sufficient to provide a risk-based check on the proposed THC emissions limit. Further, the Agency's evaluation of the emissions limit provides some evidence of adequate safety. The concept of using CO and/or THC to control PICs is reasonable.

The Subcommittee addressed research needs. Since only a small fraction of the total number of compounds produced during upset conditions can be monitored, there is a need to relate the simple measures of emissions produced by a CO, THC, or other detection surrogates to risk. Emission of PICs from incinerators are a potential problem that forms part of the broader problem of organic emissions from combustors. Comparative emissions and risk assessments of different combustion categories would be desirable in order to assign priorities for risk reduction measures.

Overall, the Subcommittee believes that the general concept of using CO and THC for the purpose of ensuring that PIC emissions are below levels of public health concern is reasonable. The Subcommittee, however, is concerned about the averaging method, the averaging period, and the concentrations chosen for the CO and THC standard. The Subcommittee understands that these parameters and values were chosen primarily based on informed judgments using the best available data. However, the supporting documentation does not convincingly demonstrate that a CO concentration of 100 ppm is better than 50 ppm or 150 ppm, nor that a one-hour rolling average is better than an eight-hour rolling average for CO.

## 2. BACKGROUND

### 2.1 Process

In a memo dated June 28, 1988, Mr. Joseph Carra, Director of the Waste Management Division of the Office of Solid Waste (OSW), requested a meeting with Dr. Donald Barnes, then Acting Director of the Science Advisory Board, to discuss how and when SAB could review OSW's proposed approach to control the potential for emissions of products of incomplete combustion (PICs) that occur during the incineration of hazardous wastes.(57) The memo also described the basic approach of OSW in the control of potential PICs. The memo acknowledged that "the approach is based on a number of assumptions and a relatively thin data base. However, we know of no viable alternative. SAB comments on improvements to this approach or alternative approaches to control PIC emissions would be helpful." Accompanying the memo was a draft of the proposed rule and supporting background documents for SAB staff review.

Following initial consideration of the matter, the SAB Executive Committee approved formation of a "PICs Investigative Group" to focus the review and to select reviewers, once the charge was clear. The PICs Investigative Group was composed of SAB Executive Committee members, Dr. Raymond Loehr, Dr. Rolf Hartung, and Dr. Richard Griesemer. Background materials were provided in July 1988. A teleconference August 30, 1988 sharpened the scope and focus of the review.

This activity produced a charge (Section 2.2) setting forth the questions to be addressed by the PICs Subcommittee. The SAB and OSW agreed this review need not address metals, residues, or specific organic emissions such as dioxin because of extensive SAB reviews of single chemical risk assessments and prior reviews of incineration issues. Participants identified the expertise needed to address these questions including: engineering, instrumentation, risk assessment, and human health. The PICs Investigative Group also established a preliminary schedule.

The SAB PICs Subcommittee held its first meeting December 15-16, 1988, drafted a report, and held a second meeting January 26-17, 1989, at which the report was extensively revised. Both meetings were held in Washington and were open to the public. An additional publicly announced meeting was held by conference call on September 15, 1989. All revisions made to the report prior to its submittal to the Executive Committee were made by mail and telephone. The Executive Committee recommended improvements and considered the report at a public meeting July 17-18, 1989, in Washington and approved it at a public meeting October 23-24, 1989, also in Washington.

The Subcommittee's task was to review the documents provided, to provide advice on the technical and scientific adequacy of the indicated approaches, and to suggest how to improve the approaches. The task was not to provide on-going continuing oversight of the EPA effort as it may have evolved since the Subcommittee meetings.

Agency staff were present at the Subcommittee meetings, participated in the discussions and heard the comments of the Subcommittee members. In addition, Agency staff were provided with drafts of this report as it was being prepared. This report has been compiled from information obtained and discussions held at the Subcommittee meetings (including the publicly announced conference call meeting of September 15), from written comments submitted by the Subcommittee members and from comments supplied from the members as they reviewed earlier drafts of this report.

## 2.2 The Charge for the PICs Subcommittee

OSW has developed a regulatory program to control emission of PICs based on limiting CO and THC concentrations in stack emissions of incinerators, boilers, and industrial furnaces. In establishing concentration limits on CO and THC that would ensure emission of PICs did not pose a significant health risk, OSW developed a risk assessment methodology to conservatively estimate the inhalation risk posed by THC.

OSW requested that the PICs Subcommittee provide comments on the technical merits of the proposed approach to control emission of PICs. Specifically, OSW requested comments on:

- o Whether limiting CO and THC is a reasonable approach to control emission of PICs, given the current data base and statutory time constraints?
- o What is the feasibility of monitoring THC to determine the aggregate emission rate of organic compounds?
- o Whether the proposed approach to assess the health risk from THC emissions is reasonable, given the current data base and statutory time constraints?

## 2.3 Regulations

Hazardous waste incinerators have been subject to controls under the Resource Conservation and Recovery Act (RCRA) since 1981. The existing regulations control emissions of organic compounds by requiring a 99.99% Destruction and Removal Efficiency (DRE) for Principal Organic Hazardous Constituents (POHC) in the waste feed. While these standards do not directly control emissions of Products of Incomplete Combustion (PIC), the quality of operation needed to achieve a 99.99% DRE also generally results in low emission of PICs.

Trial burn data have shown, however, that hazardous waste incinerators can operate at CO levels indicative of combustion upset conditions and still achieve 99.99% DRE. Under these high CO conditions, the EPA is concerned that PICs could be present at concentrations that pose unacceptable health risks. Therefore, the Office of Solid Waste (OSW) proposes to amend the existing regulations to control emission of PICs from hazardous waste incineration using the same limits on carbon monoxide (CO) and total hydrocarbons (THC) that are being proposed for control of PICs from boilers and industrial furnaces (1 - 5).

The OSW staff believes that requiring incinerators to operate at high combustion efficiency will minimize the potential health risk posed by emission of PICs. Stack gas CO is a conventional indicator of combustion efficiency and a sensitive indicator of poor efficiency under most combustion conditions. THC is a surrogate for PICs. When THC is high, CO is always high. However, when CO is high, THC may or may not be high. THC is currently measured as part of routine operations at a number of incinerators and is a better indicator of poor efficiency than CO when CO is high. Therefore, PICs and thereby the toxic fraction of PICs could be controlled by ensuring that hazardous waste incinerators operate at high combustion efficiency through limits on stack gas concentrations of CO and/or THC.

Studies characterizing PICs formed during the incineration of hazardous waste largely represent good combustion conditions where CO and THC are low. While a large fraction (that is, from 40 to 99%) of the hydrocarbon emissions at any particular facility have not been identified, and health data do not exist for many of the compounds that have been identified, many identified hydrocarbons are known to cause adverse human health effects.(4) EPA's risk assessments indicate that while emission of PICs at the currently measured levels are not likely to cause significant human health problems, the current 4-nines (99.99%) DRE standard could theoretically allow PICs emission levels which could present significant human health risks.(2,3,4) These observations are consistent with the findings of the SAB in its "Report on the Incineration of Liquid Hazardous Wastes."(7) Given the uncertainty about the health risk emission of PICs posed, and the strong public concerns about risks from incineration, OSW believes it is prudent to institute additional regulatory requirements controls to minimize the potential for health risks from possible elevated concentrations of PICs.

The proposal for controls was made even though OSW has not established that emission of PICs from hazardous waste incinerators currently pose a substantial risk. EPA's risk assessments indicate that emission of PICs at currently measured levels are not likely to produce significant human health effects. However, since the current DRE standard applies only to designated POHCs, a 4-nines



(99.99%) DRE does not preclude the possibility that emission of PICS could present significant human health risk.

## 2.4 Technical

### 2.4.1 Chemistry

Combustion is a chemical process. In the incineration of hazardous wastes, waste and air are combined with heat to produce major products, by-products, and unburned wastes. The major products for incineration are simple molecules such as water, carbon dioxide, and hydrochloric acid; these simple molecules make up approximately 99.99% of the emissions. Organic components in the emissions are generally referred to as "Products of Incomplete Combustion (PICS)" which include various hydrocarbons (THC) including chlorinated hydrocarbons. Metals present in the waste are not destroyed by incineration and will be found in the emissions and in the residue of incineration.

The incineration of wastes proceeds by means of a series of complex parallel and sequential processes, including the heating and volatilization of the waste, mixing of the vapor feed or volatile products with the oxidant, and the chemical reaction of the gaseous species. The oxidation reactions may involve several hundred elementary reactions, but with very few exceptions, carbon monoxide (CO) is an intermediate product between the carbon in the waste being incinerated and the most oxidized form of carbon, which is carbon dioxide (CO<sub>2</sub>).

On a weight basis, the majority of the PICS are CO and methane.(34) The others are trace amounts of the various partially oxidized organics, polynuclear aromatic hydrocarbons, and soot.(34,44)

### 2.4.2 Incinerators

If an incinerator is properly designed and operated to provide adequate time, temperature and turbulence, the dominant factor which impacts on the PICS emission level is the excess air or combustion chamber oxygen level. When there is adequate oxygen supply in a properly designed combustion chamber or chambers, and adequate air/fuel mixing, the emission of PICS is extremely low. The concentrations of PICS increase when the oxygen content is close to the stoichiometric requirement. When less than the stoichiometric amount of oxygen exists in the combustion chamber, PICS increase even more.(27)

Very high destruction efficiencies can be attained in the high temperature oxidizing environment of an incinerator. However, the destruction of the organic hazardous compounds in a waste does not guarantee the absence of by-products formed from the waste during combustion. High concentrations of such products of incomplete

combustion (PICs) usually are a consequence of a perturbation in the incinerator operation resulting from rapid transients in feed rate or composition, failure to adequately atomize a liquid fuel, excursions in operating temperature, instances where the combustible mixture fraction is outside the range of good operating practice, or inadequate mixing between the combustibles and oxidant. Modern incinerators are equipped with a large combustion chamber or secondary combustion chamber to minimize the impact of these perturbations. Waste feed management and sound process control systems further reduce or compensate for any adverse impact. The amount and composition of PICs will depend in a complex and unpredictable way on the nature of the perturbation.

Current data have indicated that the state-of-art incinerators can be operated extremely efficiently. Under good combustion conditions, the combustion efficiency (conversion to  $\text{CO}_2$ ) is typically higher than 99.9%. The destruction efficiency of the parent compounds are typically around 99.999%.

A study of combustion test data obtained from various types of incinerators, boilers, and process furnaces reveals that under normal operating conditions, about 80% of the principal organic hazardous constituents (POHC) and the major compounds in PICs (with the exception of methane) are found in the flue gas at concentrations between 0.1 and 20 ppbv. (10, 11, 12, 13, 14, 15, 22, 50, and 51) This relatively narrow concentration range was observed even though the data were obtained from tests on facilities of many different designs, operating at different conditions, burning different types of wastes with different POHC compounds selected, and operated by different personnel. This indicates that there is a wide range of designs and operating conditions which achieve good combustion performance. However, the compounds that were analyzed in the gaseous emissions were often limited in number and types.

The flue gas POHC and PICs levels in state-of-the-art incinerators, if operated properly, may be limited by reaction and reactor kinetics, or by some other type of limitation due to quenching effects. Studies conducted on several new/innovative incineration technologies indicate that their performance may be no better than existing incinerators. (11)

#### 2.4.3 Measurements

Emission of PICs composed of thousands of different compounds, some of which are present in very minute quantities and cannot be detected and quantified without very elaborate and expensive sampling and analytical (S&A) techniques. Such S&A work is not feasible in trial burns for permitting purposes and can only be done in research tests. Very few research tests have been conducted to date which attempted to identify and quantify all the PICs in a typical emission sample. Such tests were unsuccessful

because sampling and analysis techniques are not available to identify or quantify many of the potential compounds emitted, nor are toxicity data available for all the compounds.(2)

In view of the large number of possible compounds that can be produced and their presence at concentrations approaching their practical detection limits, it is at present impractical to design a monitoring scheme to identify and quantify the individual toxic compounds in incinerator stack emissions. What is needed is a robust, continuous monitor to measure a compound or class of compounds, the concentration of which correlates with those of the toxic PICs.

Carbon monoxide, being an intermediate in the combustion process and one for which continuous detectors are available, is a candidate for such monitoring. The rate of oxidation of carbon monoxide is slow relative to that of most organic compounds and, as a consequence, perturbations in combustion conditions, will usually result in an increase in carbon monoxide concentration well before that of other PICs.(13) CO is expected to persist beyond the completion of combustion of other combustion intermediates. Total hydrocarbons (THC) provides an alternative measure of PICs, because the concentration of THC may better correlate with the large number of PICs which are hydrocarbons.

The results of several studies on the use of CO and THC as surrogates for PICs are summarized in a document made available to the Subcommittee.(3) Figure A from that document (which can also be found on page 12 of this report) plots the concentration of benzene as a function of the CO concentration and the total hydrocarbon concentration for data obtained at several sites. Benzene was the only compound for which some general correlation could be found within the data obtained from different facilities. Whenever the benzene concentration is high, the CO or THC is also high; however, there are a significant number of measurements in which the CO or THC concentration is high but the benzene level is low. These data indicate that the use of CO and THC as a surrogate for benzene will protect against high levels of benzene, but may also give false positives, i.e., high readings when the concentrations of benzene is low. The potential for false positives is also seen in Figures B and C taken from the same reference (and which can be found on page 12 of this report). Figures B and C plot vinyl chloride and methyl chloride data from one test facility against the carbon monoxide and THC concentrations. Since the data came from a single test facility, there was no impact of design parameters on the results. Benzene, vinyl chloride, and methyl chloride are individual PICs. While the concentrations of these PICs did correlate with CO and THC, the concentrations of other PICs did not. The high concentration of CO or THC may instead reflect high concentrations of other PICs.

#### 2.4.4 Risk Reduction, Upsets, and Emissions

Risks are involved in all human activities. Risks are also involved with any waste treatment and disposal operations, including waste minimization efforts.

In the case of PICs, risk may be associated with exposure to PICs. Controlling the concentration of PICs in emissions is one approach to reducing the risks PICs may present. Incinerators monitor CO as an indicator of combustion efficiency. CO may be high for a variety of reasons. For example, some incinerators may have high CO (but low emission of PICs) because of the type of waste burned; generally, this situation is identified in the test burn and requires no additional action to reduce risk. CO may be high for very short periods because of small perturbations in the flame zone; typically those perturbations last seconds to minutes and may actually be over before they are detected. In such cases, corrective action to reduce emission of PICs is virtually impossible and very likely unnecessary. Longer lasting high CO concentrations do call for corrective action and a variety of these are possible (such as readjusting combustion air, increasing turbulence, or decreasing the rate at which waste is fed). In some cases, corrective action requires shutting down the incinerator to fix the problem. These temporary elevations in CO concentration are often called upsets.

High concentrations of PICs may be associated with major upsets in incinerator operations. Sudden significant changes in feed rate or composition can cause such upsets. While it may seem counter-intuitive, very strict controls could, by leading to more frequent shutdowns, actually increase emission of PICs rather than decrease them. A good control system will minimize both false positives (shutting down when the incinerator is operating correctly) and false negatives (operating the incinerator when it is running inefficiently).

#### 2.4.5 PICs in Perspective

The emission of PICs is a consequence of any combustion process. (44,45,46,47,48,49, and 50) Emissions from hazardous waste incinerators contribute a relatively small fraction of the total combustion emissions released into the environment each year. However, with PICs the concerns are effects on the local environment, not the aggregate national emissions, and the local impacts may vary considerably.

Present analytical methods do not allow scientists to identify and measure all compounds in incinerator emissions--or in many other materials. The best studies characterizing PICs have accounted for about 60% of the mass, some studies have accounted for as little as 1% of the mass. (4)

The available data show that a well designed and operated incinerator does not emit PICs in substantially greater quantities than fossil fuel combustion processes.

