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Technical Issues Concerned With PCDD and PCDF Formation and Destruction in MSW Fired Incinerators

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U.S. DEPARTMENT OF COMMERCE, Malcolm Baldrige, ***Secretary***
NATIONAL BUREAU OF STANDARDS, Ernest Ambler, ***Director***

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1. EXECUTIVE SUMMARY

This report has been written in response to a series of questions dealing with the chemical and physical properties of polychlorodibenzo-p-dioxins (PCDDs) and polychlorodibenzofurans (PCDFs) and the possibility of their being emitted from municipal solid waste (MSW) fired incinerators. The questions taken as a whole ask if there is reason to expect that PCDD and PCDF emissions can be minimized when an MSW fired incinerator is properly operated. Answering the questions that have been posed shows that:

- In terms of their implications for proper incinerator operation, one must consider both possibilities that chlorinated precursor compounds are found in MSW and that chlorinated precursors are being formed from chlorination reactions that occur within the incinerator.

- No one has yet conclusivley shown by experiments or testing of pilot or full scale MSW fired incinerators that PCDDs and PCDFs will be formed in the post-flame combustion zone of an incinerator from surface reactions on fly ash particles. If such surface reactions occur:

    - Catalytic PCDD and PCDF formation may take place in the post-flame combustion zone of an incinerator at temperatures in the range of about 400°C up to temperatures at which thermal destruction of these compounds and their precursors occurs.

  - Combustion factors, e.g., mixing, cold surfaces, etc., which can perturb the uniformity of the high temperature combustion process, may tend to increase the concentration of precursor compounds.

  - The role of HCl in the formation of PCDD and PCDF in this type of surface reaction is probably unimportant due to the complexities of any likely chlorination mechanism and limited reaction times. Even if HCl could play a role, attempts at separation of chlorine from MSW prior to incineration would likely have no effect on this role due to the high percentage of chlorine-containing waste that would have to be removed.

- If a fly-ash catalyzed post-flame combustion zone process produced PCDDs and PCDFs, increases in precursor compounds should have no effect on the production rate when available reaction sites are limited by slow thermal desorption. If condensed phase (grate bed) reactions are the principal mechanism for PCDD and PCDF production, an increase in the level of chlorinated precursor compounds could affect the level of PCDD and PCDF emissions if the incinerator combustion efficiency was low.

- The key to minimizing concentrations of chlorinated precursor compounds in the combustion zone is to assure as nearly so as possible that they are uniformly mixed with sufficient air and uniformly heated to flame temperatures.

- If the PCDD and PCDF precursor compounds are effectively destroyed in the combustion zone, it is not possible for them to reform at any significant levels after the combustion zone.

- In or on the grate bed some chlorination of lignin may take place. The nature and source of the chlorinating agents are not well known. Chlorinated lignin material, when heated, may depolymerize to produce chlorinated compounds, such as chlorinated phenols. The chlorinated phenols and other compounds that may be produced could be destroyed by further thermal stressing.

- Improper operation of the incinerator could increase the precursor concentrations found in the stack through mass transport of these compounds when combustion efficiency is low and control devices do not contain these furnace emissions. In principle, this can be corrected. However, even if precursor compounds are transported to the stack, no significant PCDD or PCDF formation is expected to occur in the stack.

2. GOAL OF THIS REPORT

- Have an answer, which is supported by valid scientific evidence, to each technical question about PCDD and PCDF formation and destruction in MSW fired incinerators posed by Mr. Casowitz.

3. OBJECTIVES OF THIS REPORT

- Extract from published material information which is pertinent to questions that have been raised concerning PCDD and PCDF formation and destruction in MSW fired incinerators.

- Utilize information obtained from literature reports to analyze technical issues concerned with PCDD and PCDF formation and destruction in MSW fired incinerators.

- Relate analyses to practical implications for minimization of PCDD and PCDF emissions from MSW fired incinerators.

- Identify and discuss uncertainties of analyses of technical issues concerned with PCDD and PCDF formation and destruction in MSW fired incinerators.

- With respect to Mr. Casowitz' inquiry, achieve an understanding of technical issues concerned with PCDD and PCDF formation and destruction in MSW fired incinerators.

4. BACKGROUND

Large municipalities are rapidly running out of landfill space in which to dispose of municipal solid waste (MSW). Waste disposal in MSW fired incinerators is an alternative. The City of New York is currently attempting to develop a safe and economical means to dispose of its municipal waste through incineration.

Technical issues have been raised concerning prospects for minimizing PCDD and PCDF emissions from incinerators. Mr. Paul Casowitz, Deputy Sanitation Commissioner, Office of Resource Recovery and Waste Disposal Planning, the City of New York Department of Sanitation, requested the National Bureau of Standards (NBS) to provide technical expertise to analyze the issues which are of concern. Subsequently, questions concerning PCDD and PCDF formation and destruction in MSW fired incinerators were posed to NBS by Mr. Casowitz.

5. INTRODUCTION

This work is based upon an analysis of current literature reports and the personal expertise of Dr. Walter M. Shaub, who has conducted extensive analyses of the physical and chemical properties and behavior of dioxins and related compounds in thermal environments. References [1,2] of this report can be used as an extensive bibliography to this field. The latter reference can be used as a sourcebook about NBS related research.

