



Project Summary

Potential Emissions of Hazardous Organic Compounds from Sewage Sludge Incineration

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Very little field data is available concerning organic emissions from sewage sludge incinerators. This is of particular concern because hydrophobic hazardous organic compounds, such as certain pesticides, polynuclear aromatic hydrocarbons, and polychlorinated biphenyls, have been shown to partition onto the sludge during the wastewater treatment process. The environmental fate of these compounds during sewage sludge incineration is largely unknown.

Laboratory thermal decomposition studies were undertaken to evaluate potential organic emissions from sewage sludge incinerators. Precisely controlled thermal decomposition experiments were conducted on sludge spiked with mixtures of hazardous organic compounds, on the mixtures of pure compounds in absence of sludge, and on unspiked sludge. These experiments were conducted using laboratory flow-reactor systems interfaced with a gas chromatograph or gas chromatograph-mass spectrometer for product analysis. Issues which were addressed included the effect of the sludge matrix on the thermal decomposition behavior of the hazardous sludge contaminants; potential emissions from incineration of contaminated and uncontaminated sludge; the relative contributions of the biomass and the contaminants to mass emissions in sewage sludge incineration; and potential emissions due to volatilization of organics from sludge in the drying zones of multiple hearth incinerators.

In addition to the global thermal decomposition studies describe above, elementary reaction kinetic studies were conducted using a laser photolysis/

laser-induced fluorescence technique. To permit an in-depth understanding of some of the fundamental chemistry occurring in sewage sludge incinerators, the reaction rates of OH radicals with model chlorinated hydrocarbons were measured.

This Project Summary was developed by EPA's Water Engineering Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

While incineration has been used to dispose of sewage sludge since the 1930's, concern regarding potential environmental insult due to organic emissions from this disposal method has developed only recently. Very little is known about organic emissions from municipal sludge incinerators, and the research program described herein was designed to begin filling in such a data base, and to support the development of regulations for sewage sludge incinerators.

The Domestic Sludge Exclusion removes from hazardous waste status the solvents, industrial effluents, process wastes, etc., which are discharged to publicly owned treatment works. As a result, some 20,000 metric tons of priority organic pollutants enter wastewater treatment plants in the United States each year. It is documented that priority pollutants such as pesticides, polychlorinated biphenyls, phenols, phthalates, polynuclear aromatic hydrocarbons, diazo dyes, common solvents, and nitrosamines

concentrate on sewage sludge. Most of these contaminants are found in concentrations of 0.1 to 100 $\mu\text{g/g}$ (ppm), based on the dry weight of the sludge. Some potentially toxic organics found in sewage sludge are biodegradation products from less toxic precursors. For example, nonylphenol, a biodegradation product from nonylphenol ethoxylates (common nonionic surfactants), has been detected at levels around 1000 $\mu\text{g/g}$ in sewage sludge.

While emissions of metals, particulates, and gases such as SO_x and NO_x have been characterized to some extent for sludge incinerators, very little data exists concerning organic emissions. Limited field data indicates that polynuclear aromatic hydrocarbons and chlorinated dioxins and furans are emitted from sludge incinerators.

Assessment of organic emissions from municipal sludge incineration is further complicated by the wide range of incineration conditions which occur. Incineration parameters are not generally as well characterized or controlled as they are for hazardous waste incineration. This is particularly true for the multiple hearth incinerators, which constitute about 80% of the incinerators used for sewage sludge disposal. The other 20% are primarily fluidized bed incinerators, in which conditions are better defined and controlled.

The laboratory studies described herein were designed to generate a data base on potential organic emissions from sewage sludge incinerators. The research is broken down into three major areas:

1. Potential emissions of hazardous sludge contaminants and products

of incomplete combustion (PIC's) from sludge incineration;

2. Potential emissions of organics due to volatilization in the drying zone of the multiple hearth incinerator; and
3. Elementary reaction rates of hydroxyl radicals with model sludge contaminants.