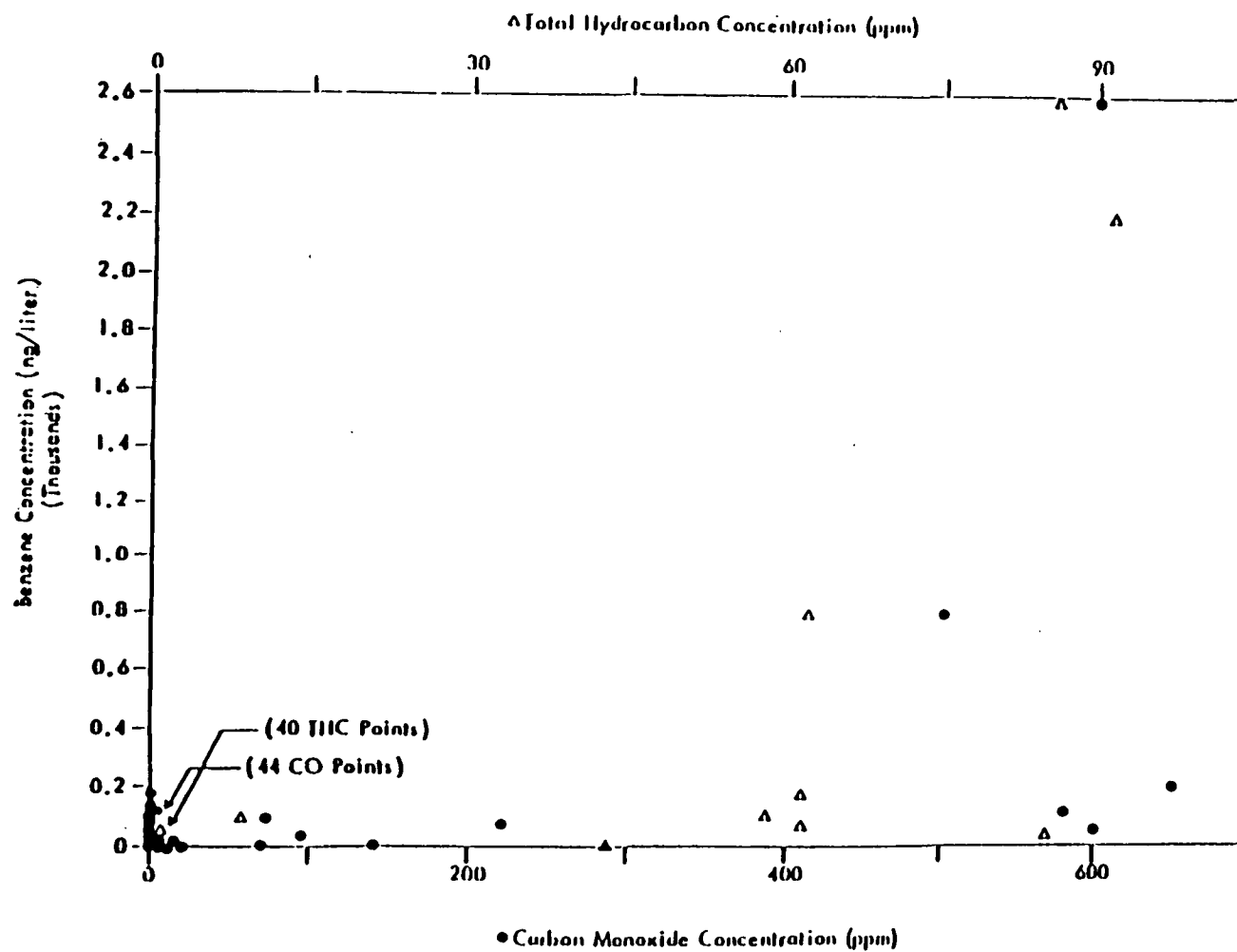


FIGURE A - Benzene (a PIC) Concentration Versus Those of CO (Bottom Scale) and THC (Top Scale)

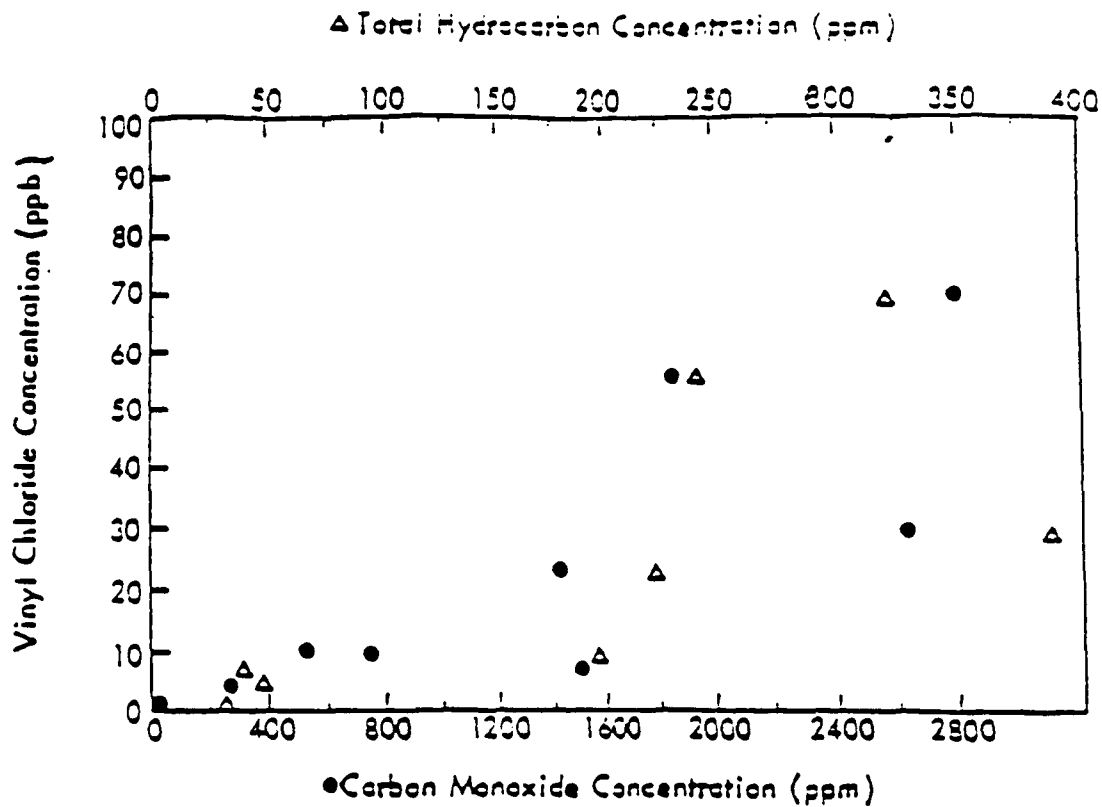


FIGURE B - Vinyl Chloride Concentration Versus Those of CO (Bottom Scale) and THC (Top Scale)

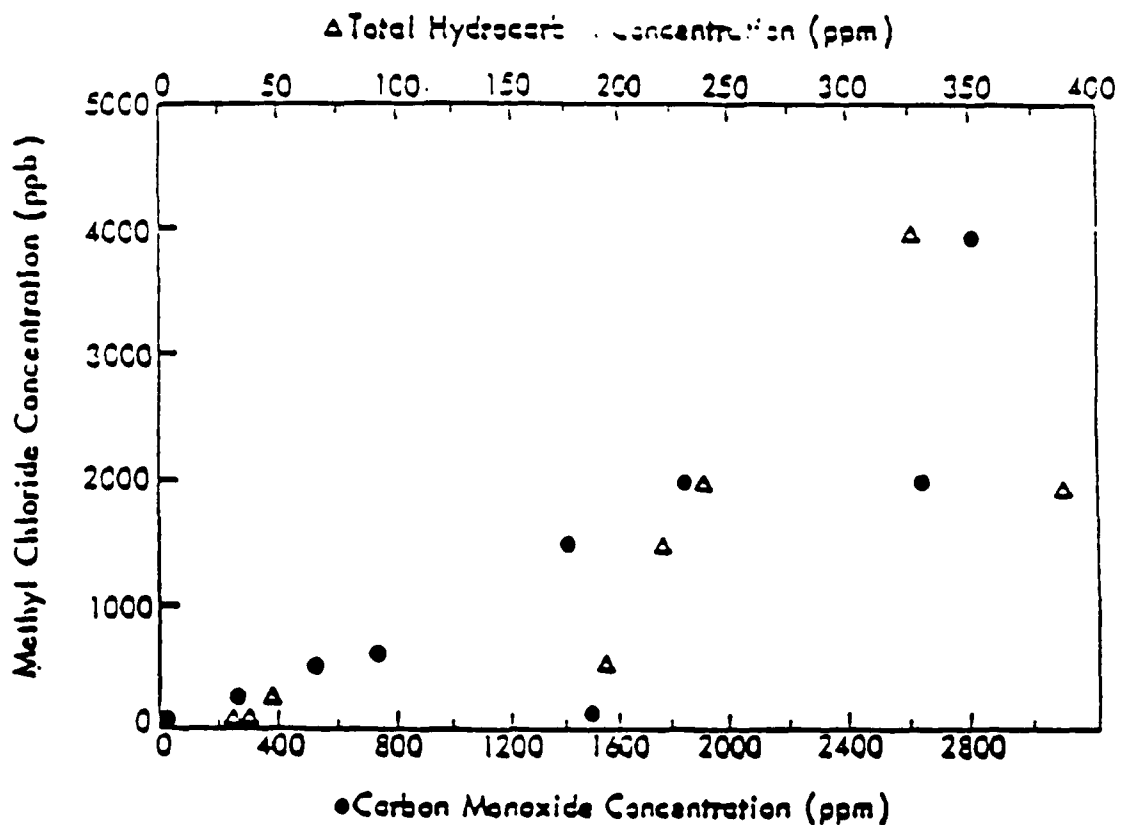


FIGURE C - Methyl Chloride Concentration Versus Those of CO (Bottom Scale) and THC (Top Scale)

### 3. RESPONSE TO THE FIRST QUESTION

The first question the PICs Subcommittee considered was "Whether limiting carbon monoxide (CO) and total hydrocarbon emissions (THC) is a reasonable approach to control emission of PICs, given the current data base and statutory time constraints?"

#### 3.1 Comments on the General Concept

Both the laboratory and field test data, and both the non-flame and flame test data have indicated that CO is a good conservative indicator of combustion performance. (3,4,6,10,13,24,25) Combustion of CO requires very high ignition energy. CO is the dominant combustion by-product. Combustion of other organics requires much lower ignition energy and the reactions proceed more quickly. While poor combustion conditions are always indicated by high CO levels, a high CO level may not indicate poor combustion conditions.

THC level, as measured by a flame ionization detector (FID) with a heated sampling line, is a measure of carbon-hydrogen based volatile and semi-volatile organics. While there are indications that a FID detector may be inappropriate for chlorine based compounds such as carbon tetrachloride, test data indicated that this is not important for regulatory control purposes. Carbon tetrachloride is very difficult to oxidize by itself and has to be burned with large amounts of carbon-hydrogen based high heating value fuel or wastes. Most EPA sponsored combustion tests and industry sponsored trial burn tests used carbon tetrachloride as a POHC.

Abundant test data indicate that CO and associated carbon based PICs are the dominant compounds in the flue gas. If both CO and PICs are low, the carbon tetrachloride level also is low. Hence, the available test data indicates that CO and/or THC concentration may be a good indicator of the emission level of PICs in stack flue gas even when carbon tetrachloride is burned.

Some test data indicate that under certain conditions the flue gas THC level may be higher than the CO level. At other conditions, the flue gas soot level is higher than the CO and the THC level. Further evaluation of those test conditions (31, 32) indicated that when the THC level is higher than the CO level, there was no excess oxygen in the combustion region and the system was in a reducing environment.

Under extreme reducing or pyrolyzing conditions where less than the stoichiometric amount of oxygen is available and the temperature is high, most organics will be thermally cracked into soot. Under this condition, the THC reading may be close to zero because the carbon is in the soot. However, the observed CO level



will be in the percent range and much higher than the 100 ppm range which is of interest for regulatory compliance purposes. Therefore, reducing conditions will be identified by the CO compliance concentration or low excess oxygen concentrations and not by a high THC concentration.

### 3.2 The Critical Linkage Between EPA's Proposed Two-Tier Approach and the Capability for Continuous or Frequent THC Monitoring

In its September 1988 guidelines, EPA originally proposed a two-tiered approach to applying limits on CO in the stack exhaust gas as a surrogate for emission of PICs. (3) Under Tier I, CO emissions would be limited to 100 ppm (corrected to 7 percent oxygen, based on an hourly rolling average); compliance with this limit would be demonstrated initially during the trial burn and thereafter through continuous emissions monitoring for CO. EPA's rationale for this approach is based on data demonstrating that at CO levels below 100 ppm, PICs appear to generally pose acceptably low risk.

EPA's Tier II approach was developed for facilities which, despite operating at higher CO levels, may nevertheless produce PICs at acceptably low levels. (3) If CO levels are found to exceed 100 ppm during the trial burn, the highest hourly CO average would serve as the CO limit in the permit, and operation would be permitted up to this level if total hydrocarbon (THC) emissions measured during the trial burn are sufficiently low. EPA's rationale for this approach is that, when CO levels are above 100 ppm, there is virtually no correlation between CO and emission of PICs; that is, when CO is high, emission of PICs may be high or low. Under Tier II, therefore, THC levels (which serve as a surrogate for emission of PICs) would need to be measured to determine whether they are acceptably low. EPA has proposed that measured THC emissions levels would be required to either meet specified screening limits or be demonstrated on a site-specific basis not to pose an unacceptable risk. The agency is considering modifying this proposal by placing an upper limit of 20 ppmv on THC emissions.

While this general approach appears to be a reasonable one, given the available data, it contains one serious deficiency that must be addressed. As proposed, THC emissions would be measured only during the trial burn. If found acceptable, operation at permitted CO levels (above 100 ppm) would be presumed to produce THC emissions on a routine basis that are not greater than those measured during the trial burn; no verification would be required. Yet the entire basis of Tier II is the lack of any correlation between CO and THC when CO exceeds 100 ppm. Thus, THC levels measured during the trial burn cannot be assumed to be representative of routine THC emissions.

EPA indicates that it is considering requiring continuous emissions monitoring (CEM) of THC, because of the limitations of CO as a surrogate for THC. Significant questions have been raised, however, regarding the current feasibility and reliability of CEM capability for THC. CEM is necessary for the viability of the entire Tier II approach. At the very least, frequent (weekly or on some other time frame determined by appropriate testing) routine stack testing for THC must be conducted as an alternative to CEM, to provide a basis for assessing both compliance with THC limits and the correlation (if any) between CO levels and THC emissions, waste feed characteristics, and operating conditions.

### 3.3 Current Available Data Correlating CO and Organic Emissions

In the past few years, EPA has spent extensive effort in studying the emission of products of incomplete combustion from hazardous wastes. In most of those studies, EPA has only attempted to analyze and quantify Appendix VIII toxic compounds. In only one study, has EPA tried to identify and quantify all compounds found in incinerator emissions. (19)

As discussed in Section 2.4.3, the Subcommittee agrees that due to the large number of possible compounds and their typical presence in the stack flue gas at concentrations approaching their practical detection limits, it is difficult to identify and quantify all the PICs. However, due to public concern over emission of PICs, the Subcommittee considers the available data on PICs is still sparse and more study should be conducted. The ultra-low level of PICs and the similarity to those emitted from other combustion devices (22,44,45,46,47,48,49,50), however, suggest that this is not an important or unique problem associated with hazardous waste incinerators.

Below is a brief summary of the data presented by EPA to date, trying to find correlations among CO, specific PICs, DRE and THC. Specific relationships normally can be found for data obtained at the same facility where most of the parameters which have impact on combustion performance are fixed. However, only general correlation can be found for data obtained at different facilities where many parameters were changed in the data collection process.

#### 3.3.1 Investigations of Potential Correlation of CO with Specific PICs:

- a. One study of four full-scale incinerators found that three of four PICs (benzene, toluene, carbon tetrachloride) were low (on the order of 0.1 ng/L) when CO was below 100 ppm; a fourth (trichloroethylene), however, did not show this correlation with CO. (22)

- b. Another study of a pilot-scale facility examined 11 PICs; while the two most abundant PICs showed a good correlation with CO, the other nine did not.(40)
- 3.3.2 Investigations of Potential Correlation of CO with DRE at Low CO Levels:
- a. One study of a bench-scale facility revealed little effect on DRE at CO levels ranging between 15 and 522 ppm.(42)
  - b. Another study of a pilot-scale facility found that DRE was fairly constant at CO levels up to 220 ppm.(41)
- 3.3.3 Investigation of Potential Correlation of CO and THC:
- a. Data from 9 full-scale incinerators of various designs at many operating conditions and burning various types of wastes demonstrated that when CO levels were below 100 ppm, THC levels were almost always below 20 ppmv. Higher CO levels were usually associated with higher THC emissions.(33)
  - b. Data from 11 industrial boilers of various designs and at different operating conditions, co-firing hazardous waste indicate a similar correlation, with the exception of one firetube boiler burning natural gas.(43,51)
  - c. Data from 10 cement kilns co-firing hazardous waste indicate the same correlation; however, at CO levels higher than 100 ppm, no clear trend was seen because both high and low THC emissions were observed.(43)
- 3.4 Summary

In the Subcommittee's view, the available data correlating CO with THC emissions at low CO levels are sufficient to support the Agency's concept of limiting CO as a means of ensuring high combustion efficiency and reducing total organic emissions. The data do not, however, provide a sufficient basis for assessing emission levels for specific PICs. The data also do not convincingly support EPA's choice of a limit as low as 100 ppmv for CO.

#### 4. RESPONSE TO THE SECOND QUESTION

The second question asked of the PICS Subcommittee was, "What is the feasibility of monitoring THC to determine the aggregate emission rate of organic compounds?"

The feasibility of continuously monitoring THC to determine the aggregate emission rate of organic compounds can be subdivided into several parts:

- a. Is there an available detection system that is responsive to "total hydrocarbons"?
- b. Is there an available sampling system that can reproducibly deliver to the detection system a sample of stack gas that is representative of the actual stack gases?
- c. Are the detection and sampling systems sufficiently rugged for use in a continuous monitoring mode during routine or trial burn hazardous waste combustion operations?
- d. Has the feasibility of the overall THC system been sufficiently well documented to serve as a basis for regulation?

Each of these issues is discussed separately below.

##### 4.1 Availability of a "Total Hydrocarbon" Monitor

Accurate determination of the "aggregate emission rate of organic compounds" requires a detection system whose response depends on, and only on, the mass of organic material present in the stack gas. The Flame Ionization Detector (FID) represents a commercially available detector that comes close to meeting this criterion, in that it is responsive to most classes of organic chemicals, including those likely to be most abundant as PICS in hazardous waste combustor emissions, at sub-ppm (v/v) concentrations in air.