In the section which follows this introduction, each question associated with the technical points posed by Mr. Casowitz is analyzed and answered.

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September 19, 1984

Dr. Walter Shaub
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Dear Dr. Shaub:

I want to thank you again for taking time to speak with me about your report Containment of Dioxin Emissions from Refuse Fired Thermal Processing Units - Prospects and Technical Issues.

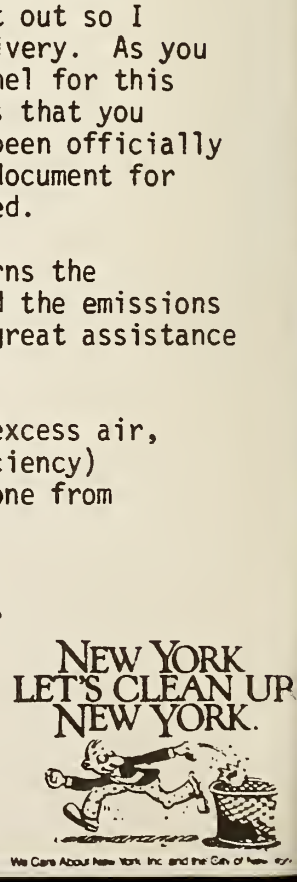
Your approach establishes a theoretical framework that provides an extremely useful perspective for evaluating both the available experimental evidence and also the design of future experiments.

I had been under the false impression that Dave Lipsky of Fred C. Hart Associates had sent you a copy of their report on the potential public health risks from dioxin and furan emissions from the resource recovery facility proposed for the Brooklyn Navy Yard. Apparently, your copy was not sent out so I have enclosed a copy with this letter. I apolcgize for the late delivery. As you are aware, I very much wanted you to be part of the expert review panel for this report. I would still greatly appreciate any comments or suggestions that you might care to make in regard to the Hart Study. The report has not been officially released yet. I would ask that you treat it as an internal working document for the next four weeks by which time the report should have been released.

One of the policy issues that Barry Commoner has raised concerns the relationship between the PVC content of the municipal solid waste and the emissions of PCDD's and PCDF's from an MSW fired incinerator. It would be of great assistance to me if you would comment briefly on the following points:

(1) In a properly operated incinerator (i.e., where temperature, excess air, mixing and residence time are set to maximize combustion efficiency) dioxins and furans may still be formed after the combustion zone from surface reactions on fly-ash particles.

  - What temperatures would favor the formation of PCDD and PCDF from chlorinated phenols or other likely precursors?



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- What combustion factors would tend to increase the concentration of precursor compounds?

- What role, if any, would the presence of HCl be likely to have in the formation of PCDD and PCDF in this type of surface reaction?

(2) What effect would an increase in the level of chlorinated precursor compounds have on the levels of PCDD and PCDF emissions?

(3) Could improper operation of the incinerator increase the precursor concentrations found in the stack? How?

(4) What combustion conditions would be required to effectively destroy chlorinated precursors in the combustion zone? Could these precursor compounds reform after the combustion zone?

(5) Could PVC or other sources of chlorine play a role in the formation of chlorinated phenols or other organic compounds by combustion in combination with paper on the grate? Barry Commoner has stated that the lignin in paper will give rise to phenols which will combine with the chlorine.

(6) Can the levels of chlorinated precursor compounds likely to be found in MSW account for their concentrations in the emissions or is it more likely that these precursors are being formed from chlorination reactions that occur within the incinerator?

(7) Are the emissions of PCDD and PCDF likely to be limited by the levels of these precursor compounds or by the available surface area provided by the particulate?

I hope I am not imposing too much on your time. New York City has a tremendous waste disposal problem (we generate over 20,000 tons each day and we are rapidly running out of landfills. We want to select the safest and most reliable technology for meeting this waste disposal need. If removing PVC is likely to further reduce PCDD or PCDF emissions, we will pursue the feasibility of this alternative. If on the other hand the PCDD and PCDF are independent of the PVC content of the waste or there are better control techniques, we do not want to waste time and resources with PVC removal.

Any help you could provide would be most appreciated.

Sincerely,

Paul Casowitz

Paul Casowitz, P.E.
Deputy Sanitation Commissioner

PC:rl
Enclosure

6. ANALYSIS OF TECHNICAL QUESTIONS

CAN THE LEVELS OF CHLORINATED PRECURSOR COMPOUNDS LIKELY TO BE FOUND IN MSW ACCOUNT FOR THEIR CONCENTRATIONS IN THE EMISSIONS OR IS IT MORE LIKELY THAT THESE PRECURSORS ARE BEING FORMED FROM CHLORINATION REACTIONS THAT OCCUR WITHIN THE INCINERATOR?

There are insufficient amounts of PCDDs or PCDFs in uncombusted MSW waste streams to account for their emissions from stacks [2]. Fewer data are presently available about the sources of chlorinated precursor compounds in uncombusted waste. The identities of all the chlorinated precursor compounds are uncertain. Chlorophenols appear to be precursor compounds [2]. Other chlorinated precursor compounds have been suggested [2].

The amounts of chlorinated precursor compounds found in MSW are highly variable. Thus, it is difficult to quantitatively measure concentrations of these compounds in a statistically representative manner [2]. Consequently, the levels of the precursor compounds, particularly on or in the mass of municipal waste which is burned on the grates, are not known with certainty.