Thermal Decomposition of Spiked Sludges and Spiking Mixtures

Experimental

To study the thermal decomposition of common sewage sludge contaminants, and to identify products of incomplete combustion (PIC's) from contaminated sewage sludge, thermal decomposition studies were conducted on the Thermal Decomposition Unit-Gas Chromatographic (TDU-GC) system and the Thermal Decomposition Analytical System (TDAS). Block diagrams of these systems are given in Figures 1 and 2, respectively. Both systems include thermal decomposition units in which temperature, atmosphere, and mean residence time can be precisely controlled. In the case of the TDU-GC, this thermal unit is interfaced with an in-line gas chromatograph (GC), while in the case of the TDAS, the analytical instrumentation is an in-line gas chromatograph-mass spectrometer (GC-MS). Details concerning these systems are given in the full report.

Thermal decomposition studies were conducted on a relatively clean sludge spiked with mixtures of contaminants, on mixtures of pure contaminants (without sludge), and on unspiked sludge. Con-

taminants were studied in three mixtures rather than as pure compounds so that a number of compound classes could be investigated within the constraints of the program. The contaminants which were studied were heptachlor; pentachlorophenol; diphenylnitrosamine; pyrene; butyl benzyl phthalate; 2,3',4,4',5-pentachlorobiphenyl; azobenzene; and technical-grade nonylphenol.

Sewage sludge used for these studies was a filter-cake sludge containing 17% solids, and was obtained from a local wastewater treatment plant from a primarily residential municipality. This sludge was not adequately dewatered for efficient incineration, but was otherwise similar in composition to sludges which are incinerated. The sludge was spiked at about 1 mg/g with the organic components, except nonylphenol, which was spiked at 10 mg/g. These levels are at least an order of magnitude greater than those typically found in "real world" sludges, but such spike levels were required to minimize interferences on the TDU-GC from the sludge matrix.

Variables investigated in these studies included gas phase temperature (300°C to 1000°C), oxygen level (air for combustion studies and nitrogen for pyrolytic studies), and sample matrix (spiked sludge versus mixtures of pure spike compounds). For spiked sludges and mixtures of pure compounds, the TDU-GC was used to generate thermal decomposition curves as a function of reactor temperature and oxygen level. The TDAS was then used to identify products of incomplete combustion (PIC's) by selecting reactor temperatures that, based upon TDU-GC data, would yield the majority of the PIC identi-

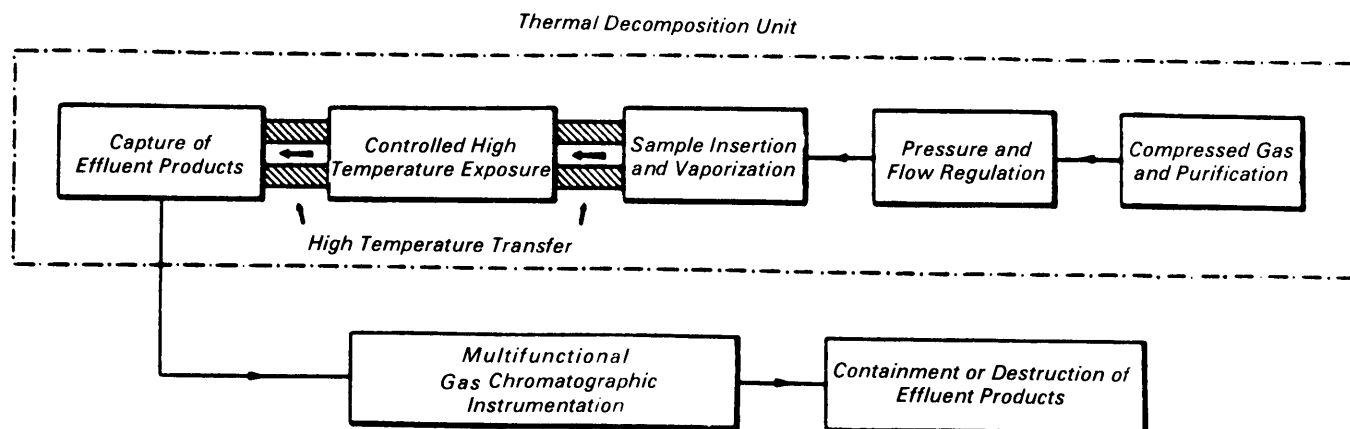


Figure 1. Block diagram of TDU-GC.