However, the magnitude of the FID response depends both on the concentration and the composition of the organic material present. A report presented to the Committee notes that "The response (relative to methane taken as 1.0) varies from 0 for formaldehyde and formic acid to 0.4 for methylamine ( $\text{CH}_3\text{NH}_2$ ) and 0.76 for dichloromethane ( $\text{CH}_2\text{Cl}_2$ ). In general, each chlorine atom makes a reduction in response by 0.12 units."(38)

While the most abundant compounds in hazardous waste stack emissions (up to 50% of the total mass) are simple hydrocarbons

(methane, etc.), some of the methane could have been unburned fuel rather than a product from the waste since auxiliary fuel is, in some cases, burned at the time of sample collection. Since compounds such as methane have high FID response factors, they will tend to dominate the magnitude of the total hydrocarbon analyzer signal. A 10- or 100-fold increase in the concentration of a low response factor but highly toxic, organic compound might go undetected against the background signal of high response factor nontoxic hydrocarbons. Many different mixtures of chlorinated and nonchlorinated organics could give rise to exactly the same total FID response.

The Office of Solid Waste addressed the response factor issue by developing a "weighted average response factor" based on a hypothetical worst case composition of PICs in incinerator emissions.(38) However, in actual hazardous waste combustion processes, the composition of the organic species will not necessarily approximate this hypothetical distribution and the actual average response factor will differ. Further, the composition of organics in the stack gas, and thus the average response factor, will vary. Thus, even for a single incinerator burning a single waste, it will not be possible to deduce whether a change in the FID signal represents a change in the emission rate or a change in composition.

Despite these caveats, the Subcommittee thinks it probable that the average response factor of the organic species present in relatively high concentration in the stack gas will be sufficiently constant that the FID response could provide a useful approximation or estimate of the level of PICs. Such an estimate could serve as an indicator of good combustion control (but not as the basis for a health risk estimate).

#### 4.2 Availability of a Sampling System

The FID monitor responds only to organic compounds that reach the detector in the vapor phase. In order to achieve an estimate of the aggregate emission rate of organic compounds, it is necessary to use a sampling system that delivers, at a minimum, a constant fraction of the total organics present in the original flue gas to the detector.

The Office of Solid Waste asked the Subcommittee to address the question of using a "hot" (150°F) versus "cold" (ambient temperature) transfer line to deliver the stack gas sample to the FID. A 150°F transfer line may not eliminate sorption problems, although the hot line should allow a broader range of compounds to reach the detector. The proposed regulations assume that a constant fraction (25%) of the THC (the "missing carbon") will be lost due to absorption effects.(38) No evidence was presented to the Committee to document that the "missing carbon" percentage will be constant. In fact, data were presented which show "missing

carbon" percentages ranging from 2% to 71.1%.(4) It was not possible to determine whether the variability was due to differing degrees of absorption/condensation in the sampling system or to differences in the composition of organics present or both.

With a cold transfer line, most lower volatility, higher molecular weight organics will condense out of the vapor phase. Cold sampling systems typically include a condensate trap to collect these non-volatile organics, along with water. The relatively volatile compounds will reach the detector and the variability in their concentration should be mainly a function of stack gas composition, rather than sampling train problems. This may be advantageous relative to using hydrocarbons as a measure of good combustion, but not for risk estimates because the risk assessment relies on the accuracy of mass emission rate of the pollutant. Using a method which measures only a portion of the THC is acceptable in view of EPA's proposed technology based 20 ppm THC limit, although it is desirable to measure the total THC or at least a relatively constant fraction of the total. However, the reliability and operability of the system in all modes of operation is also important so that a comparative picture of the emissions is available on a continuous basis. Heated THC systems, although potentially detecting a greater fraction of the THC, have been observed to experience problems attributable to plugging of sample extraction lines due to heavy particulate loading and/or condensed organics. Unheated THC systems have a longer history of use and have a much higher availability. A recent survey of continuous THC monitoring systems reported that 6 facilities have been continuously monitoring THCs using "cold" or "conditioned" systems for periods ranging from 1 to 7 years and did not have any significant loss of availability due to breakdowns or malfunctions. Moreover, the Subcommittee has learned that continuous THC monitors are required by regulations in Germany and Switzerland and the facilities reported no major problems with routine (daily) maintenance.(58) The Subcommittee believes that "cold" or "conditioned" monitoring systems for hazardous waste incinerators are available at this time.

Under upset conditions, the presence of high-surface-area particulate matter (soot) in the stack could act as condensation nuclei or absorption sites, thus reducing the quantity of organic material reaching the FID. However, excessive levels of soot would be likely to be accompanied by other indications of upset conditions, such as high CO readings and/or low excess oxygen readings (see Section 3.1).

#### 4.3 Ruggedness (Operability and Maintainability) of THC-CEM Systems

The feasibility of monitoring hydrocarbons using heated systems in hazardous waste incinerator stack emissions on a continuous basis during routine operations was not documented.

While such systems (like the Beckman 402 and Ratfisch 455) have been available for a long time and used in trial burn test or research tests, their continuous usage for any extended period of time (such as a month) could not be documented either in the U.S. and Europe. In fact, the Subcommittee heard anecdotal evidence that the "hot" THC system(s) can present reliability difficulties even under trial burn conditions.

Commercially available "total hydrocarbon analyzers" using sample conditioning lines and a cold FID system are considerably more rugged than typical laboratory instruments such as gas chromatographs. However, the FID-based monitors are still subject to corrosion and plugging under conditions that may exist in hazardous waste incinerator gaseous emissions. Use of the FID as a continuous monitoring system may require considerable (probably daily) maintenance under the direction of a reasonably experienced chemist or chemical technician.

The "hot" sampling line may also require periodic (frequent) maintenance or cleaning to prevent build-up of condensable organics and losses of THC over time. This could require the installation of two parallel sampling lines - one in service and the other being washed/baked-out at any given time. Another alternative might be frequent replacement of a short section of transfer line close to the stack.

The Subcommittee is convinced that successful implementation of a continuous THC monitoring system will require rigorous attention to Quality Assurance/Quality Control (QA/QC) protocols, as well as requiring the careful training of skilled operators.

A single gaseous organic, such as propane, is conventionally used to calibrate continuous hydrocarbon monitors. This may also be appropriate for hazardous waste combustion purposes. However, two caveats need to be made. It is critically important that the calibration standard(s) be introduced at or immediately behind the probe; this will be the only way to approximate the kinds of absorption losses that have been postulated. Also, some checks of the monitoring system should be made using calibration gases containing less-volatile organics (perhaps naphthalene, or tri- or tetrachlorobenzene). Preferably, these compounds would be introduced into the stack gas stream by the method of standard additions; this could provide a check on the constancy of the "response factor" and also on absorptive losses.

#### 4.4 Documentation of THC-CEM System Feasibility

While there are limited data available on the accuracy and precision of continuous THC measurements over time periods of days to weeks, OSW did not provide documentation of the operability and maintainability of the FID detector and sampling system by facility personnel under routine operations until late in the Subcommittee's

review process. As discussed above, the OSW recently submitted to the Subcommittee a survey of continuous THC monitoring systems that indicates that "cold" or "conditioned gas" systems can be operated continuously without unusual operation or maintenance problems. (58) Although the Subcommittee has not reviewed the report in detail, it appears to document the feasibility of continuous cold THC monitoring.

Notwithstanding the field experience with continuous THC monitoring, there is a need to investigate and document the magnitude of effects such as rate of condensation, build-up of non-volatile organics, flue gas moisture effects, and effects of particulate matter on the medium- to long-term performance of the system. The selection of appropriate calibration compounds and determination of precision and accuracy data over various time periods and concentrations is also a subject for further investigation. There is evidence indicating that a cold THC analyzer with a flue gas pre-conditioning system can function reasonably reliably. The reliability is improved due to the fact that those components which cause corrosion and plugging problems have been removed, but, at the same time, these chemicals have been removed from the system and have not been detected.

#### 4.5 Summary

The feasibility of using a heated line to continuously monitor total hydrocarbons (THC) has not been documented. However, recent survey data appear to show that unheated THC monitors using sample conditioning systems (refrigerated condensate traps) are feasible and already in operation at several facilities in the United States and Europe.



## 5. RESPONSE TO THE THIRD QUESTION

The third question asked of the PICs Subcommittee was, "Whether the proposed approach to assess the health risk from THC emissions is reasonable given the current data base and statutory time constraints?"

### 5.1 A Brief Description of EPA's Risk Assessment and Two Regulatory Approaches

To support its proposal to limit THC emissions as a means of reducing the potential risks posed by PICs, EPA developed a means of estimating the human carcinogenic risk posed by inhalation of THC at a given level. Specifically, the EPA derived a unit cancer risk value for a mixture of compounds assumed by EPA to represent THC (elsewhere in this section this mixture will be referred to as "estimated THC".) using a set of assumptions to predict the array of specific PICs actually present in THC.

EPA's starting point for deriving the unit risk value is its historical data base on emissions of individual compounds from hazardous waste incinerators, boilers, and industrial furnaces. Several hundred toxic compounds which have been found in wastes are listed in Appendix VIII of the Code of Federal Regulations (CFR 261). For each Appendix VIII compound identified in the emissions data base, EPA assumed that it is present in THC at its 95th percentile concentration, as a "reasonable worst-case value" (EPA's wording). (4) However, as Appendix B shows, this assumption may not be conservative in this particular instance. For each Appendix VIII compound that has not been detected in emissions and is therefore not in the data base, but for which adequate health effects data are available to establish a risk-specific dose, EPA assumed it is present in THC at a nominal detection limit of 0.1 ng/L.

The list was further expanded by including methane and ethane emissions from fossil fuel combustion and formaldehyde concentrations from municipal waste incinerators also at their 95th percentile concentration. In recognition of the fact that even the most complete analyses of incinerator emissions have failed to account for all of the emissions, the list of compounds was further expanded by including all compounds that have been quantitatively assessed by the Cancer Assessment Group (CAG) of the Agency.

Table I indicates the number of Appendix VIII compounds (out of a total of more than 350 and not all are organic compounds) used to calculate the THC unit risk value and the basis for their assumed concentrations.

**Table I: The Number of Appendix VIII Compounds Used to Calculate the THC Unit Risk Value and the Basis for Their Assumed Concentrations**

No. of App. VIII Compounds Detected in Emissions (including formaldehyde)	25
No. of App. VIII Compounds Assumed at 0.1 ng/L	45
Total No. of App. VIII Compounds Used to Calculate the THC Unit Risk Value	70

Approximately 70% of the identified emissions (on a weight basis) from these facilities are associated with known systemic toxicants; 30% of the identified emissions are associated with known carcinogens.(37) All of the individual systemic toxicants occurred at concentrations that were calculated to be lower than the Reference Air Concentration (RAC). The reference air concentration (RAC) is an estimate (accurate within an order of magnitude) of the concentration to which humans could be exposed for a lifetime without suffering adverse effects. EPA assumed that the individual non-carcinogenic compounds in the mixture did not act additively and that consequently, because the exposures to systemic toxicants were estimated at sub-threshold concentrations, EPA reasoned that exposure to the mixture would not generate health concerns for systemic toxicity.

EPA then applied compound-specific unit cancer risk factors to each concentration value to obtain a risk level for each compound. A unit risk factor is the upper bound estimate of the excess lifetime cancer risk associated with a lifetime of exposure to one unit of concentration (usually one milligram per cubic meter). A unit risk value of zero was assumed for all non-carcinogens (e.g., methane). Finally, these risk levels were summed to produce a weighted 95th percentile unit risk value for estimated THC. This unit risk factor was then used to calculate the risk associated with inhalation of estimated THC emissions at particular levels using a variety of additional assumptions regarding dispersion and point of exposure.

## 5.2 Discussion of Assumptions Used in Risk Assessment

The estimation of potential risks associated with various levels of total hydrocarbon (THC) emissions involves many assumptions. In addition, the many assumptions required to derive the unit risk factor and to calculate risks arising from exposure to estimated THC render the methodology even more unreliable for the purposes of site-specific regulation. These assumptions are commonly used in EPA risk assessments and while the Subcommittee did not consider it within its charge to challenge the assumptions. Additional comments relating to the general issue of risk assessment and which are relevant in part to this particular instance, are found in Appendix C.

Below are listed some of the assumptions with commentary from the Subcommittee and Executive Committee. Some of these assumptions are clearly conservative, while others are not. Some of the conservative assumptions are the following:

- a. Compounds that have been determined by EPA to be carcinogenic in any context, but which have not been identified in the emissions data base, are nevertheless assumed to occur in emissions at their approximate

detection limits. A more realistic risk assessment should omit from consideration those compounds which are highly unlikely to be present in incinerator emissions, for example diethylstilbesterol.

- b. Individual risks are calculated at upper plausible limits to risk. A different approach is described in Appendix C.
- c. Although not measured in the studies of hazardous waste incinerator emissions contained in the data base, it is assumed that formaldehyde is emitted at a level corresponding to the 95th percentile of the available data from municipal waste combustors.
- d. The receptor is a Maximum Exposed Individual (MEI) who is postulated to reside continually at the site of maximum annual average calculated ground level concentration for a full 70 years.
- e. The estimated THCs are assumed to reach a postulated receptor (the MEI) after dilution in ambient air, based on the use of conservative dispersion coefficients for reasonable worst-case facilities.
- f. Individual unit risk(s) are added, assuming that carcinogenic risks are additive. Appendix C shows how the addition of upper 95% bounds of risk for individual compounds leads to a higher percentile bound for the combined risk.

The following assumptions in the risk assessment are either neutral or insufficient data exist to determine whether their effect would be conservative or non-conservative:

- a. Although EPA uses 95th-percentile emission levels in calculating risk from emission of PICs, this risk is not significantly conservative compared with one calculated using "median" levels. Factors leading to this result are: the high degree of skewness of emission level distributions, the assignment of 0.1 nanograms/liter to some supposed PICs (especially diethylstilbesterol with its high contribution to risk at the "median" levels) at both levels and the zero risk contribution of C1 and C2.
- b. Synergistic or antagonistic effects among carcinogens or between carcinogens and non-carcinogens are not considered.
- c. Only Appendix VIII compounds for which adequate health effects data exist are considered in calculating the

unit risk factor for estimated THC. Because this unit risk value is applied to the entire mass of estimated THC, the aggregate of all other compounds present in the emissions is assumed to pose the same risk. Data indicate that non-Appendix VIII compounds are present in estimated THC in at least the same order of magnitude as Appendix VIII compounds; semi-volatile compounds not in Appendix VIII are a particularly high fraction of the total.(4) These compounds may pose lesser or greater risk than those included in calculating the unit risk value.

- d. It is assumed that a single THC unit risk value, based on a hypothetical reasonable worst-case composition, can be applied to all incinerators.
- e. In calculating RACs for compounds lacking direct inhalation data, oral RfDs are used, assuming a conversion factor of 1 between the two routes of exposure.
- f. Exposure to the same carcinogenic compounds contributed by other sources (combustion or otherwise) is not considered in assessing overall risk.

Finally, certain assumptions are clearly non-conservative:

- a. The emissions data base is derived in large part from facilities operating under good combustion conditions (e.g., research tests), which is likely to underestimate, to an unknown degree, the emissions that occur during routine operations; the nature and magnitude of emissions under the range of conditions which may be experienced during the lifetime of a facility's operation is poorly understood. A more realistic assessment would not be restricted to good operating conditions. Continuous CO monitoring records could be inspected to estimate the amount of time spent in excursions.
- b. Direct inhalation of carcinogenic PICs is the only route of exposure considered; indirect exposure through other routes (e.g., the food chain) are not included, although available data indicate that such routes may produce exposures that may be much greater than direct inhalation, particularly for environmentally persistent compounds.(39)
- c. Reliance on RfDs, which are based on risks to the general population, may not adequately protect sensitive members of the population. RfDs include a factor of ten for the extrapolation from animal studies to human

health effects and another factor of ten because of the variability of sensitivity in human populations; in many cases this appears to be adequate, but not in all cases. (2,52,53)

- d. No consideration is given to environmental effects due to a lack of sufficient information. These effects may occur at levels of exposure lower than those affecting human populations. (2)

In the THC risk assessment process, conservative assumptions are used to compensate for many sources of uncertainty and areas of insufficient information. However, the toxicity of the total estimated THC mixture cannot be assessed, in part because of the great likelihood of the emission of unknown compounds. In addition, humans can also suffer adverse effects from pollutants to which they are indirectly exposed (through the food chain or by breathing resuspended dusts which contain contaminants, etc.). Other living creatures may also be affected by pollutants. To the extent that the risk assessment excludes these effects, it is not conservative.

### 5.3 Evaluation of the Risk Assessment

EPA has proposed two different regulatory applications of its risk assessment methodology (including use of the THC unit risk value). The first application involves its use as a risk-based check on the Agency's proposed technology-based THC emissions limit of 20 ppm. (5) The second application involves its use in site-specific risk assessments conducted to support facility operation at CO flue gas concentrations in excess of 100 ppmv. (3) These two applications are discussed separately below, since the Subcommittee reached different conclusions regarding the adequacy of the two approaches.

#### 5.3.1 Is the Use of the Risk Assessment Methodology Reasonable and Appropriate as A Risk-Based Check on the Proposed Technology-THC Limit (20 ppm)?

EPA has proposed to limit THC emissions to 20 ppm, based primarily on consideration of the actual THC levels achieved by units operating under good combustion conditions that is, based on good operating practice. In further evaluating the choice of this value, EPA employed the THC unit risk value described above (as well as other assumptions regarding dispersion of and exposure to THC emissions) to provide a risk-based check on the technology-based limit of 20 ppm, in order to determine whether such a limit will be generally protective of human health and the environment.