Therefore, in terms of their implications for proper incinerator operation, one must consider both possibilities that chlorinated precursor compounds are found in MSW and that chlorinated precursors are being formed from chlorination reactions that occur within the incinerator.

In the following questions which Mr. Casowitz has raised, these implications are examined.

IN A PROPERLY OPERATED INCINERATOR (I.E., WHERE TEMPERATURE, EXCESS AIR, MIXING AND RESIDENCE TIME ARE SET TO MAXIMIZE COMBUSTION EFFICIENCY) MAY DIOXINS AND FURANS STILL BE FORMED AFTER THE COMBUSTION ZONE FROM SURFACE REACTIONS ON FLY ASH PARTICLES?

It has not been demonstrated that PCDDs and PCDFs "will" be formed at significant levels in properly operated incinerators. What is known is that under some conditions, some incinerators will at times emit detectable levels of PCDDs and PCDFs [1]. These findings do not exclude the possibility that proper operating conditions can be determined that will promote the minimization of PCDD and PCDF emissions.

Theoretical studies conducted at the NBS suggest that conditions may sometimes exist in which PCDDs and PCDFs may be formed in the post-flame combustion zone of an incinerator from surface reactions involving chlorinated precursor compounds and fly-ash particles [2]. Catalytic formation of PCDDs and PCDFs on surfaces can be made to occur under some laboratory conditions [2-6].

Therefore, no one has yet conclusively shown by experiments or testing of pilot or full scale MSW fired incinerators that PCDDs and PCDFs will be formed in the post-flame combustion zone of an incinerator from surface reactions on fly-ash particles.

WHAT TEMPERATURES WOULD FAVOR THE [POST-FLAME COMBUSTION ZONE] FORMATION OF PCDD AND PCDF FROM CHLORINATED PHENOLS OR OTHER LIKELY PRECURSORS?

High temperatures which can promote the thermal and oxidative destruction of PCDDs, PCDFs and precursor compounds (e.g., chlorophenols) in the gas phase, should also promote the destruction of these compounds on the surface of fly-ash particles. There is no known unique thermal kinetic stability attributable to these compounds when they are adsorbed on fly ash surfaces [2].

The lower temperature limit for PCDD or PCDF formation from chlorophenols or other likely precursors is set by the temperature required for effective thermal desorption of these compounds and other competitively adsorbed species in periods which are short relative to the post-flame combustion zone transit time [2]. At temperatures lower than about 400°C, the rate of thermal desorption of these compounds from fly-ash becomes slow compared to the transit time of the fly-ash particles through the incinerator. This means that at low temperatures, sites for PCDD and PCDF formation on fly-ash are unavailable. Under such conditions, PCDD and PCDF production is insufficient to account for reported emissions. This is one reason, for example, why the possibility for PCDD or PCDF formation from reactions in the stack of an incinerator can be discounted.

Therefore, catalytic PCDD and PCDF formation may take place in the post-flame combustion zone of an incinerator at temperatures in the range of about 400°C up to temperatures at which thermal destruction of these compounds and their precursors occurs.

WHAT COMBUSTION FACTORS WOULD TEND TO INCREASE THE CONCENTRATION OF PRECURSOR COMPOUNDS?

To answer this question precursor compounds must be suggested. To do this requires an examination of possible environments in which PCDD and PCDF formation may take place. There are at least two possible environments to consider: (a) reactions involving surfaces of fly-ash in the post-flame combustion zone of an MSW fired incinerator [2]; or, (b) reactions involving condensed phase environments, e.g., on or in the grate beds of an MSW fired incinerator.

Kinetic modeling of a worse case (beyond that which is reasonably likely to happen) formation model for PCDD formation conclusively eliminates the possibility of gas phase formation of PCDDs from any precursor compounds, with or without HCl present [2]. The possibility that PCDFs may be formed in the gas phase by radical abstraction of oxygen from PCDDs has not been studied by experiment. This latter statement does not exclude PCDF formation from precursor compounds due to non-gas phase formation processes.

(a) Post-flame combustion zone environments:

The formation of PCDDs or PCDFs from fly-ash catalyzed post-flame combustion zone reactions may involve chlorobenzenes or chlorophenols. (In a combustion environment, chloro-2-phenoxyphenols are probably best thought of as short-lived reactive intermediates rather than as precursors [2]). Except as discussed below, possibilities for other post-flame combustion zone precursors may not be important: in terms of chemical kinetics, when reaction times are limited, the possibility for postulating realistic PCDD or PCDF formation mechanisms from precursor compounds that are very much structurally unlike PCDDs or PCDFs is small. This is because when a precursor is structurally unrelated to PCDDs or PCDFs, a very complex pathway must be postulated to account for PCDD or PCDF formation. As the postulated mechanism necessarily becomes more and more complicated the reaction probability for PCDD or PCDF formation becomes small [2]. These arguments can be demonstrated by analytical and numerical techniques [2,8].