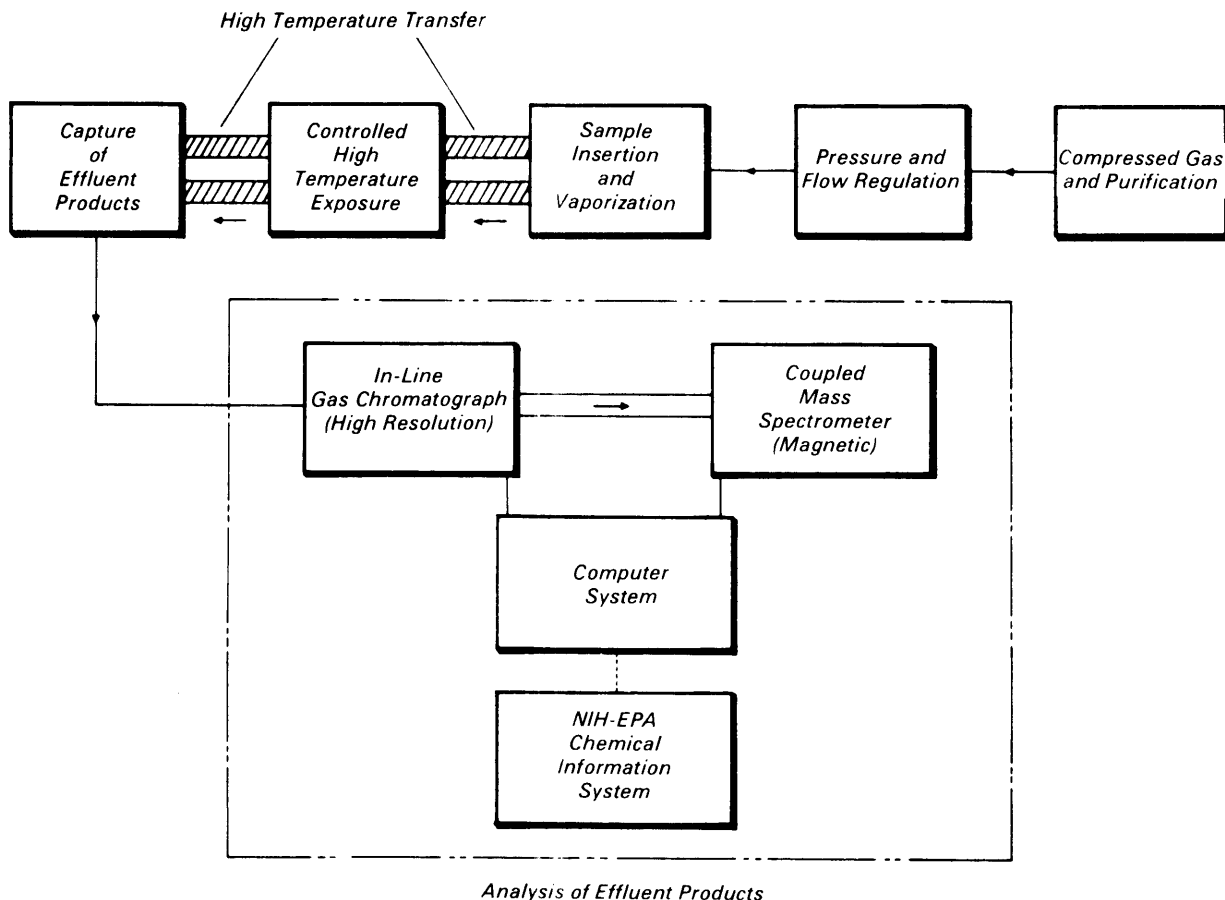


Figure 2. Block diagram of TDU-GC.

cations. The unspiked sludge was studied using the TDU-GC only, since there were no contaminant thermal decomposition profiles to generate.