Despite the limitations of the emissions data and the large degree of uncertainty introduced by various assumptions employed in the risk assessment methodology, the Subcommittee considers that the methodology is sufficient to provide a risk-based check on the

proposed THC emissions limit, and that the Agency's evaluation of the emissions limit provides evidence of adequate safety.

Therefore, considering the results of the THC risk assessment calculations presented, measured THC emissions of 20 ppmv are likely to present actual carcinogenic risks below the suggested limit of 1 in 100,000 in the majority of cases. However, given the assumptions and uncertainties discussed above, the Subcommittee concludes that (a) it is not possible to calculate reliable total THC risks--to both human health and the environment and (b) at present, the method is not suitable for setting specific limits based upon THC levels alone.

5.3.2 Is the Use of the Risk Assessment Methodology in Site-Specific Assessments Reasonable and Appropriate to Support Facility Operation at CO Levels in Excess of 100 ppm?

While EPA's risk assessment approach follows previously accepted methodologies, because of the data limitations, the Subcommittee believes that the risk assessment lacks both the precision and accuracy needed to be useful in a site-specific regulatory context. For site-specific applications EPA would need to replace the assumptions currently used with hard data. Such data would have to include at least: wind direction, the nature of the waste mixture, and the specific concentrations of individual compounds found in the emissions. The Subcommittee is not recommending a large data gathering effort to OSW, but only recognizing that the data requirements for site-specific applications are very high.

THC is used as a surrogate for PICs and for those compounds in the PICs which may cause cancer. Since THC does not correlate well with CO when the concentration of CO is higher than 100 ppmv, reliance on these data, however necessary, introduces considerable uncertainty into risk estimations. The Subcommittee therefore considers the Agency's risk assessment methodology, which would rely on THC concentrations obtained during trial burn tests only, to be inadequate for site-specific applications, as proposed under the original Tier II.(3) The revision made by requesting continuous THC monitoring using a cold system should be satisfactory. (37)

5.4 Summary

The Subcommittee considers EPA's risk assessment adequate to provide a risk-based check on the proposed THC emissions limit of 20 ppm. However, because high levels of CO do not necessarily mean THC is high, the risk assessment methodology is inadequate for site-specific applications, as proposed under the initial Tier II approach. (3)

## 6. VIEWS ON OTHER TECHNICAL ISSUES

### 6.1 Risk Assessment and Exposure Modeling Considerations

#### 6.1.1 Atmospheric Dispersion Simulation

##### 6.1.1.1 Introduction

The approach to dispersion modeling employed in the evaluation of exposure and the risk assessment associated with hazardous waste incinerators is reasonable and appropriate, especially in view of the relatively small uncertainty in these estimates when compared with uncertainties associated with other components of the risk assessment, such as emission estimates and risk factors. There are a few areas where the procedures are in need of some "tightening" or clarification, and in one or two areas, minor revision. These include: so-called dispersion coefficients; sensitivity analyses; representative meteorological data; and low stack-height considerations.

##### 6.1.1.2 Dispersion Coefficients

The dispersion modeling discussion refers to the use of 'dispersion coefficients' whereas, in fact, a more appropriate term would be "dilution factor." The coefficient or factor referenced is the modeled atmospheric concentration (C) normalized by the stack mass emission rate (Q); i.e.,  $C/Q$ . This ratio is a factor that denotes the effluent dilution, normalized by the rate. Convention considers dispersion factors to characterize the rate (temporal or spatial) at which the atmospheric motions cause a volume of some additive to spread. The two concepts are quite distinct and use of 'dispersion coefficients' as originally drafted is inappropriate and misleading.

##### 6.1.1.3 Sensitivity Analyses

Applicants and regulators would be helped by sensitivity analyses of the relative impact of stack height and ambient meteorology on dilution factors. Selecting worst-case dilution factors from multiple-year applications of a dispersion model eliminates most of the site-specific meteorological variability and emphasizes the importance of effective stack height. This emphasis may be appropriate because stack height is an applicant-controlled variable, whereas meteorology can only be controlled by relocating the plant. Given these considerations, the type of sensitivity analysis suggested would be beneficial.



#### 6.1.1.4 Representative Meteorological Data

EPA's "Information Requirements" section also addresses representative meteorological site data, and indicates virtually any data should be used if representative site-specific data are not available.(4) This is a significant weakness of the requirements section. In the absence of representative data, other data should only be allowed on an interim basis if such data meet identified acceptance criteria; such criteria need to be included in the document.

#### 6.1.1.5 Low Stack-Height Considerations

The preamble to the hazardous waste incinerator regulation presents many tables that illustrate feed rate screening limits for various compounds in both complex and non-complex terrain. These tables illustrate effective stack heights that vary from 4 m to 120 m. Inclusion of the smaller stack-height values in the tables suggests that these are acceptable values. However, as a general practice, small stack heights are to be discouraged; specific guidance can only be given in combination with information on aerodynamic roughness ( $z^0$ ) of the local environment and the height and fetch of nearby tall buildings. Such information should also be required specifically under the data needs enumerated in Part Four: Section VI "Information Requirements."(4)

Sites where potentially adverse ambient concentrations may be found are apt to be associated with plants whose effective stack heights are small relative to the height of nearby buildings or where the fetch to nearby buildings is small (or both). In such cases, mathematical dispersion modeling may not be the preferred simulation methodology, and fluid modeling in a boundary-layer wind tunnel may be desirable. The draft regulations do not address this issue and should be amended to reflect a selected preference for fluid modeling in certain situations. The Agency already has in place guidelines for good engineering practices in the application of fluid modeling, and these should be referenced and cited as an acceptable (or preferred) alternative to mathematical modeling.(1,2,8.9)

#### 6.1.2 Recommendations

- a. Replace so-called 'dispersion coefficients' in the context presently used with the term 'dilution factor' and clarify related ambiguities.
- b. Present a sensitivity analysis that illustrates the relative impact on dilution factors of: stack height and ambient meteorology.
- c. Develop guidelines for acceptable representative meteorological site data.

- d. Identify and support the role of fluid modeling for site-specific assessments involving low stacks and/or tall buildings.

## 6.2 Selection of CO and THC Levels

EPA's proposed strategy for reducing the risk from emission of PICs is to stop all hazardous waste feeds when the allowed CO limit is exceeded. The incinerator operator is encouraged to set an alarm level at a lower level at which corrective action would be initiated with the aim of avoiding waste feed cutoff. Such an alarm level will reduce frequent transient startups and shutdowns which could become the source of increased emission of PICs. The proposed CO and THC regulatory limits should be set at concentrations that provide enough margins above the background levels to provide the incinerator operator sufficient leeway to take corrective action. The CO and THC regulatory limits are for measurements corrected to 7 percent oxygen. In cases in which oxygen is added after the combustion chamber, incinerators operating at higher flue gas oxygen levels will have lower actual or "uncorrected" CO and THC concentration readings because of dilution. Those incinerators which operate at high oxygen levels normally are burning high BTU waste and require extra air as a heat sink. Flame temperatures will be high. Some carbon monoxide may come from dissociation of carbon dioxide as discussed below and the carbon monoxide level may be relatively high. THC will be lower due to better air/fuel mixing. In this case, excess air is not a dilution air, but combustion air. OSW has taken this into account by proposing a CO waiver if THC is less than 20 ppm.

The Subcommittee was provided with data (summarized in Table II) from research tests on nine industrial hazardous waste incinerators.(4) These show that six of the units meet the proposed standards for CO and THC by a wide margin.

The results of tests on such incinerators are not necessarily representative of those on other combustion devices. Two examples where the CO and THC concentrations may not be related to the efficiency of combustion were brought up during the Subcommittee's deliberations. Cement kilns involve the countercurrent flow of limestone and the combustion products. In calcining limestones with a high organic content, CO and THC may be produced during the heat up of the limestone and will yield high exit concentrations unrelated to the efficiency of the combustion process.

SITE ID	RUN NO.	O <sub>2</sub> (PERCENT)	AVERAGE CO (ppm DRY)* (AS MEASURED) (ppm 7% O <sub>2</sub> )		AVERAGE THC (ppm DRY)* (AS MEASURED) (ppm 7% O <sub>2</sub> )		HIGHEST RECORDED VALUES (ppm DRY @ 7% O <sub>2</sub> ) CO THC	
			(AS MEASURED)	(ppm 7% O <sub>2</sub> )	(AS MEASURED)	(ppm 7% O <sub>2</sub> )	CO	THC
Mitchell	1	9.4	1.4	1.7	< 1	1.2	6.1	1.3
	2	10.5	1.8	2.4	< 1	1.3	4.1	1.4
	3	9.9	< 1	1.2	0.6	0.7	16.3	2.3
	Average	9.9	1.4	1.8	0.9	1.1	-	-
DuPont	1	9.2	666	790	75.9	90.1	1,364.4	166.1
	2	9.6	422	518	47.6	58.5	1,854.4	105.4
	3	10.3	624	816	58.1	76.0	1,975.7	112.9
	Average	9.7	571	708	60.5	74.8	-	-
TWI	1	12.4	4.3	7.0	2.5	4.1	107.9	4.7
	2	13.0	0.9	1.6	1.9	3.3	24.2	3.7
	3	13.2	1.2	2.2	1.7	3.1	4.1	3.9
	4	15.6	0.6	1.6	0.8	2.1	5.2	5.4
	Average	13.6	1.8	3.1	1.7	3.1	-	-
DOW	1	10.1	1	1.3	2.5	3.3	110.5	11.6
	2	11.1	NA	NA	2.3	3.2	-	11.2
	3	11.5	1	1.5	2.1	3.0	3.7	14.7
	4	11.2	10	14	2.9	4.2	1,028.6	230.0
	Average	11.0	4.0	5.6	2.5	3.4	-	-

Sources: MRI "Performance Evaluation of Full-Scale Hazardous Waste Incinerators. Volume 2. Incinerators Performance Results," EPA-600/2-84-181b, PB85-129518, Nov. 1984.

MRI "Total Mass Emissions from a Hazardous Waste Incinerator," MRI Project No. 8671-L(1), May 1987.

- \* All THC data are measured propane with the exception of DOW Site where THC was measured as methane. Heated extraction system and heated THC monitor was used. The THC data for this Site was converted to propane using the following equation:

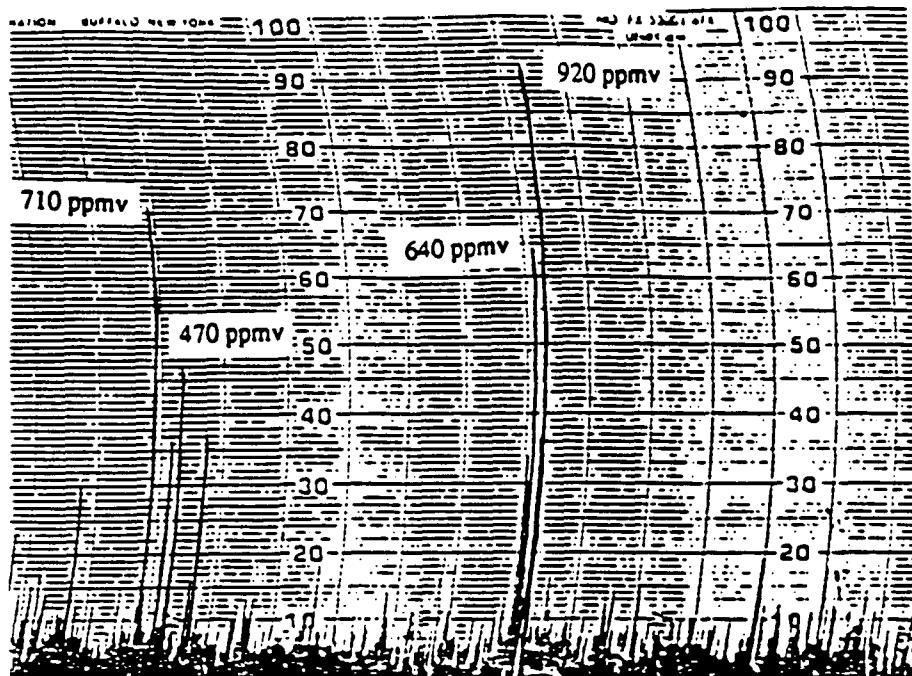
$$\text{THC (propane)} = \text{THC (methane)}/3 \text{ (to account for the FID response factor)}$$

TABLE II- Incinerator CO/THC Data from Research Tests

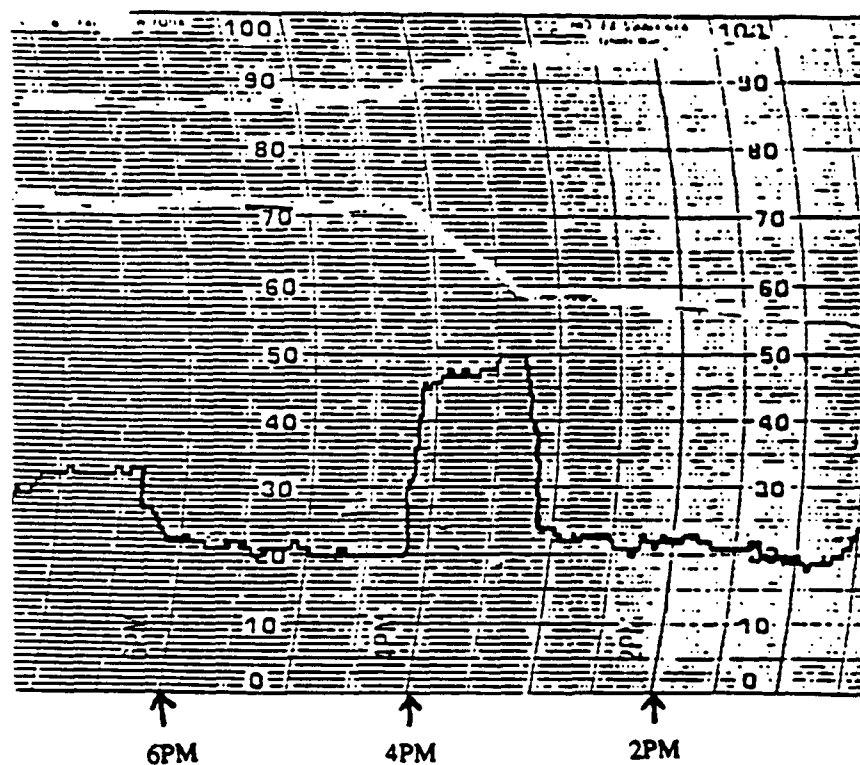
SITE ID	RUN NO.	O <sub>2</sub> (PERCENT)	AVERAGE CO (ppm DRY)*		AVERAGE THC (ppm DRY)*		HIGHEST RECORDED VALUES (ppm DRY @ 7%O <sub>2</sub> )	
			(AS MEASURED)	(@ 7% O <sub>2</sub> )	(AS MEASURED)	(@ 7% O <sub>2</sub> )	CO	THC
Plant B	1	11.8	14.8	22.5	< 1	1.5	34.2	1.5
	2	10.3	< 1.0	1.3	< 1	1.3	1.3	1.3
	3	10.7	6.9	9.4	< 1	1.4	14.5	2.6
	4	14.3	7.2	15.0	< 1	2.1	17.6	2.3
	5	10.1	4,300	5,523	341	438	6,935.8	671.7
	Average	11.4	866	1,114	69	89	-	-
Ross	1	10.4	4.8	6.3	< 1	1.3	9.8	1.3
	2	10.8	9.1	12.5	0.9	1.2	21.3	3.2
	3	10.7	4.7	6.4	1.0	1.4	11.8	3.1
	Average	10.6	6.2	8.4	1.0	1.3	-	-
Up John	1	8.1	10.5	11.4	8.9	9.6	7.3	7.9
	2	8.3	11.2	12.3	6.0	6.6	7.6	6.0
	3	8.4	9.9	11.0	3.9	4.3	6.7	4.1
	Average	8.3	10.5	11.6	6.3	6.9	-	-
Zapata	1	8.2	1,275	1,394	71.0	77.7	1,717.2	235.2
	2	12.0	22.2	34.5	1.9	3.0	612.9	63.6
	3	11.8	7.5	11.4	< 1	1.5	13.4	1.5
	4	11.9	8.8	13.5	< 1	1.5	28.2	4.5
	Average	11.0	328.4	363.5	18.7	20.9	-	-
A. Cyanamid	1	10.3	6.7	8.8	< 1	1.3	40.2	2.1
	2	12.4	19.3	31.4	< 1	1.6	60.7	4.2
	3	-	-	-	-	-	-	-
	4	12.7	13.8	23.3	< 1	1.7	43.0	1.7
	5	13.0	14.3	25.0	< 1	1.8	45.0	1.9
	Average	12.1	13.5	22.1	1.0	1.6	-	-

TABLE II- Incinerator CO/THC Data from Research Tests (Continued)

IN-SITU ACTUAL FLUE GAS CO  
MONITORING DATA (Scale  $\times 10$  ppmv)



UNCORRECTED ROLLING HOUR AVERAGE  
CO MONITORING DATA (ppmv)



100 PPM CUTOFF POINT AFTER CORRECTION  
FOR MOISTURE AND OXYGEN.

← TIME OF THE DAY

FIGURE D - In-Situ CO Monitoring Data and Rolling Hour Average Data  
Uncorrected for Moisture and Oxygen at a Multipurpose Rotary  
Kiln Incinerator (Plant A)

Another situation that may lead to high CO concentrations that are not representative of poor combustion is that in which the products of combustion are rapidly cooled. CO is produced in combustion chambers operated at high temperatures by the dissociation of CO<sub>2</sub>. When the combustion products are rapidly quenched, the high CO concentrations inevitably present in a well-operated high temperature combustor will persist. This source of CO will not correlate with emission of PICs, but THC will be less than 20 ppm if combustion is efficient.