In the post-flame combustion zone, two other possibilities to consider are that the unchlorinated phenols or unchlorinated benzenes may be precursor compounds. If so, this would require the presence of a high density of chlorinating agent on the surface of fly-ash particles and/or in the gas phase of the post-flame combustion zone and that additionally, chlorination of the unchlorinated compounds on the surface of the fly-ash be both very rapid and very extensive - in order to account for the often reported [1,2] skewed distribution of chlorinated PCDD emissions towards the more highly chlorinated isomers. Note that preferential reactive destruction of the less chlorinated PCDD isomers by hydroxyl radicals is likely to be much less extensive in the post-flame combustion zone than in the flame combustion zone.

It is interesting to note that at least in the case of a silica surface, HCl is a very poor compound for promoting surface chlorination by displacement of hydroxyl groups [8,10] even at elevated temperatures. This would seem to imply that chlorination of unchlorinated organics takes place by surface activation of the organic species. It is not known to what extent surface condensed heavy metal halides [11] may promote post-flame combustion zone chlorinations or whether CCl_4, which is a more effective chlorinating agent than HCl [10], may play some role. The conceptual complexities of these reactions [8,11] and the limited reaction time in the post-flame combustion zone suggest that these possibilities are not significant except under some unusual circumstances.

Experiments have been performed [3-6] which suggest that some catalytic chlorination of PCDDs and other organic compounds can occur under controlled laboratory conditions. More research is necessary to conclusively show whether or not and to what extent such reactions can occur in the post-flame combustion zone of MSW fired incinerators.

Of the possible precursor compounds suggested above, concentration increases in the post-flame combustion zone may be attributable to several factors which include [2]:

(i) poor mixing efficiencies between fuel and oxidant, resulting in heterogeneous combustion conditions and wide temperature fluctuations or low average temperatures;

(ii) gasification of unburnt or partially combusted condensed phase organic material which has been buoyantly transported to the post-flame combustion zone;

(iii) boundary layer transport along cold surfaces, e.g., walls, of unburnt or partially combusted fuel to the post-flame combustion zone; and

(iv) incomplete combustion due to low average temperatures.

Research is necessary to quantify these and other possibilities. Test plans should include a consideration of the relationship of incinerator operations and design characteristics to these conditions.

(b) Condensed phase environments:

Chemical and physical processes take place in and on material which is burning on the grates of an MSW fired incinerator. These processes may produce chlorinated precursor compounds or PCDDs or PCDFs. It is difficult without conducting further research to make more than just a few qualitative observations concerning combustion factors that could increase the concentration of these compounds on or in the material which burns on grates. This is presently due to a general lack of useful information about this particular aspect of the combustion process in MSW fired incinerators. A few observations which can be made will be presented in response to additional points raised by Mr. Casowitz.

Any compounds produced on or in the material which burns on the grates of an MSW fired incinerator must subsequently pass through the rest of the incinerator in order to be emitted through the stack. This implies that combustion conditions could be established which minimize emissions of these compounds. The combustion factors cited above are likely to contribute to these emissions if not adequately controlled.

Therefore, combustion factors, e.g., mixing, cold surfaces, etc., which can perturb the uniformity of the high temperature combustion process, may tend to increase the concentration of precursor compounds. Research and testing are required to optimize these combustion factors to minimize concentrations of precursor compounds.

WHAT ROLE IF ANY WOULD THE PRESENCE OF HCl BE LIKELY TO HAVE IN THE FORMATION OF PCDD AND PCDF IN THIS TYPE OF SURFACE REACTION?

Some numerical estimates are made to suggest what role if any the presence of HCl may have in promoting the surface catalyzed formation of PCDDs or PCDFs.

Emission levels of HCl from municipal incinerators are on the order of 100 ppm by weight [12-15]. The concentration level of HCl in the post-flame combustion zone is about the same order of magnitude. This means that at one atmosphere pressure and a temperature of about 600°C there are about $6 \times 10^{+14}$ HCl molecules per cm^{+3} in the post-flame combustion zone. (The arguments made here are not critically sensitive to the assumed temperature.)

The maximum number of chlorine atoms that can be adsorbed on a silica surface is reported to be between three and four chlorine atoms per 100 square Angstroms under favorable conditions [10-16]. On fly-ash in an MSW fired incinerator the maximum number of chlorine atoms which can be adsorbed per 100 square Angstroms is probably much less than this, e.g., due to competitive adsorption, steric effects, variations in fly-ash surface composition, etc. Assume that the maximum coverage of fly-ash particles is no more than about 3.5 chlorine atoms per 100 square Angstroms [10]. Assume that the average fly-ash particle diameter is about 10 micrometers, that the fly-ash particles are approximately spherical, and that the fly-ash loading in the post-flame combustion zone is about 10^{-6} grams per cm^{+3} [2]. With these assumptions the maximum number of adsorption sites for HCl is about $8 \times 10^{+11}$ sites per cm^{+3} of fly-ash laden gas in the post-flame combustion zone.

When the above assumptions are made, the ratio of HCl in the gas phase of the post-flame combustion zone to the maximum amount of HCl that can be surface adsorbed on fly-ash is about 750. For reasons mentioned above, this figure is only an estimate. The actual ratio may be much larger.