A thermal decomposition run was initiated by inserting the sample, contained in the sludge probe, into the sample insertion region of the TDU-GC or TDU-GC. After allowing laboratory air to be purged from the system, the insertion region was programmed from 50°C to 200°C at 15°C/min. During sample heating, the vaporized sample components were conveyed into the reactor using either nitrogen or air. The reactor temperatures were varied over the range of 300°C to 1000°C, and a 2-second gas-phase mean residence time was maintained in the reactor. The reactor effluent (both undecomposed parents and products of incomplete combustion) was trapped at the head of the in-line gas chromatographic column. After purging the system with a helium carrier gas, the GC was programmed to elute the trapped species,

which were detected using an FID detector for the TDU-GC, or a mass spectrometer for the TDU-GC. Frequent method blanks and duplicates were run to ensure the integrity of the data.

Results and Discussion

The thermal decomposition of nonylphenol typifies the behavior observed for the majority of the sludge contaminants. Thermal decomposition profiles for nonylphenol as a function of matrix (spiked onto sludge versus run in a mixture of pure compounds) and of atmosphere (nitrogen versus air) are shown in Figure 3. These curves indicate that for a given matrix, the compound was more stable in nitrogen than in air. This is typical behavior for many organic compounds and was not surprising here. Figure 3 indicates that sample matrix also affected the thermal decomposition, with nonylphenol being more difficult to destroy in the presence of sludge than in the presence of the pure mixture.

While the sludge appeared to stabilize most of the contaminants studied, there were some cases where the sludge enhanced the thermal decomposition, and some where the sludge exerted little effect. Based on the limited data from eight hazardous contaminants, the following trends were observed:

- The sludge exerted little if any effect on the ease of destruction of very fragile contaminants.
- If a contaminant was intermediate in thermal stability, it was more difficult to destroy in the presence of the sludge.
- If a contaminant was very stable in the pure mixture, the sludge enhanced its ease of destruction.

Comparing the overall thermal stability of the eight sludge contaminants, pyrene was the most stable and butyl benzyl phthalate was the least stable. The relative ease of incineration of the eight hazardous contaminants increases in the following order: pyrene < pentachloro-