The Subcommittee suggests that the facilities be encouraged to set an alarm level which helps an individual facility improve its operations. Alarm levels for CO and THC should be designed to provide enough margin above background concentrations but below shutoff values to provide the incinerator operator sufficient leeway to take corrective measures. The individual operator can best determine how much lead time is needed to take corrective measures. For liquid injection incinerators, the lead time could be very short, while for rotary kiln incinerators, it could be very long. Further the Subcommittee does not think it is appropriate to, in effect, raise the CO limit by providing for a phase down period. The intention is to reduce the number of automatic waste feed cutoffs which could potentially increase emission of PICs due to frequent shutdowns and restarts.

### 6.3 Choice of Averaging Method

The Subcommittee believes that there is a need to justify the particular selection of the proposed averaging technique. Although OSW proposes use of a one-hour rolling arithmetic average, OSW presented no statistical analysis of CO monitoring data from well-operated incinerators to evaluate the impact of the proposed regulation on incinerators operating under realistic conditions.

The Subcommittee has obtained access to data from four plants which are discussed in some detail in Appendix A in order to elaborate on the issues that need to be addressed when selecting an averaging method.

The Subcommittee believes that the selection of levels of CO and THC and averaging procedures in the short term will involve a certain element of judgment. It could be argued that an arithmetic mean is preferable for the following reasons. The geometric mean is substantially lower (by a factor of three) than the arithmetic mean with CO and THC levels are relatively steady. The SAB does not believe that these lower values should be considered for conformance with the limits because: (1) CO and THC are indicators of combustion efficiency, a parameter which is based on an instantaneous measure of CO; (2) EPA is allowing for inevitable spikes in the CO/THC levels that occur even when facilities are well designed and operated by allowing the CO/THC levels to be averaged; (3) the flexibility provided by the arithmetic average

is sufficient to enable the vast majority of incinerators to routinely meet the recommended Tier I CO limit; and (4) for facilities that cannot easily meet the 100ppmv CO limit, EPA is providing a waiver that would allow higher CO levels provided that the THC levels do not exceed an hourly rolling average of 20 ppmv, a THC level that the vast majority (perhaps all) of the well designed and well operated incinerators meet. It should, therefore, be recognized that the values may need to be revised in the future as new information becomes available.

#### 6.4 Alternative Approaches

EPA's proposed approach to controlling emission of PICs is to stop all hazardous waste feeds when the allowed CO concentration is exceeded, without considering whether the shutdown will actually increase emission of PICs. Three major conditions may result in high emission of PICs at properly designed incinerators. These conditions are inadequate oxygen or too much fuel, too high instantaneous thermal load for batch feed, and too low a temperature in the incinerator. Parameters other than CO and THC concentrations can be used for making control decisions and actions other than automatic shutdown can be used to control emission of PICs.

##### 6.4.1 Alternative Measures of Performance

While CO monitoring data provide a very good indicator for combustion performance, CO alone may not be appropriate for combustion control. Oxygen monitoring should be considered for all hazardous waste incinerator operations because oxygen monitoring provides much better guidance to the operator when the fuel feed rate is getting too high or the air supply rate is getting too low.

For incinerators with batch feed, there is a special CO spike problem. As long as there is some oxygen available (1-3%), little emission of PICs occurs. However, if oxygen is completely depleted, high emission of PICs is possible.

Besides oxygen control, possible alternates include combustion chamber temperature or the rate of change of combustion chamber temperature. A high temperature or high rate of increase usually indicates that the waste feed rate is getting too high. A low temperature or fast decrease in temperature usually indicates that the waste feed is getting too low or the waste feed does not have enough heating value.

While these alternative measures of performance are useful to operators and such monitoring could be required, because of the complexity of incinerator operations, particular concentrations, temperatures, or rates of change should not be made permit conditions.

#### 6.4.2 Alternative Actions

Once an "upset" condition has been identified, it is desirable to correct the situation without causing increased emission of PICs. With an automatic shutdown strategy, the change in fuel property or quality (from hazardous waste to supplementary fuel), the change in fuel quantity, and the restart of hazardous waste feeds all have the potential to upset operations and increase emission of PICs.

Therefore, the Subcommittee proposes use of a corrective action approach as the first response to high CO and THC followed by a facility before considering an automatic waste feed shutoff. For example, a staged reduction in waste feed or other operational controls (such as readjusting combustion air or increasing turbulence) seem more appropriate in reducing emission of PICs than a shutdown. It is probably not possible to specify corrective action (or "alarm") concentrations except on a facility specific basis. While the practice of corrective action could be required based on generally applicable criteria, the concentrations are best developed at the facility.

For example, high CO spikes due to momentary depletion of oxygen can occur for certain types of waste material. From trial burn tests and past operating experience, the operator should have a pretty good idea on the limitation of batch feed size. However, flame combustion of solid waste is an extremely complex process and there is always the possibility that a certain material performs differently in the combustion chamber. Those CO spikes can be identified from the oxygen monitoring data. Since there is a time lag between the waste feed and the time that the CO analyzer recorded a super-high CO spike, or the oxygen analyzer recorded a zero oxygen period, the automatic cutoff of all waste feeds will not solve the problem but may create more problems. If the CO spike causes the hourly rolling CO level to approach the permitted level, a 20% (or other appropriate number), cutback of waste feeds as discussed previously may avoid an exceedence and the problems that an automatic waste shutoff can cause without further upsetting the operation.

#### 6.5 Research Needs

One long-term research need, which hazardous waste incineration has in common with other combustion systems, is for the development of continuous fast-response monitors. Additional research questions are: (a) how to develop reliable continuous monitors, (b) how to convert measurements made by the monitors to indicators of risk, and (c) how to correct operations of a unit when emissions approach unacceptable levels.



Short-term continuous monitoring research needs to include better definition of the limits of existing monitors for CO, O<sub>2</sub>, and "total hydrocarbons." In addition, considerable research is needed on: (a) developing flue gas conditioning systems for THC monitors that would preclude the plugging up of sample extraction lines and also provide a reasonably accurate measure of mass emission rates, and (b) on developing procedures for quality control and quality assurance (QC/QA) of monitors during extended operations.

Longer-term research should be undertaken to evaluate or develop alternate monitoring methods for initial use as research tools, and eventually for more routine monitoring or audit purposes. A number of promising techniques already exist, but have had little or no practical application to combustion sources. A few examples of devices with high potential for application are Fourier Transform infrared spectroscopy (FTIR), photoionization detectors, molecular beam mass spectroscopy, laser spectroscopy of several kinds including absorption, fluorescence, laser activated infrared spectroscopy and Raman spectroscopy.

FTIR has the potential to monitor approximately twenty-two flue gas components simultaneously including carbon monoxide, water, hydrochloric acid, and sulfur dioxide many individual organic compounds, and a measure of "total organics." A laser fluorescence monitor for PAHs has been demonstrated in research. With some additional modification and further testing, development, and simplification of these systems might then be ready for use in industrial application.

The current cost of some of these devices is relatively high, but this could be reduced dramatically with further research. The potential returns on such research are very high. A continuing program to evaluate the most promising monitoring techniques and to adapt them for application to a variety of combustion sources would strengthen the ability to control pollution from these sources.

Since only a small fraction of the total number of compounds produced during upset conditions can be monitored, there is a need to relate the simple measures of emissions produced by a CO, THC, or other detection surrogates to risk. Emission of PICs from incinerators are a potential problem that forms part of the broader problem of organic emissions from combustors. Comparative emissions and risk assessments of different combustion categories would be desirable in order to assign priorities for risk reduction measures.

The presence of spikes of CO during operation of rotary kilns raises the question on the best averaging method for emissions. There is insufficient data on whether any PICs are emitted with the episodic CO emissions and if these emissions are at levels of

concern. A lack of correlation of PICs with CO during the spikes could favor a geometric averaging, but more data are needed to provide an evaluation of the problem.

The current incinerator permitting process is costly and time consuming. A better understanding of the relationship of operating parameters to emissions is needed in order to judiciously select the parameters to control and to establish their limits. A goal would be to use continuous monitors such as oxygen and temperature to provide an early warning of equipment malfunction to provide the operator with time to take corrective actions.

## 7. CONCLUSIONS AND RECOMMENDATIONS

### 7.1 Conclusions

The Products of Incomplete Combustion (PICs) Subcommittee of the EPA's Science Advisory Board reviewed the Office of Solid Waste's (OSW) proposal to control emissions of PICs from hazardous waste incinerators by instituting process controls based on CO and THC emission concentrations. Because compounds known to cause adverse human health effects have been detected at very low concentrations in PICs, it is prudent to take precautionary measures to control PICs. However, the linkages between emission concentration, exposure, and effects (health and environmental) were not documented.

The proposal for controls was made even though OSW has not established that emission of PICs from hazardous waste incinerators currently pose a substantial risk. EPA's risk assessments indicate that emission of PICs at currently measured levels are not likely to produce significant human health effects. However, since the current DRE standard applies only to designated POHCs, a 4-nines (99.99%) DRE does not preclude the possibility that emission of PICS could present significant human health risk.

Overall, the concept of using CO and THC for the purpose of regulating PICs is reasonable. However, EPA has not convincingly documented the superiority of the selected averaging period, the concentrations chosen for the CO and THC standard, and has not evaluated emissions problems associated with unnecessary automatic shutdowns. Other values or approaches may be better. Individual conclusions, referenced to the relevant sections of this report appear below.

1. PICs, including compounds known to have adverse effects on human health, have been detected at concentrations in the ppbv and pptv range in the emissions of hazardous waste incinerators, boilers, industrial furnaces and other combustion sources. (Section 5.1)
2. Carbon monoxide (CO) is a good, but conservative indicator of combustion performance. Poor combustion conditions are always indicated by high CO levels. A high CO concentration may not indicate poor combustion conditions. (Section 3.1)
3. CO does not correlate with THC when CO exceeds 100 ppm. In addition, THC concentrations measured during the trial burn cannot be assumed to be representative of routine THC emissions even if CO concentration remains unchanged. (Section 3.2)

4. Even frequent routine stack testing for THC may not be adequate to provide a basis for assessing compliance with THC limits. (Section 3.2)
5. Continuous emissions monitoring (CEM) of THC is desirable because of the limitations of CO as a surrogate for THC. (Section 3.2 and 4.3)
6. While there are data relating CO and THC emissions at low CO concentrations sufficient to support the concept of limiting CO to ensure high combustion efficiency and reduced total organic emissions, the existing data base is not sufficient for assessing emission concentrations for potential PICs. (Section 3.4)
7. Although the commercially available flame ionization detector (FID) responds to those classes of organic chemicals most abundant as PICs in hazardous waste combustion emissions, the magnitude of the FID response varies with the composition of the organic material present. While the FID response could provide an approximation of the PICs concentration good enough to serve as an indicator of good combustion control, it is not appropriate as the basis for a health risk estimate. (Section 4.1)
8. In principle, a hot transfer line is better than a cold one. However, the 150°C transfer line proposed by EPA has not been validated for reliability and maintenance problems. Anecdotal evidence was presented that THC systems can present reliability difficulties even during trial burns. (Section 4.2)
9. A recent survey was presented to indicate hydrocarbons in hazardous waste emissions are being monitored on a continuous basis during routine operations in several facilities for periods ranging from 1 to 7 years using unheated FID systems. A cold THC system may be more practical to serve as a combustion performance indicator. A hot THC system would detect a larger fraction of the THC if operability and maintenance problems could be overcome. (Section 4.3 and 4.4)
10. Use of a "cold" or "conditioned gas" FID as a continuous THC monitor will, however, require routine maintenance and rigorous attention to QA/QC protocols, and the careful training of skilled operators. (Section 4.3)
11. Despite the limitations of the data and the uncertainties introduced by the assumptions, the risk assessment methodology is sufficient to provide a risk-based check on the proposed THC emissions limit. (Section 5.3.1)

12. Although the toxicity of the total THC mixture cannot be assessed, the measured THC emissions of 20 ppmv are likely to present carcinogenic risks below the suggested limit of 1 in 100,000 in most cases. Thus, EPA's evaluation of the emissions limit provides evidence of adequate safety.
13. The approach to dispersion modeling employed by the Office of Solid Waste in the evaluation of exposure and the risk assessment associated with hazardous waste incinerators is reasonable and appropriate. (Section 6.1.1)
14. Sensitivity analyses of the relative impact of stack height and ambient meteorology on dilution factors would be helpful to applicants and regulators. (Section 6.1.1.3)
15. In cases where stack heights are low relative to the height of nearby buildings or where the fetch to nearby buildings is small, fluid modeling in a boundary-layer wind tunnel may be preferable to mathematical dispersion modeling. (Section 6.1.1.5)
16. While CO monitoring data provide a good indicator of combustion performance, CO alone may not be sufficient for combustion control purposes. Oxygen monitoring data provides better guidance to the operator. (Section 6.2)
17. Other controls, related to change in temperature, can be used as alternatives to oxygen control. (Section 6.2)
18. Sudden changes in fuel feeds can cause upsets to incinerator operation. Such upsets may produce increased emissions of PICs. (Section 6.2)
19. The most likely cause for continuous high CO concentrations in a large-scale incinerator with multiple feeds is that the total waste feed is too high; the same is generally true for small liquid injection type incinerators. Low incinerator operating temperature may also cause high CO. (Section 6.2)
20. Unnecessary shutdown of the waste feed to incinerators may be counterproductive to control of PICs in some cases and should be discouraged. Alternate approaches, including taking corrective measures to avoid an automatic wastefeed cutoff or phased shutdown, may be more effective. Facility operators should be encouraged to set an alarm level to alert of impending waste feed cutoffs and take remedial measures to avoid them.
21. A major research need which hazardous waste incineration shares with other combustion systems, is for the development of continuous fast-response monitors that could be used for feedback control. (Section 6.3)

22. Combustion devices differ and the differences between devices, such as those between cement kilns and hazardous waste incinerators, need to be accounted for in developing a strategy for controlling PICs. (Section 3.3.3)
23. The risk assessment methodology should not be applied to specific sites as proposed under Tier II by using THC data obtained during trial burn tests only because of the lack of assurance that THC will remain low during routine operations if carbon monoxide alone is continuously monitored. Routine monitoring of THC is necessary. (Section 5.2)

## 7.2 Recommendations

1. EPA should conduct more studies to better define whether or not a problem exists with the emission of PICs, the source(s) of the problem if it exists, and how to minimize the problem.
2. To assure that THC remains low even when CO is high, the Tier II approach should require CEM of THC. This is necessary because CO concentration does not correlate with THC concentrations when CO exceeds 100 ppm. Therefore, even if a CO limit is set and monitored for, the THC concentrations measured during the trial burn cannot be assumed to be representative of routine THC emissions. (Section 3.2)
3. EPA should develop and validate a heated sampling system. Until such a line is validated, the continued use of a cold transfer line may be appropriate because the cold transfer line has been shown to operate successfully under the temperature and operating conditions expected. (Section 4.2)
4. EPA should investigate and document the magnitude of effects such as rate of condensation, build-up of non-volatile organics, flue gas moisture effects, and effects of particulate matter on the medium- to long-term performance of the monitoring system. The selection of appropriate calibration compounds and determination of precision and accuracy data over various time periods and concentrations is also a subject for further investigation. (Section 4.4)
5. EPA should revise its discussion of dispersion modeling to employ standard terminology. (Section 6.1.1.2)
6. EPA should include sensitivity analyses in the supporting documentation for the regulation. (Section 6.1.1.3)
7. EPA should expand on the data needs enumerated in Part Four of its document to include more information on terrain. (4) (Section 6.1.1.3)

8. Fluid modeling in a boundary-layer wind tunnel should be considered where stack heights are small relative to the height of nearby buildings or where the fetch to nearby buildings is small. In such cases, mathematical dispersion modeling may not be the preferred simulation methodology. (Section 6.1.1.5)
9. An oxygen concentration limit should not be used as a permit condition although it provides useful guidance to operators for decisions on corrective actions. Controls related to temperature may be considered as alternatives to provide information for corrective action. (Section 6.2.1)
10. A corrective action system should be considered as a first response to CO/THC concentrations that approach permit limits in order to avoid unnecessary automatic waste cutoffs because sudden changes in fuel feeds may create major upsets in incinerator operations which may lead to the release of more PICs to the environment than are associated with a CO spike. Nonetheless, an automatic waste shutoff should be triggered when CO and THC levels reach the permit limit. (Section 6.2)
11. EPA should conduct research on how to develop reliable THC continuous monitors, how to convert measurements made by the monitors to indications of risk, and how to correct operations of a unit when emissions approach unacceptable levels. (Section 6.3)

## APPENDIX A

### A Discussion of Averaging as it Applies to Emissions Data Controls

One problem results from occasional momentary high CO spikes which may give one-hour rolling average CO values above the current proposed CO standard. If the CO remains higher than normal for a prolonged period of time, it is likely that there is a combustion problem and the waste feeds should be shutoff to inspect the problem. The current proposed standards adequately address this concern. However, since CO is a conservative indicator for combustion performance, CO spikes will be observed during the normal incinerator operation. Any disturbance in the flame zone may produce a CO spike which can be large or small. The CO spike data will form a skewed (lognormal) distribution with most of the data being very low (around 20-30 ppmv), but some of the spike values will be very large (higher than 1,000 ppmv). Depending on the cause, those spikes may last from only a few seconds to one or two minutes in the combustion chamber, but will show up as a wider peak at an extractive CO monitor due to the baffling and damping effect of the air pollution control equipment, the sampling line, and the flue gas sample conditioning system.