In chlorination experiments reported by Eiceman and Rghei [4,5] an attempt was made to chlorinate dioxins on fly-ash with a mixture of HCl in air at elevated temperatures. The nominal fly ash size used was between 100 and 140 mesh (an average particle size diameter of about 63.5 micrometers). Eiceman and Rghei [4,5] used a typical fly ash loading of 1.6 grams per 3.76 cm^{+3}. Therefore in these experiments, the maximum number of adsorption sites for chlorine atoms was about $2.8 \times 10^{+16}$ sites per cm^{+3} of fly-ash loaded gas volume, assuming as before that the fly-ash particles were approximately spherical and that the maximum possible chlorine atom loading was about 3.5 chlorine atoms per 100 square Angstroms [10]. The instantaneous gas phase molecular number density of HCl at a reported loading of one percent by volume of HCl in air at one atmosphere pressure and a temperature of 300°C was about $1.3 \times 10^{+17}$ molecules of HCl per cm^{+3}. Therefore in this reported experiment, the ratio of the gas phase HCl to surface adsorbed HCl was about five. This is a ratio which is smaller by about a factor of 100 than the value of a typical ratio calculated above for HCl in an MSW fired incinerator. Eiceman and Rghei [4,5] report that even at this low ratio of five, promotion of chlorination reactions was found to be independent of the HCl concentration. This independence of chlorination reactions from HCl concentrations was reported for ratios from about five to about 250 [4,5].

Benzene and phenol are in some respects structurally similar to PCDDs and PCDFs. This implies that the same results might be observed for HCl promotion of fly-ash catalyzed chlorination of these precursors [3]. This supposition needs to be verified by experiment.

Polyvinyl chloride (PVC) in municipal waste streams is reported to account for no more than about 25% of the HCl which is produced and emitted during the combustion process which takes place in MSW fired incinerators [15,17]. Therefore removal of all PVC from municipal waste streams prior to incineration would reduce the level of HCl such that the ratio of the gas phase HCl to the maximum value for surface adsorbed HCl (actually surface adsorbed chlorine atoms) would still be very large (about 560 based on the above assumptions) compared to the ratios studied in the experiments reported by Eiceman and Rghei [4,5]. The fact that the extent of chlorination is independent of HCl concentration even at the low ratio of five, implies that if all PVC were removed from municipal waste streams prior to incineration, no effect on the level of PCDD and PCDF emissions would result if PCDD and PCDF formation critically involved surface catalyzed HCl chlorination reactions in the post-flame combustion zone.

It has previously been suggested in this report that given the likely complexities of a multiple chlorination mechanism and the limited reaction time available in the particle laden gas flow stream of the incinerator, extensive fly-ash catalyzed chlorination reactions appear to be unlikely. However, if such reactions could occur, the above discussion implies that extensive removal of chlorine, by as much as a 99+% reduction of chlorine content from the MSW stream prior to introduction into the incinerator, would likely have no effect on the extent of such reactions. This author is not aware of any pre-treatment technology which could effectively remove 99+% of the chlorine from an MSW stream prior to incineration.

Therefore, the role of HCl in the formation of PCDD and PCDF in this type of surface reaction is probably unimportant due to the complexities of any likely chlorination mechanism and limited reaction times. If HCl could play a role, attempts at separation of chlorine from MSW prior to incineration would likely have no effect on the role due to the high percentage of chlorine that would have to be removed.

WHAT EFFECT WOULD AN INCREASE IN THE LEVEL OF CHLORINATED PRECURSOR COMPOUNDS HAVE ON THE LEVELS OF PCDD AND PCDF EMISSIONS?

(a) Post-flame combustion environment:

Assume that the principal mechanism for PCDD and PCDF formation is due to catalytic reactions which take place upon the surface of fly-ash in the post-flame combustion zone. Assume that the concentration of polychlorinated precursor compounds in the gas phase of the post-flame combustion zone is significantly greater than the number of available surface reaction sites per unit volume of fly-ash laden combustion gas. A typical chlorophenol loading level is about 300 micrograms per M^{+3} [2]. Then the rate determining step for PCDD and PCDF formation should depend upon the number of available surface reaction sites, and the emissions of PCDDs and PCDFs should not be affected by or correlated to any further increase in the level of chlorinated precursor compounds. In this instance the level of emissions would depend upon other factors, e.g., the rate of desorption of chemisorbed species, competitive species adsorption, etc. Consider the following example of what the above discussion implies.

At a fly-ash mass loading of 3.5×10^{-6} grams per cm^{+3} (about 0.1 gram per $foot^{+3}$) in the post-flame combustion zone of an MSW fired incinerator it has been estimated that the number of surface reaction sites does not exceed about $3 \times 10^{+12}$ sites per cm^{+3} [2] of fly-ash laden combustion gas. This is an upper limit estimate for the reasons discussed previously, i.e., the actual number of available reaction sites is probably much less due to heterogeneties in particle morphology, steric effects, competitive adsorption, etc. For example, if competitive adsorption is accounted for, an estimate for the available number of reaction sites is about 3 x 10^{+10} sites per cm^{+3} of fly-ash laden combustion gas [2].