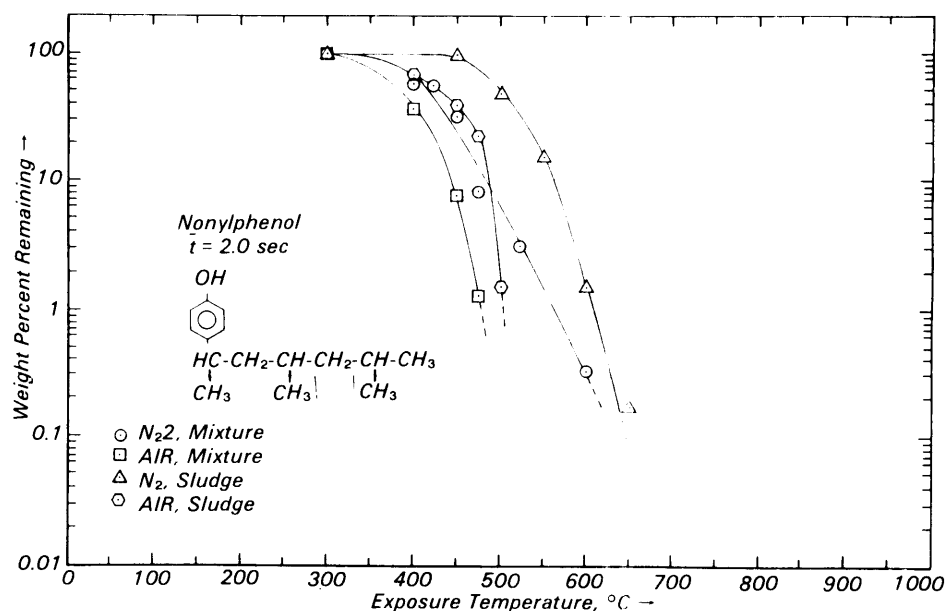


Figure 3. Thermal decomposition profiles for nonylphenol

biphenyl < pentachlorophenol < diphenylamine < azobenzene < nonylphenol < heptachlor < butyl benzyl phthalate.

A multitude of thermal reaction products were identified for spiked sludge, and mixtures of pure spiking compounds. Analysis of the data indicates that some PIC's could be attributed to the sludge, while others could be attributed to the contaminants, and still others may have formed through an interaction of the sludge and the contaminants. Interaction between the sludge and chlorinated contaminants may be the source of the trace emissions of chlorinated dioxins and furans from certain sludge incinerators.

The majority of the PIC's were aromatic, and the remainder were primarily chlorinated or unchlorinated short-chained unsaturated aliphatic hydrocarbons. The reader is referred to the final report for a complete discussion and tabulation of PIC's, since only a few examples can be given here. Pentachlorophenol, for example, yielded chlorinated benzenes, tetrachlorophenol, tetrachloropropyne, hexachlorodihydro-naphthalene, and other PIC's. Diphenylnitrosamine was 100% converted to diphenylamine at very low temperatures; this primary PIC was then the precursor for carbazole, benzonitrile, biphenyldicarbonitrile, and possibly other PIC's.

The sludge itself yielded a number of PIC's which are of environmental concern.

At relatively low temperatures (~500°C), desorption/decomposition products from the sludge included primarily compounds having the cholesterol-fused ring structure and alkenes or cycloalkanes. At higher temperatures (~800°C), benzene, styrene, toluene, benzaldehyde, ethylbenzene, xylene, and various polynuclear aromatic hydrocarbons were formed as PIC's. A number of these are on the Appendix VIII list of hazardous compounds and/or have produced positive results in various toxicological tests. Since the sludge used for these experiments originated in a relatively nonindustrialized municipality, these PIC's are attributed to the biomass rather than to environmental contaminants.

These laboratory studies indicate that PIC's from the sludge contributed much more to the total mass emissions than did PIC's from the contaminants. This is primarily because the contaminants were spiked at only parts-per-thousand levels in the sludge, meaning that the relative weight of the starting sludge was orders of magnitude greater than that of the starting contaminants. For "real world" sludges, which generally contain contaminants as parts-per-million rather than parts-per-thousand levels, the relative contribution of the biomass to total mass emissions is expected to be even greater.

The fact that potentially toxic compounds were formed from the sludge, combined with the fact that the total

levels of PIC's were many times greater for the sludge than for the trace contaminants, indicates the importance of incinerating all sludges under highly controlled and environmentally safe conditions.

Multiple Hearth Approximation

Experimental

Because both temperatures and residence times in the drying zone of the multiple hearth incinerator are relatively low, it was hypothesized that incineration efficiency would be poor in this zone. The temperature appeared to be high enough to volatilize many organic species, but not sufficiently high to initiate their thermal decomposition. For this reason, an experiment was designed to determine the potential for emissions from the drying zone of a multiple hearth incinerator.