There are many reasons for the generation of such spikes. The major ones are:

- (a) the combined effect of a particular batch feed has too high a volatilization rate and too high heat content;
- (b) purging clean a plugged feed line;
- (c) loss of feed in one of the burners due to line plugging or failure in the flame management system and the associated safety shutdown;
- (d) switching feeds and the associated shutoff and startup; and
- (e) waste feed rate change due to control response or mechanical response.

The CO spikes generated are lognormally distributed. Based on some preliminary discussion with rotary kiln operators, the Subcommittee offers the following as a typical scenario. A 5,000 ppmv CO spike may occur once every few months. A 2,000 ppmv CO spike may occur a few times per week. A 500 ppmv CO spike may occur a few times per day. There will be times when CO spikes occur more or less frequently.

The impact of those CO spikes on the rolling hour average is shown in Figure A-1 for an in-situ mounted CO analyzer (Plant A).



Figure A-2 shows similar monitoring data for an extractive CO analyzer at a different facility (Plant B). As can be seen, those rare high CO spikes will cause incinerator operation to be shut down if the CO standard is not set properly. Such CO spikes cannot be entirely avoided, due to random statistical variation as the result of complexities of a multiple-purpose rotary kiln operation and high sensitivity of CO as a combustion performance indicator. During Plant A's RCRA trial burn compliance test, it was shown that as long as the flue gas oxygen level is higher than 1%, the CO spikes did not cause deterioration in destruction performance.

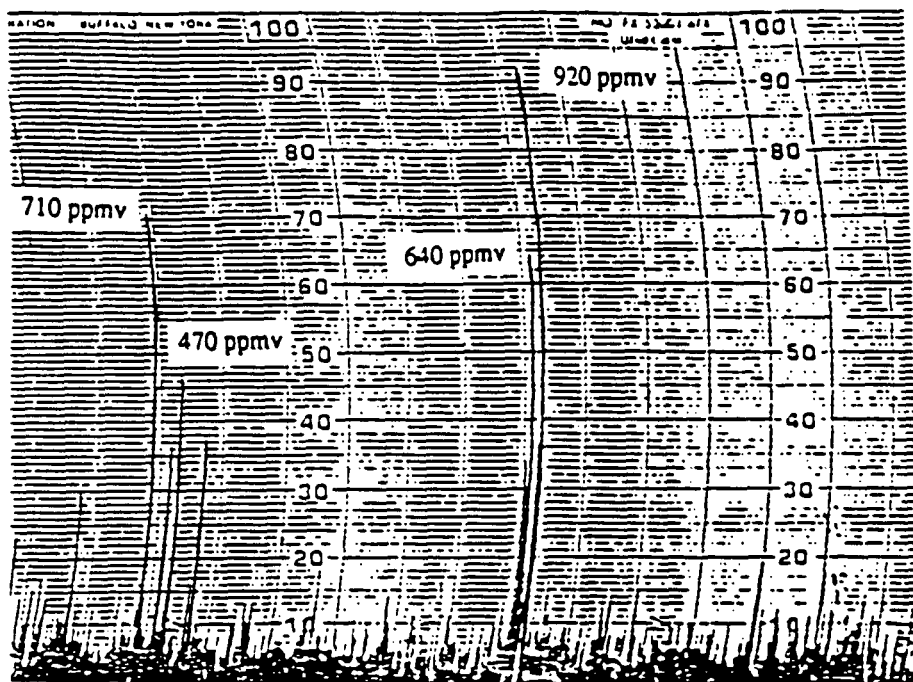
In Figure A-2, each temperature peak represents a batch feed. As can be seen, the majority of the batch feeds did not cause a high CO spike problem. Since the solids volatilization and the associated combustion phenomena are very complex, and due to the fact that CO is a very sensitive indicator, certain batch feeds will generate high CO spikes. The same situation applies to burner switchover; it may or may not generate high CO spikes.

During Plant B's RCRA trial burn compliance test, the batch feed rates were accelerated to produce as many high CO spikes as possible (over ten spikes higher than 2,000 ppmv uncorrected were produced). During the trial burn test, flue gas organics level was continuously monitored with a MS/MS (two Mass Spectroscopies in series for better compound speciation) mounted in a mobile van. There was no deterioration in destruction performance during those high CO spikes observed. However, there is insufficient data on other compounds to be confident that no other PICs were present.

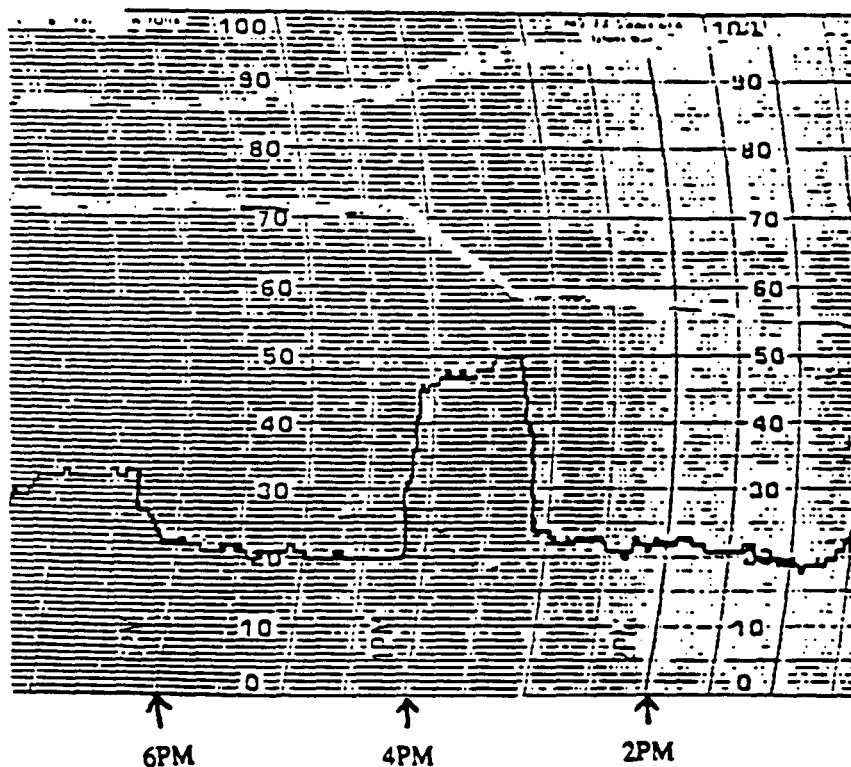
Figure A-3 shows a two-hour period, extractive CO monitoring data (adjusted from 13% to 7% oxygen) at a third plant (Plant C). Four methods to calculate the rolling average data were used and will be discussed. Figures A-4 and A-5 extended the data to a ten-hour period to show the long-term trend.

Figure A-4 shows extractive CO monitoring data (uncorrected) at a multiple-chamber incinerator with multiple feeds (Plant D). During one of Plant D's RCRA trial burn compliance tests, pint bottles of four different materials (solid, slurry, and two liquids) were burned. Forty pint bottles (ten of each material) were burned in controlled order (one bottle followed with another of different content) during each VOST sampling period. Figure A-6 shows data for three VOST sampling periods under the same operating conditions. The resulting measurements were different even though the content and operating conditions were the same. The highest CO spike observed was the result of emergency shutdown, since the facility was operated under a permit which allows a CO spike no higher than 150 ppm. The test results differed because each bottle had been subjected to a different flame condition and broke in a different manner. However, test data indicated no deterioration in destruction performance.

IN-SITU ACTUAL FLUE GAS CO  
MONITORING DATA (Scale x10 ppmv)



UNCORRECTED ROLLING HOUR AVERAGE  
CO MONITORING DATA (ppmv)



100 PPM CUTOFF POINT AFTER CORRECTION  
FOR MOISTURE AND OXYGEN.

← TIME OF THE DAY

Figure A-1 In-Situ CO Monitoring Data and Rolling Hour Average Data Uncorrected for Moisture and Oxygen in a Multipurpose Rotary Kiln Incinerator (Plant A)

EXTRACTIVE ACTUAL FLUE GAS CO MONITORING DATA (ppmv)

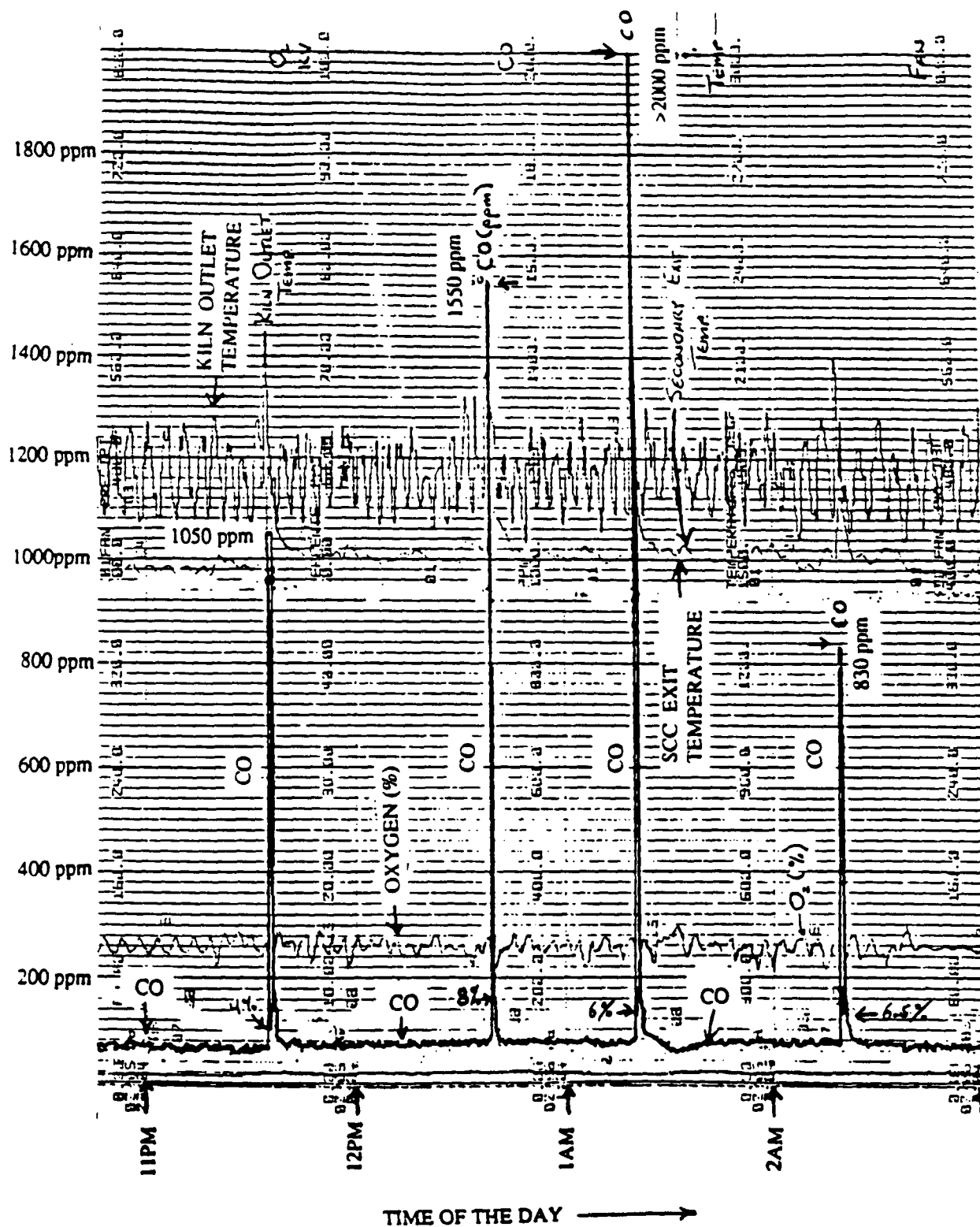


FIGURE A-2 Extractive CO Monitoring Data Uncorrected for Oxygen at a Multipurpose Rotary Kiln Incinerator (Plant B)

The Subcommittee recommends that EPA evaluate the impact of those occasional CO spikes which would occur in real-world incinerator operation. The Subcommittee also recommends that EPA evaluate the use of geometric average (GA) as an alternative to the arithmetic average (AA). If the intent of the regulation is to regulate the total amount of CO discharged at an incinerator, an arithmetic mean is more appropriate and will account for the total amount of CO discharged. Since the Subcommittee understands the intent of the regulation is to use CO as a surrogate combustion performance indicator, then a geometric mean may be more appropriate, because the CO data are lognormally distributed.

The relationship between the GA and AA can be expressed by the following equation:

$$GA = \frac{AA^2}{AA^2 + S^2}$$

where "S" is the standard deviation of the data points used to calculate AA and GA. Table A-I shows the ratio of GA to AA and its relationship with standard deviation, S, at three CO hourly rolling average levels observed in Figure A-3. The three levels were: AA at 32 ppmv between 0 to 20 minutes, AA at 112 ppmv between 20 to 50 minutes, and AA at 185 ppmv between 60 and 80 minutes.

During normal CO variation between 10 to 60 ppmv (as shown between 0 to 20 minutes in Figure F) the AA was 32 ppmv, the standard deviation(s) was about 10 ppmv, and the GA was 31 ppmv, which was almost the same as AA (GA/AA = 0.96). If the standard deviation increased to 20 ppmv, the CO spikes would have to vary, repeatedly, between approximately 10 to 100 ppmv. Even so, the ratio of GA/AA would be 0.87.

Between 20 to 50 minutes, the observed AA was 112 ppmv and GA was 39 ppmv, which was 35% of AA. This means the standard deviation of the data points had to be 300 ppmv. As shown in Figure F, the increase in AA was caused by only two large CO spikes. If the operation was seriously faulty, there would be repeated CO spikes and the standard deviation would be narrower. For example, if the CO spikes had varied repeatedly between 50 and 250 ppmv, the standard deviation would be about 50 ppmv. The observed GA would then be approximately 102 ppmv, which is 91% of the observed AA.

A-6

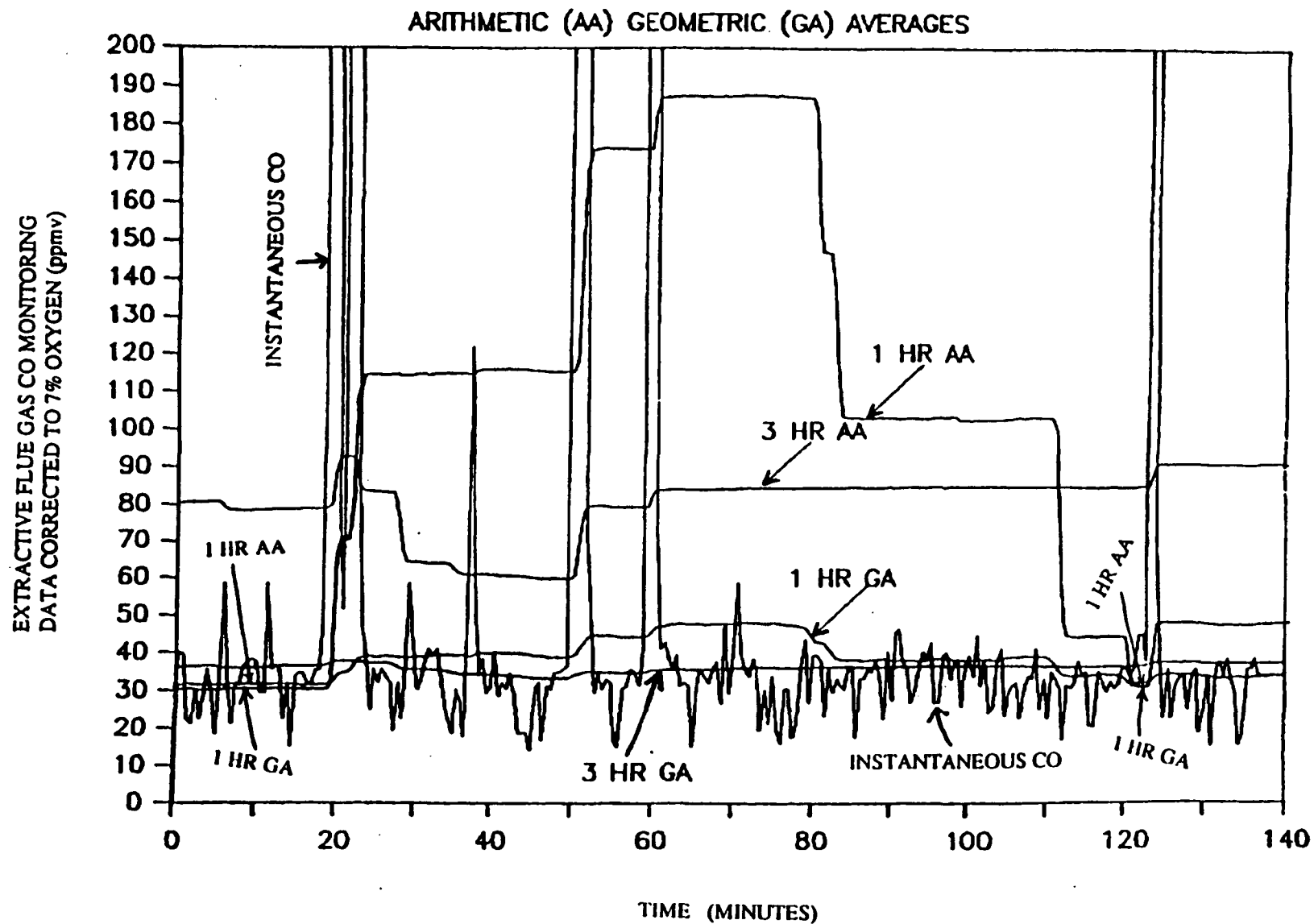


FIGURE A-3 Extractive CO Monitoring Data Corrected for Oxygen with  
Four Rolling Average Scenarios, for a Multipurpose  
Rotary Kiln Incinerator (Plant C)