In the post-flame combustion zone, a gas phase mass loading of 10 micrograms per M^{+3} of a trichlorophenol corresponds to a molecular gas density of about 3 x 10^{+10} molecules per cm^{+3}. This is about equal to the number of available reaction sites. Therefore an increase in the mass loading of trichlorophenol, e.g., to a value of 100 micrograms per M^{+3} would not necessarily result in an increase in the level of, e.g., PCDD emissions. Other factors would have to be examined such as the rate of desorption of chemisorbed species from the fly-ash surface [2]. Under these circumstances, in which PCDD emissions are not related to precursor concentrations, the level of PCDD emissions would be more sensitive to the time dependent temperature distribution function for the incinerator than to the ambient level of precursor compounds.

(b) Condensed phase environment:

If the principal driving force for PCDD and PCDF formation is attributed to mechanisms which occur on or in the mass of waste which burns upon the grate bed of an MSW fired incinerator, the effect of an increase in the level of chlorinated precursor compounds on the level of PCDD or PCDF emissions is difficult to predict or estimate. Almost no useful information is reported in the literature from which to draw conclusions. Additional discussions of grate bed chemistry will be presented in response to the following questions raised by Mr. Casowitz.

If under some conditions increases in precursor compounds promote increased production of PCDDs and PCDFs in the condensed phase environment, other factors may compensate for this enhancement and promote destruction of these compounds. Potential controlling factors associated with the combustion environment have been suggested in this report and in reference [2].

Therefore, if a fly-ash catalyzed post-flame combustion zone process produced PCDDs and PCDFs, increases in precursor compounds should have no effect on the production rate when available reaction sites are limited by slow thermal desorption. If condensed phase (grate bed) reactions are the principal driving force for PCDD and PCDF production, an increase in the level of chlorinated precursor compounds could affect the level of PCDD and PCDF emissions if the incinerator combustion efficiency were low.

ARE THE EMISSIONS OF PCDD AND PCDF LIKELY TO BE LIMITED BY THE LEVELS OF THESE PRECURSOR COMPOUNDS OR BY THE AVAILABLE SURFACE AREA PROVIDED BY THE PARTICULATE?

A response to this question is predicated on the presumption that the principal means for PCDD and PCDF formation is by catalytic reactions due to the interactions of fly-ash with precursor compounds in the post-flame combustion zone. This presumption has been suggested [2] but not proven at the present time. If this presumption is true, then the preceding discussions in this report are pertinent and should be referred to for a response to this question. In addition, the NBS report mentioned in the references should be referred to for further information [2].

Therefore, if a fly-ash catalyzed post-flame combustion zone process produces PCDDs and PCDFs, increases in precursor compounds should have no effect on the production rate when available reaction sites are limited by slow thermal desorption.

WHAT COMBUSTION CONDITIONS WOULD BE REQUIRED TO EFFECTIVELY DESTROY CHLORINATED PRECURSORS IN THE COMBUSTION ZONE?

The key to minimizing concentrations of chlorinated precursor compounds in the combustion zone is to assure as nearly so as possible that they are uniformly (homogeneously) mixed with sufficient air and uniformly thermally heated to flame temperatures [2]. (Actually temperatures as low as about 900°C should be more than adequate to destroy most organic compounds efficiently during available transit times if mixing and thermal stressing are efficient.)

In practice the above conditions are sometimes difficult to achieve. In large scale combustion devices such as MSW fire incinerators, considerable effort is required to minimize thermal fluctuations and uniformly heat a particulate laden gas stream. Particles, e.g., fly-ash in combustion streams, have size and composition dependent heating times [2].

Compensations can be made for these spatial and temporal heterogeneties by use of e.g., excess air, staged combustion, increased hot gas furnace residence times, afterburners, etc. The effectiveness of each of these approaches to minimization of PCDD and PCDF emissions can in principle be determined by a carefully designed testing program.

Therefore, the key to minimizing concentrations of chlorinated precursor compounds in the combustion zone is to assure as nearly so as possible that they are uniformly mixed with sufficient air and uniformly heated to flame temperatures.

COULD THESE PRECURSOR COMPOUNDS REFORM AFTER THE COMBUSTION ZONE?

If the PCDD and PCDF precursor compounds are effectively destroyed (completely oxidized to CO_2, H_2O and HCl) in the combustion zone, it is not possible for them to reform at any significant levels after the combustion zone [2]. Any apparent reformation of these compounds would be attributable to and depend upon the extent of any incomplete combustion.

If the formation of PCDDs and PCDFs were to depend upon the reformation of precursor compounds, the probability for PCDD and PCDF formation would be much reduced from the case of PCDD and PCDF formation from pre-existing precursor compounds [2]. This is because the probability for formation of any compound is generally sensitive to the complex interactions and effects of all of the pathways of a formation mechanism. Generally, the more complex the mechanism for compound formation and the more there are opposing characteristics in the mechanism (e.g., destruction pathways or alternate product formation pathways), the lower the probability that the particular compound will be formed [2].

Therefore, if the PCDD and PCDF precursor compounds are effectively destroyed in the combustion zone, it is not possible for them to reform at any significant levels after the combustion zone.

COULD PVC OR OTHER SOURCES OF CHLORINE PLAY A ROLE IN THE FORMATION OF CHLORINATED PHENOLS OR OTHER ORGANIC COMPOUNDS BY COMBUSTION IN COMBINATION WITH PAPER ON THE GRATE? IT HAS BEEN SUGGESTED THAT THE LIGNIN IN PAPER WILL GIVE RISE TO PHENOLS WHICH WILL COMBINE WITH THE CHLORINE.