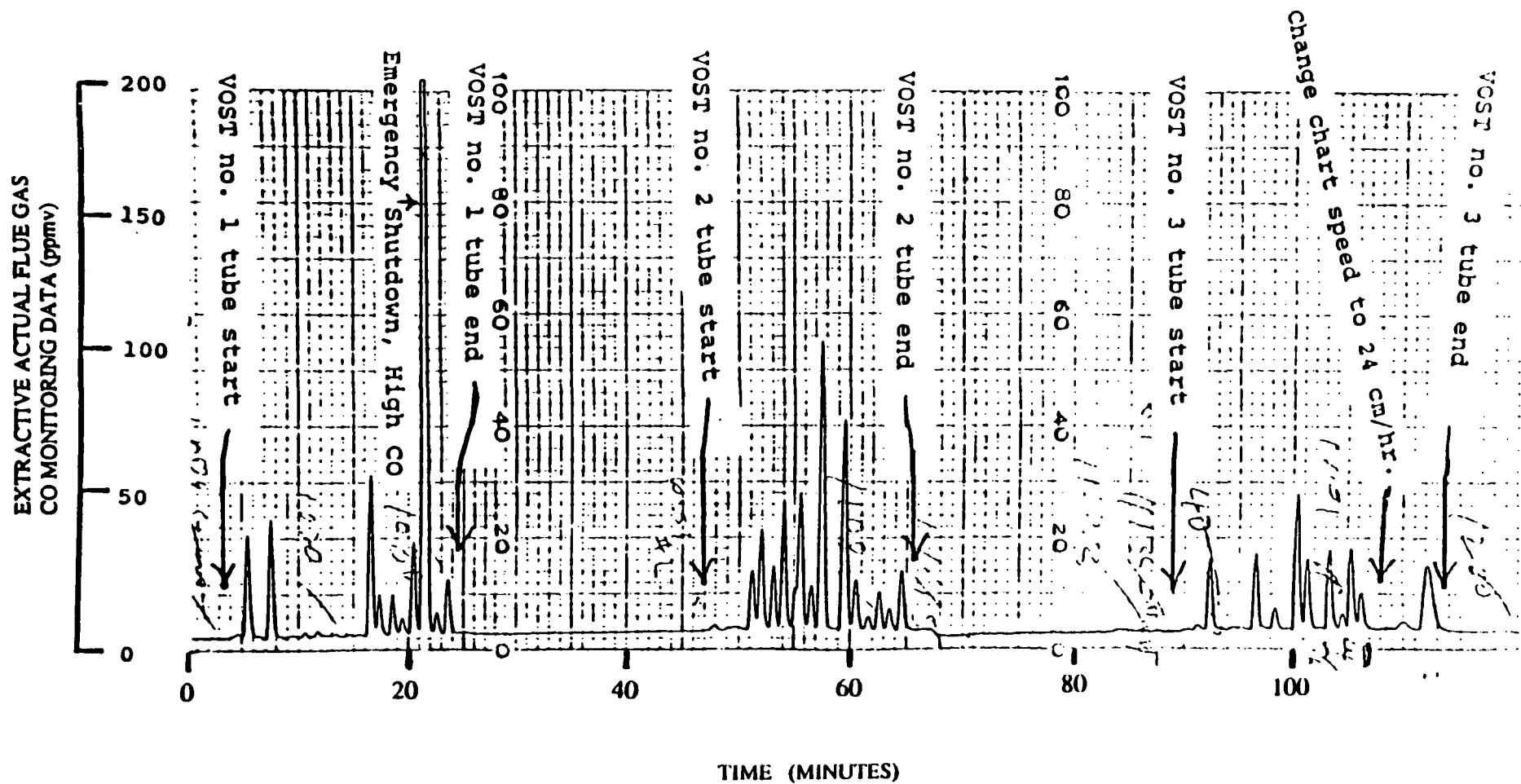


FIGURE A-4 Extractive CO Monitoring Data Uncorrected for Oxygen at a Multipurpose Multiple-Chamber Incinerator (Plant D)

Between 60 to 80 minutes, the observed AA was 185 ppmv and GA was 44 ppmv, which was 24% of the AA. This means the standard deviation of the data points had to be 750 ppmv. As shown in Figure A-3, the increase in AA was caused by the two additional large CO spikes. If the operation was seriously faulty, there would also be repeated CO spikes. For example, if the CO spikes had varied repeatedly between 30 to 500 ppmv, the standard deviation would be about 200 ppmv. The observed GA would then be approximately 125 ppmv which is 68% of the observed AA. The difference between GA and AA will be less if the standard deviation is smaller.

As shown in the above discussion, the geometric average removes the effect of a few very large values which will occur occasionally in incinerator operation. However, the difference between the geometric average and arithmetic average will be small, if the combustion conditions is seriously faulty as indicated by repeated CO spikes or continuous high CO levels.

EPA should also evaluate the averaging time, which will have major impacts as well. Figures A-5 and A-6 illustrated the impact of averaging time (one hour and three hours were used) to the arithmetic average and to the geometric average for operation at Plant C.

In Figure A-5, continuous CO values are plotted for a period of 600 minutes (10 hours). For the entire period, 97.3% of all values (adjusted to 7% oxygen) were less than 200 ppmv and 96.5% were less than 100 ppmv.

The one-hour and three-hour rolling geometric averages (1 hr GA, 3 hr GA) and arithmetic averages (1 hr AA, 3 hr AA) are plotted for the same 600 minute period in Figure A-6. During periods of relatively constant operation, the CO is more normally distributed and the AA and GA approach each other. Examples are shown at times 0-130, 200-240, and 340-400 minutes. Although the instantaneous CO value exceeded 100 ppmv less than 3.5% of the time, the one-hour AA appears to exceed 100 ppmv about 25% of the time. The arithmetic average, therefore, exaggerates relatively short events.

In summary, a good control strategy should not only address the limit, and averaging times, but also the frequency of both false positives (shutting down when the incinerator is operating correctly) and false negatives (operating the incinerator when it is running inefficiently). A problem is that too many false positives may result in higher overall emissions. As was discussed earlier, the CO level is a conservative indicator of combustion performance, so modifying the standard to reduce false positives might not increase the false negatives.

<u>AA = 32 ppmv</u>		<u>AA = 112 ppmv</u>		<u>AA = 195 ppmv</u>	
<u>S</u>	<u>GA/AA</u>	<u>S</u>	<u>GA/AA</u>	<u>S</u>	<u>GA/AA</u>
5	.99				
10	.95				
15	.91				
20	.85				
30	.73				
50	.54	50	.91	50	.96
		100	.74	100	.88
		150	.59	150	.78
		200	.48	200	.68
		250	.40	250	.60
		300	.34	300	.53
				500	.35
				700	.26
				750	.24
				800	.23

TABLE A-1 Relationship Between the Ratio of Geometric Average (GA) and Arithmetic Average (AA) and the Standard Deviation (S) at Three Observed CO Hourly AA Levels Shown in Figure F.



A-10

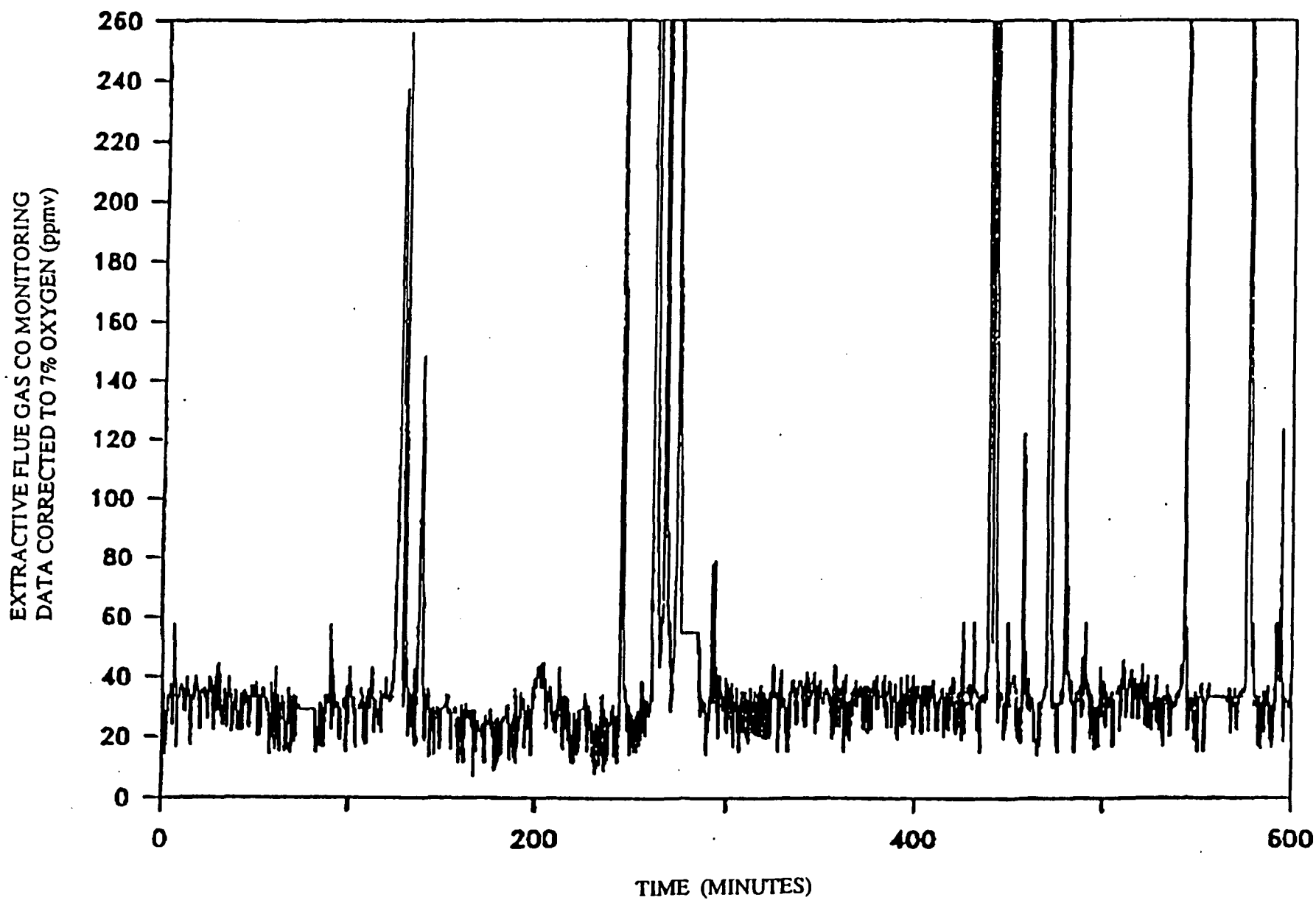


FIGURE A-5 Instantaneous CO monitoring data corrected for oxygen at a multipurpose rotary kiln incinerator (Plant C).

A-11

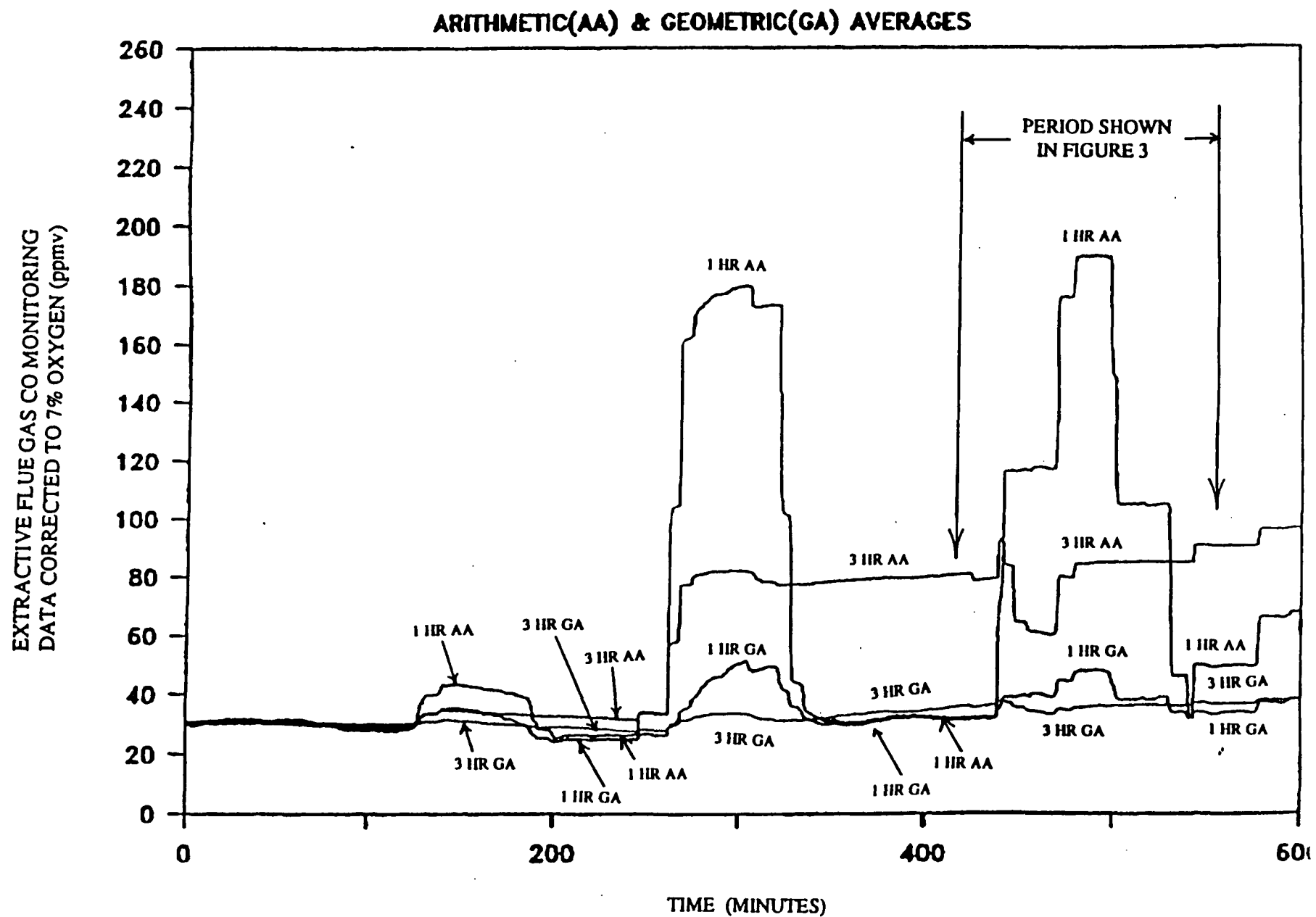


FIGURE A-6 Four rolling average scenarios for CO monitoring data shown in Figure 3A (Plant C).

# ENVIRONMENTAL DEFENSE FUND

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July 14, 1989

Kathleen White Conway  
Deputy Director, SAB  
1418 South Monroe Street  
Arlington, VA 22204

Dear Kathleen:

As I mentioned to you on the phone earlier today, I have looked in some detail at the derivation of the THC unit risk value used by EPA in its risk assessment for assessing the risk of PIC emissions from hazardous waste incinerators.

One of the assumptions used in the risk assessment that has been considered by both EPA and the PIC Subcommittee to be very conservative is the use of 95th-percentile emission levels for individual PIC compounds. I have examined this assumption more closely after noticing that EPA also used 95th-percentile values for non-carcinogenic C1 and C2 hydrocarbons. See Table 18 of the "Background Information Document for the Development of Regulations for PIC Emissions from Hazardous Waste Incinerators."

The raw C1 and C2 hydrocarbon emission data used by EPA were actually measured in fossil fuel burning devices, and are listed in Attachment 1. As you can see, the 95th percentile values used by EPA (17575 ng/L for C1 and 34200 ng/L for C2) are heavily influenced by the single high values measured in the wood boiler, test #1.

To test the actual conservatism of EPA's use of the 95th percentile values, I calculated the THC unit risk value that would be predicted using median (rather than 95th percentile) emission values for both individual carcinogenic PICs and C1 and C2 hydrocarbons. While my calculation did not include all of the carcinogenic compounds EPA included (see Table 14 of the Background Information Document), it included all of the compounds that contributed significantly to the calculated risk, the mass of PIC emissions, or both. The compounds I included account for 96% of the total THC risk and 98% of the total THC mass in EPA's calculation.

My analysis is shown in Attachment 2. It shows that use of median values predicts a THC unit risk value that is almost 90% of that predicted using the 95th percentile emission values.

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Conway  
July 14, 1989  
Page 2

In short, and perhaps contrary to intuition, EPA's assumption is not at all conservative. This is because EPA's use of 95th percentile values for C1 and C2 hydrocarbons (which do not contribute at all to risk) downwardly skews the weight fractions, and therefore the weighted unit risks, of the individual carcinogenic PIC compounds.

Given that this factor was assumed by the PIC Subcommittee to very significantly contribute to the overall conservatism of EPA's risk assessment, we may need to re-evaluate the language pertaining to this issue in our report.

Please feel free to call me if you have questions on this matter.

Sincerely,



Richard A. Denison, Ph.D.  
Senior Scientist

Attachments

cc: SAB PIC Subcommittee  
Jack Kooyoomjian  
Bob Holloway

# Attachment 1

C<sub>1</sub> AND C<sub>2</sub> CONCENTRATIONS BASED ON DATA IN TABLE 2

Case no. from Table 2	Feed type	Test	C <sub>1</sub> (ng/L)	C <sub>2</sub> (ng/L)
2	Wood	1	18,500	36,000
		2	2,500	5,000
3		Baseline	0	3,600
		Low NO <sub>x</sub>	0	2,800
4			200	0
5	Coal/water	1	3,500	10,500
		2	3,000	5,800
6	Coal/water/oil	1	0	900
		2	0	0
8	Coal	Dry bottom	2,330	0
		Wet bottom	3,330	630
		Cyclone	610	270
		Stoker	970	5,770
	Lignite	Dry bottom	2,570	810
		Cyclone	6,440	500
		Stoker	1,780	330
	Residual oil	Tangentially fired	1,450	260
		Wall fired	5,910	520
	Natural gas	Wall fired	330	330
10 <sup>a</sup>			929	0

<sup>a</sup> Data from "Total Mass Emissions from a Hazardous Waste Incinerator," Final Report, MRI Project No. 8671-L(1).

## Attachment 2

Recalculating risk using median instead of 95th percentile emission values

[The compounds listed below account for 96% of the risk, 98% of the total mass, and 90% of the non-C<sub>1</sub>/C<sub>2</sub> mass that were calculated using the 95th percentile emission values.]

	Median	Weight Fxn	Unit Risk	Weighted Unit Risk	% of Total Risk
Benzene	48	1.49e-02	7.10e-06	1.06e-07	1.30
Carbon Tetrachloride	5.1	1.58e-03	1.50e-05	2.37e-08	0.29
Chloroform	31	9.62e-03	2.30e-05	2.21e-07	2.72
Chloromethane	474.6	1.47e-01	3.30e-06	4.86e-07	5.98
1,2-Dichloroethane	4.8	1.49e-03	2.60e-05	3.87e-08	0.48
1,1-Dichloroethylene	2.6	8.07e-04	-3.30e-04	2.66e-07	3.28
Diethylstilbestrol	0.1	3.10e-05	1.40e-01	4.34e-06	53.44
Formaldehyde	398.5	1.24e-01	1.30e-05	1.61e-06	19.78
Hexachlorobenzene	2.3	7.14e-04	5.00e-06	3.57e-09	0.04
2,3,7,8-HxCDD	0.0000425	1.32e-08	2.00e+00	2.64e-08	0.32
Methylene Chloride	21	6.52e-03	4.20e-06	2.74e-08	0.34
2,3,7,8-PeCDD	0.0000053	1.64e-09	2.50e+01	4.11e-08	0.51
2,3,7,8-TCDF	0.0000190	5.90e-09	5.00e+00	2.95e-08	0.36
2,3,7,8-TCDD	0.0000425	1.32e-08	5.00e+01	6.59e-07	8.11
Other TCDDs	0.00029	9.00e-08	5.00e-01	4.50e-08	0.55
1,1,2,2-Tetrachloroethane	5.7	1.77e-03	5.90e-05	1.04e-07	1.28
Tetrachloroethylene	7.3	2.27e-03	4.80e-07	1.09e-09	0.01
1,1,2-Trichloroethane	15	4.66e-03	1.60e-05	7.45e-08	0.92
Trichloroethylene	6.2	1.92e-03	1.30e-06	2.50e-09	0.03
2,4,6-Trichlorophenol	8.3	2.58e-03	5.60e-06	1.44e-08	0.18
Vinyl Chloride	1.7	5.28e-04	5.00e-06	2.64e-09	0.03
C1 Hydrocarbons	1615	5.01e-01	--	--	--
C2 Hydrocarbons	575	1.78e-01	--	--	--
TOTAL	3222.2	1.000	.	8.13e-06	100

**CONCLUSION:** This risk level of 8.13e-06, calculated using median emission values, represents 88% of the risk calculated using 95th percentile emission values, demonstrating the lack of conservatism in use of the latter values.

As shown on the attached sheets, even if one eliminates diethylstilbestrol and/or formaldehyde -- the two compounds to which most of the risk is attributed -- from the risk calculation, the "median" THC risk value is still only slightly lower than the "95th percentile" risk THC value.

	Median	Weight Fxn	Unit Risk	Weighted Unit Risk	% of Total Risk
Benzene	48	1.49e-02	7.10e-06	1.06e-07	2.80
Carbon Tetrachloride	5.1	1.58e-03	1.50e-05	2.37e-08	0.63
Chloroform	31	9.62e-03	2.30e-05	2.21e-07	5.85
Chloromethane	474.6	1.47e-01	3.30e-06	4.86e-07	12.86
1,2-Dichloroethane	4.8	1.49e-03	2.60e-05	3.87e-08	1.02
1,1-Dichloroethylene	2.6	8.07e-04	3.30e-04	2.66e-07	7.04
Formaldehyde	398.5	1.24e-01	1.30e-05	1.61e-06	42.53
Hexachlorobenzene	2.3	7.14e-04	5.00e-06	3.57e-09	0.09
2,3,7,8-HxCDD	0.0000425	1.32e-08	2.00e+00	2.64e-08	0.70
Methylene Chloride	21	6.52e-03	4.20e-06	2.74e-08	0.72
2,3,7,8-PeCDD	0.0000053	1.64e-09	2.50e+01	4.11e-08	1.09
2,3,7,8-TCDF	0.0000190	5.90e-09	5.00e+00	2.95e-08	0.78
2,3,7,8-TCDD	0.0000425	1.32e-08	5.00e+01	6.60e-07	17.45
Other TCDDs	0.00029	9.00e-08	5.00e-01	4.50e-08	1.19
1,1,2,2-Tetrachloroethane	5.7	1.77e-03	5.90e-05	1.04e-07	2.76
Tetrachloroethylene	7.3	2.27e-03	4.80e-07	1.09e-09	0.03
1,1,2-Trichloroethane	15	4.66e-03	1.60e-05	7.45e-08	1.97
Trichloroethylene	6.2	1.92e-03	1.30e-06	2.50e-09	0.07
2,4,6-Trichlorophenol	8.3	2.58e-03	5.60e-06	1.44e-08	0.38
Vinyl Chloride	1.7	5.28e-04	5.00e-06	2.64e-09	0.07
C1 Hydrocarbons	1615	5.01e-01	--	--	--
C2 Hydrocarbons	575	1.78e-01	--	--	--
TOTAL	3222.1	1.000		3.78e-06	100

	Median	Weight Fxn	Unit Risk	Weighted Unit Risk	% of Total Risk
Benzene	48	1.70e-02	7.10e-06	1.21e-07	4.87
Carbon Tetrachloride	5.1	1.81e-03	1.50e-05	2.71e-08	1.09
Chloroform	31	1.10e-02	2.30e-05	2.53e-07	10.18
Chloromethane	474.6	1.68e-01	3.30e-06	5.55e-07	22.37
1,2-Dichloroethane	4.8	1.70e-03	2.60e-05	4.42e-08	1.78
1,1-Dichloroethylene	2.6	9.21e-04	3.30e-04	3.04e-07	12.25
Hexachlorobenzene	2.3	8.15e-04	5.00e-06	4.07e-09	0.16
2,3,7,8-HxCDD	0.0000425	1.51e-08	2.00e+00	3.01e-08	1.21
Methylene Chloride	21	7.44e-03	4.20e-06	3.12e-08	1.26
2,3,7,8-PeCDD	0.0000053	1.88e-09	2.50e+01	4.69e-08	1.89
2,3,7,8-TCDF	0.0000190	6.73e-09	5.00e+00	3.36e-08	1.36
2,3,7,8-TCDD	0.0000425	1.51e-08	5.00e+01	7.53e-07	30.35
Other TCDDs	0.00029	1.03e-07	5.00e-01	5.14e-08	2.07
1,1,2,2-Tetrachloroethane	5.7	2.02e-03	5.90e-05	1.19e-07	4.80
Tetrachloroethylene	7.3	2.59e-03	4.80e-07	1.24e-09	0.05
1,1,2-Trichloroethane	15	5.31e-03	1.60e-05	8.50e-08	3.43
Trichloroethylene	6.2	2.20e-03	1.30e-06	2.85e-09	0.12
2,4,6-Trichlorophenol	8.3	2.94e-03	5.60e-06	1.65e-08	0.66
Vinyl Chloride	1.7	6.02e-04	5.00e-06	3.01e-09	0.12
C1 Hydrocarbons	1615	5.72e-01	--	--	--
C2 Hydrocarbons	575	2.04e-01	--	--	--
TOTAL	2823.6	1.000		2.48e-06	100



## APPENDIX C

### Comments from Paul Diesler of the Executive Committee

1. If you have the upper 95% bounds of risk  $P_A$  and  $P_B$  at concentrations (or doses, exposures)  $C_A$  and  $C_B$ , this means that there is only one chance in twenty that the risks will, individually, equal or exceed the upper 95% bounds. If A and B occur together at  $C_A$  and  $C_B$ , the sum of the risks,  $P_{AB}=P_A+P_B$  is not at the 95% upper bound, but, rather at a higher percentile. In this case, if A and B act independently, the joint percentile is  $1-(1/20)(1/20)=1-0.0025=0.9975$ ; or 99.75%. (If A and B, and therefore  $P_A$  and  $P_B$ , are correlated in some way, constrained, etc... the calculation is less simple but the result is the same qualitatively. If instead of A and B one has A,B,C,D, etc.. the percentile becomes still greater. This is the situation when adding up the risks of many PICS in hazardous waste incinerator emissions.

2. To obtain an upper bound risk for a mixture of A,B,C, etc. at the 95% percentile (and so to be comparable to other risks at the same level of confidence) just calculate the expectations of mean risks,

$\bar{p} = \bar{p}_A + \bar{p}_B + \bar{p}_C$   
at  $C_A, C_B, C_C$ , etc...; the mean for the mixture is then

$$\bar{p} = \bar{p}_A + \bar{p}_B + \bar{p}_C + \text{etc.}$$

(at the low levels of risk involved, and assuming independence--no synergism, antagonism). Similarly the variance of the risk for the mixture can be obtained from the sum of the variances of the individual risks, from which the standard deviation (the square root of the variance) can be obtained. Given the mean and standard deviation of the mixture's risk, the upper 95% bond of risk for the mixture can be estimated--putting the estimate of the upper bound of risk for a mixture on the same basis as other such risk estimates. (Note: The regression or curve fitting method with which the upper 95% percentile risks are calculated should also estimate, if asked, the mean risks expected.)

### 3. Partial Reconstruction of the 95th Percentile Calculations

#### Case I: If all PICs were, in fact, combustion products

$S_m$  = sum of median concentrations of carcinogenic PICs

$S_{95}$  = sum of 95th percentile concentrations of carcinogenic PICs

$C_m$  = sum of median concentrations of C1 and C2

$C_{95}$  = sum of 95th percentile concentrations of C1 and C2

$\bar{r}_m$  = unit risk of the carcinogenic PICs in the median case

$\bar{r}_{95}$  = unit risk of the carcinogenic PICs in the 95th percentile case

Now:

$$A. \quad r_m = \frac{\bar{r}_m S_m}{S_m + C_m} = 8.13 \times 10^{-6}$$

$$B. \quad r_{95} = \frac{\bar{r}_{95} S_{95}}{S_{95} + C_{95}} = 9.23 \times 10^{-6}$$

$$C. \quad r_m = 0.88 r_{95}$$

where  $r_m$  and  $r_{95}$  are the weighted unit risks in the median and 95th percentile cases, respectively.

From A, B, and C:

$$0.88 = \frac{\bar{r}_m S_m (S_{95} + C_{95})}{\bar{r}_{95} S_{95} (S_m + C_m)}$$

Now:

$$C_m = 1,615 + 575 = 2,190$$

$$S_m + C_m = 3,222.2$$

$$\text{Therefore, } S_m = 1,032.2$$

$$\text{Also } C_{95} = 17,575 + 34,200 = 51,775$$

The C1 and C2 emissions are highly skewed to the right ( $C_{95} \gg C_m$ ). Suppose the other PICS are skewed and that  $S_{95} = m S_m$  (where  $m > 1$ ).

Question: could they be highly skewed?

Suppose the other (other than C1 and C2) PICS distributions are similarly shaped; then

$$\bar{r}_m \approx \bar{r}_{95} \text{ as a limit.}$$

Then:

$$0.88 \approx \frac{\bar{r}_m}{\bar{r}_{95}} \cdot \frac{\bar{s}_m}{m\bar{s}_m} \cdot \frac{mS_m + 51,775}{3222.2}$$

and, with  $S_m = 1032.2$ ,  $m \approx 29$

or, therefore, the other PICS are highly skewed, too, in Case I enough so that relative to the skewness of C1 and C2,  $S_m$  is only 88% of  $S_{95}$ .

If all the above is true (check the distributions), this result has nothing to do with the zero risk of C1 and C2 but only with the relative skewness of the distributions of C1, C2, and the carcinogenic PICS.

(Note: for various  $\bar{r}_{95}/\bar{r}_m > 1$ ,  $m$  is still large unless  $\bar{r}_{95}/\bar{r}_m$  is unbelievably large) -- Must check skewness of carcinogenic PICS (that is, actual ratio of  $S_{95}/S_m$ ).

#### Case II: Allow for effect on $r_{95}/r_m$ of diethylstilbesterol (DES)

At the median case, DES contributes more than 1/2 of total risk; same is true of  $r_m$  since C1 and C2 contribute no risk. Therefore at the 95th percentile case DES contributes very little to the average  $r_{95}$  because its concentration (0.1 nanogram/liter) does not change but that of the non-C1/C2 PICS rises. Thus, DES has the effect of decreasing average  $r_{95}/r_m$  compared to what it would be if DES concentrations behaved naturally. Skewness of the non-C1/C2 PICS still needs to be great to compensate here.

## Glossary of Terms

AA	- ARITHMETIC AVERAGE
ADI	- ALLOWABLE DAILY INTAKE
C	- MODELED ATMOSPHERIC CONCENTRATION
CE	- COMBUSTION EFFICIENCY
CEM	- CONTINUOUS EMISSIONS MONITORING/CONTINUOUS EMISSIONS MONITOR
CEMS	- CONTINUOUS EMISSION MONITORING SYSTEM
CO	- CARBON MONOXIDE
CO <sub>2</sub>	- CARBON DIOXIDE
DRE	- DESTRUCTION REMOVAL EFFICIENCY
EPA	- ENVIRONMENTAL PROTECTION AGENCY
FID	- FLAME IONIZATION DETECTOR
FTIR	- FOURIER TRANSFORM INFRARED SPECTROSCOPY
GA	- GEOMETRIC AVERAGE
GOP	- GOOD OPERATING PRACTICE
MEI	- MAXIMUM EXPOSED INDIVIDUAL
MWI	- MUNICIPAL WASTE INCINERATION
O <sub>2</sub>	- OXYGEN
ORD	- OFFICE OF RESEARCH AND DEVELOPMENT AT EPA
OSW	- OFFICE OF SOLID WASTE AT EPA
PAH	- POLYCYCLIC AND/OR POLYNUCLEAR AROMATIC HYDROCARBONS
PCDD	- POLYCHLORINATED DIBENZO-P-DIOXIN
PCDF	- POLYCHLORINATED DIBENZOFURAN
PCP	- PENTACHLOROPHENOL
PIC	- PRODUCTS OF INCOMPLETE COMBUSTION
PICS	- PRODUCTS OF INCOMPLETE COMBUSTION SUBCOMMITTEE OF THE EXECUTIVE COMMITTEE OF THE SAB
PNA	- POLYCYCLIC AND/OR POLYNUCLEAR AROMATICS
POHC	- PRINCIPAL ORGANIC HAZARDOUS CONSTITUENTS
POM	- POLYCYCLIC AND/OR POLYNUCLEAR ORGANIC MATTER
PPM	- PARTS-PER-MILLION (BY VOLUME OFTEN IMPLIED)
PPBV	- PARTS-PER-BILLION BY VOLUME
PPTV	- PARTS-PER-TRILLION BY VOLUME
Q	- STACK MASS EMISSION RATE
QC/QA	- QUALITY CONTROL AND QUALITY ASSURANCE
RAC	- REFERENCE AIR CONCENTRATION
RCRA	- RESOURCE CONSERVATION AND RECOVERY ACT
RfD	- REFERENCE DOSE
S	- STANDARD DEVIATION
SAB	- SCIENCE ADVISORY BOARD
TCDD	- 2,3,7,8, - TETRACHLORODIBENZO-P-DIOXIN
THC	- TOTAL HYDROCARBONS
TSDF	- HAZARDOUS WASTE TREATMENT, STORAGE AND DISPOSAL FACILITY
VOC	- VOLATILE ORGANIC COMPOUND
VOST	- VOLATILE ORGANICS SAMPLING TRAIN
Z <sub>1</sub>	- AERODYNAMIC ROUGHNESS

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