(a) Post-flame combustion zone environment:

On undergoing incomplete combustion wood and wood components will decompose to produce many lower weight organic compounds, including substantial amounts of alkyl- and alkoxy- substituted phenols [18-22]. The probability that these unchlorinated phenols will undergo extensive gas phase chlorination by HCl or other chlorine containing species is negligible. This statement can be substantiated by simple worse case modeling [8]. As previously discussed in this report, the probability that these unchlorinated phenols will undergo extensive chlorination in the post-flame combustion zone due to catalytic processes involving fly-ash is likely to be limited by the complexities of the chlorination reactions. Qualitatively chlorination of organic compounds has been shown to occur under some laboratory conditions [3]. The extent of the reported chlorination does not appear to account for the levels of polychlorinated phenols reported in incinerator emissions.

(b) Condensed phase environment:

Sjostrom [22] has reported that lignin is readily chlorinated. For example, extensive chlorination through substitution at C-5 and C-6 positions (and to a lesser extent at the C-1 and C-2 positions) of the guaiacyclopropane units of lignin is possible [22]. Subsequent substitutions, and oxidative or pyrolytic thermal stressing could then lead to side chain displacement, cleavage of methoxyl groups and lignin depolymerization to produce lower molecular weight compounds, e.g., chlorophenols [22]. This is evident for example from the extensive amount of chlorinated lignin products found in spent bleach liquor from chlorination and alkali extraction stages in the pulp bleaching process [23-25]. Production of some paper involves these bleaching processes. Some discarded waste paper may therefore contain significant amounts of chlorinated organic materials. On heating this may depolymerize, potentially resulting in production of chlorophenols. At the present time this is an untested suggestion.

The nature and sources of other chlorinating agents present in the mass of municipal waste which is burned on the grates of an MSW fired incinerator are not precisely known. Kinetic processes which may promote PCDD and PCDF formation in these instances have not been determined. It has not clearly been established that HCl is the principal chlorinating agent in municipal waste combustion. Carefully designed experiments would be required to resolve these issues.

As mentioned previously, it appears that PVC in municipal waste streams accounts for only about 25% of the HCl which is produced and emitted during the combustion process [15,17]. In municipal waste there are numerous other possible sources of chlorine which could contribute to production of HCl: plasticizers, plastic additives, wood preservatives, fire retardants, solvents, propellants, cutting fluids, bleaching agents, etc. [2]. In addition, it has been known since at least 1809 [27] that HCl can be produced from inorganic chlorine sources, e.g., NaCl. Uchida and co-workers [14] report that production of HCl from inorganic chlorine sources in municipal waste can be extensive. Thus, even if lignin in discarded waste paper is not already partially chlorinated from bleaching processes, formation of precursors, e.g., chlorophenols, may be promoted by a virtually ubiquitous availability of chlorine in the waste stream. Careful studies are needed to test and quantify these suggestions.

Based on the above observations it is probably advisable to focus upon minimization of PCDD and PCDF emissions by combustion control and/or post-combustion control technologies rather than attempting to remove sources of chlorinated materials by presorting municipal waste streams prior to feeding them into an MSW fired incinerator. Theoretical studies carried out at NBS suggest that minimization of PCDD and PCDF emissions in principle can be achieved by combustion control and/or application of post-flame combustion zone control technologies, without resorting to pre-sorting of municipal waste streams [2].

Therefore, in or on the grate bed some chlorination of lignin may take place. The nature and source of the chlorinating agents are not established. Chlorinated lignin material, when heated, may depolymerize to produce chlorinated compounds, such as chlorinated phenols. The chlorinated phenols and other compounds that may be produced could be destroyed by further thermal stressing.

COULD IMPROPER OPERATION OF THE INCINERATOR INCREASE THE PRECURSOR CONCENTRATIONS FOUND IN THE STACK? HOW?

If an MSW fired incinerator combustion furnace does not efficiently destroy precursor compounds they will be transported from the combustion furnace to the next sections of the incinerator. These sections may include, the energy recovery devices, scrubbers, air pollution control units, etc. These devices can be analyzed in terms of a net transport of combustion exhaust gases containing fly-ash laden with PCDDs and PCDFs. The extent to which each of these devices affects the resulting emissions levels of PCDDs and PCDFs can be suggested theoretically and measured reasonably quantitatively in principle.

An increase in the mass transport of precursor concentrations to the stack of an MSW fired incinerator can be due to a combination of incomplete minimization of PCDD and PCDF formation in the combustion furnace and/or subsequent failures of control devices to contain or minimize the resulting emissions. In principle, this problem can be corrected by improving incinerator performance.

The presence of or an increase of precursor concentrations found in the stack of an MSW incinerator is not likely to result in significant formations or increased formations of PCDDs or PCDFs in the stack. There are reasons for this. First, at stack temperatures, the rate of thermal desorption of chemisorbed PCDDs and PCDFs, chlorophenols and numerous other organic compounds is so slow that reactive sites for formation of PCDDs and PCDFs are not available during the exhaust gas transit time through the stack of the incinerator [2]. For example, the desorption time for even a small fraction of chemisorbed PCDDs and PCDFs at 400°F (about 200°C) is many millions of times longer than the stack transit time [2]. This means that PCDD and PCDF formation reactions become inoperative in the stack. Second, at stack temperatures, competitive adsorption involves not only chemisorption but also contributions due to condensation of high molecular weight species, e.g., polycyclic aromatic compounds, resulting in multiple layer rather than monolayer coverage of fly-ash particles in times which are very short compared to stack gas transit times.

The fact that PCDD and PCDF fly-ash concentrations have been found to be significantly higher in stack emissions than in fly-ash taken from electrostatic precipitators (ESPs) is probably due to the difference in particle sizes between ESP ash and stack ash and/or condensation isotherms which favor a higher fly-ash to gas phase ratio for the partioning of PCDDs and PCDFs in the stack than in the ESP unit, since the latter operates at a higher temperature.

Therefore, improper operation of the incinerator could increase the precursor concentrations found in the stack through mass transport of these compounds when combustion efficiency is low and control devices do not contain these furnace emissions. In principle, this can be corrected. However, even if precursor compounds are transported to the stack, no significant PCDD and PCDF formation is expected to occur in the stack.

7. MAJOR CONCLUSIONS

Technical issues concerned with underlying factors that can potentially affect the levels of PCDD and PCDF emissions from MSW fired incinerators have been analyzed. This analysis of the technical issues that have been raised suggests that:

- Removal of sources of chlorine by pre-sorting of MSW waste streams prior to incineration is not a reasonable option compared to attempting combustion control and/or post-combustion control options for minimizing PCDD and PCDF emissions from MSW fired incinerators.

- If precursor compounds are transported to the stack of an MSW fired incinerator, no significant PCDD or PCDF formation is expected to take place in the stack.

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9. APPENDIX

On internal review the author was advised to consider more explicitly the possible contribution of buoyantly transported uncombusted fly-ash to PCDD emissions in the post-flame combustion zone:

WHAT CONTRIBUTIONS TO PCDD EMISSIONS MIGHT BE EXPECTED FROM BUOYANT TRANSPORT OF UNCOMBUSTED OR PARTIALLY COMBUSTED FLY-ASH TO THE POST-FLAME COMBUSTION ZONE?

Sjostrom [1] has reported that the lignin content of paper (actually pulp used for the production of paper) is about 0.5 to 1.0 percent by weight and can contain about ten percent by weight of chlorine if the paper has been bleached with a chlorinating agent. Karasek and co-workers [2] have reported that about two percent by weight of fly-ash appears to be uncombusted or partially combusted when transported to the post-flame combustion zone.

Using the above information, a worse case (beyond that which is likely to occur) analysis of PCDD production from buoyantly transported uncombusted or partially combusted fly-ash can be made:

Hutzinger and co-workers [3] have studied PCDD production by strong chlorination of lignin with a source of chlorine (HCl or PVC) in heated quartz ampoules. They have reported a conversion efficiency (defined as amount of PCDD formed compared to amount of lignin burned) of lignin to PCDDs of 43.6×10^{-9}. A typical fly-ash loading in the post-flame combustion zone is about 3.5 $g \cdot M^{-3}$ (about 0.1 $g \cdot ft^{-3}$) [4]. With these assumptions the worse case total amount of PCDDs that may be produced in the post-flame combustion zone of an incinerator is equal to the product of the fly-ash loading (3.5 $g{\cdot}M^{-3}$) times the fraction of fly-ash which is uncombusted or partially combusted (0.02) times the fraction of this which could be lignin (0.01) times the conversion efficiency of lignin to PCDDs (43.6 x 10^{-9}). The resulting predicted PCDD level is about 3 x 10^{-2} $ng{\cdot}M^{-3}$. In an incinerator environment, some lignin is lost from the fly-ash due to partial combustion on passage through the flame combustion zone. Therefore this result is an upper limit worse case value. Typical PCDD emission levels may range from 10^{+1} to about 10^{+4} $ng{\cdot}M^{-3}$. Therefore, it appears that PCDD production from the transport of partially combusted fly-ash to the post-flame combustion zone is not at all sufficient to account for observed PCDD emissions.

Therefore, the contribution to PCDD emissions resulting from buoyant transport of partially combusted fly-ash to the post-flame combustion zone is not at all sufficient to account for reported emission levels of PCDDs.

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☐ Document describes a computer program; SF-185, FIPS Software Summary, is attached.

11. ABSTRACT *(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here)*

TECHNICAL ISSUES CONCERNED WITH UNDERLYING FACTORS THAT CAN POTENTIALLY AFFECT THE LEVELS OF PCDD AND PCDF EMISSIONS FROM MSW FIRED INCINERATORS HAVE BEEN ANALYZED. MAJOR CONCLUSIONS OF THIS STUDY ARE THAT PRESORTING OF MUNICIPAL WASTE PRIOR TO INCINERATION TO REMOVE CHLORINE DOES NOT APPEAR TO BE A REASONABLE OPTION AND THAT PCDD AND PCDF FORMATION IS NOT LIKELY TO TAKE PLACE IN THE STACK OF AN INCINERATOR.

12. KEY WORDS *(Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons)*

catalysis; dioxins; fly-ash; grate bed; incinerator; municipal waste; PCDD; PCDF; pre-sorting; stack emissions

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