The thermal exposure within the drying zone of the multiple hearth incinerator was best mimicked by gradually heating the sludge in the insertion region of the TDU-GC while maintaining the reactor at a low temperature. Therefore, a single sludge sample was placed in the sample insertion region of the TDU-GC, and was successively heated at 15°C/min in nitrogen over four temperature ranges. These temperature ranges were 50°C to 200°C, 200°C to 300°C, 300°C to 400°C, and 400°C to 500°C. The gas-phase residence time of desorbed species in the insertion region was less than 1 second. During the entire experiment, the reactor was maintained at a nondegradative temperature (300°C). While the sample was being heated over a given temperature range, any evolved species were condensed at the head of the in-line gas chromatographic column. After these species were collected, they were analyzed using programmed temperature capillary gas chromatography (GC), with flame ionization detection (FID). Once the GC run was complete, the same sample was then heated over the next temperature range and the analytical process repeated. This procedure was repeated a total of four times, until a final temperature of 500°C was achieved.

Results and Discussion

Results of this experiment indicate that the majority of the volatile sludge components desorbed during the initial program step between 50°C and 200°C. Significant residuals also desorbed in the 200°C to 300°C and the 300°C to 400°C ranges, but a marked decrease in desorbed or-

ganics was seen between 400°C and 500°C. Overall this experiment clearly illustrated the potential for major emissions from volatilization and/or incomplete combustion of sludge components in the drying zone of the multiple hearth incinerator.

A comparison of potential emission levels from the multiple hearth versus the fluidized bed incinerator is shown in Figure 4. The top chromatogram depicts volatile species desorbed from the sludge and conveyed through the reactor at 300°C, while the bottom chromatogram shows the remaining species after these volatilized organics have been subjected to an 800°C reactor temperature. While the thermal conditions in the top chromatogram approximate those in the drying

zone of the multiple hearth incinerator, those in the bottom chromatogram are more characteristic of the thermal regime in the fluidized bed incinerator. This indicates that the thermal regime of the fluidized bed incinerator is much less likely than that of multiple hearth to lead to major gaseous organic emissions.

Hydroxyl Radical Reactivity Studies

Experimental

For the combustion of hydrocarbons, OH radicals are the dominant reactive species under all but the most fuel-rich environments. Although it is recognized that chlorine atom reactivity may be

important for chlorinated hydrocarbons such as those produced as PIC's in the thermal degradation of contaminated sewage sludge, OH reaction kinetics are considered most significant with respect to the oxidative destruction of these materials. Since there is a general paucity of data on OH-chlorocarbon reactions and data are practically non-existent at the high temperatures which simulate incinerator conditions, the high temperature elementary reaction rates of OH radicals with select chlorocarbons were determined for this program via a laser photolysis/laser-induced fluorescence technique. This experimental approach allows the generation and detection of OH radicals in a "clean" environment where essentially only OH-chlorocarbon reactions can occur. This eliminates the complexities of rate constant determinations in multireaction media such as shock tubes, flames, and flow reactors.

The experimental test system consisted of five inter-dependent components: (1) a test cell and temperature control system, (2) the carrier gas and sample delivery system, (3) the pump laser system, (4) the probe beam system, and (5) the detection/measurement system. The test cell was a specially designed pyrex cell which allowed gas reactants to be heated, irradiated with laser beams, and observed. By monitoring relative concentrations of OH over time, the reaction rates of OH radicals with organic molecules were calculated.

The chloromethanes were chosen as model chlorocarbon compounds for this initial study because chlorinated hydrocarbons are both known sludge contaminants and stable PIC's produced from decomposition of contaminated sludge. Pseudo-first order rate constants were generated for all the chloromethanes over a temperature range of 296 to 782K.

Results and Discussion

Table 1 presents bimolecular rate constants for reactions of OH radicals with the chloromethanes over a temperature range of 571 to 782K. A statistical propagation of error analysis was applied to the data collection procedure with the results presented in Table 2. With minor exceptions, good precision was indicated as standard deviations in the rate constants were generally less than 10% of the measured value. The temperature dependence of the bimolecular rate constants were evaluated with weighted least-squares algorithms in relation to

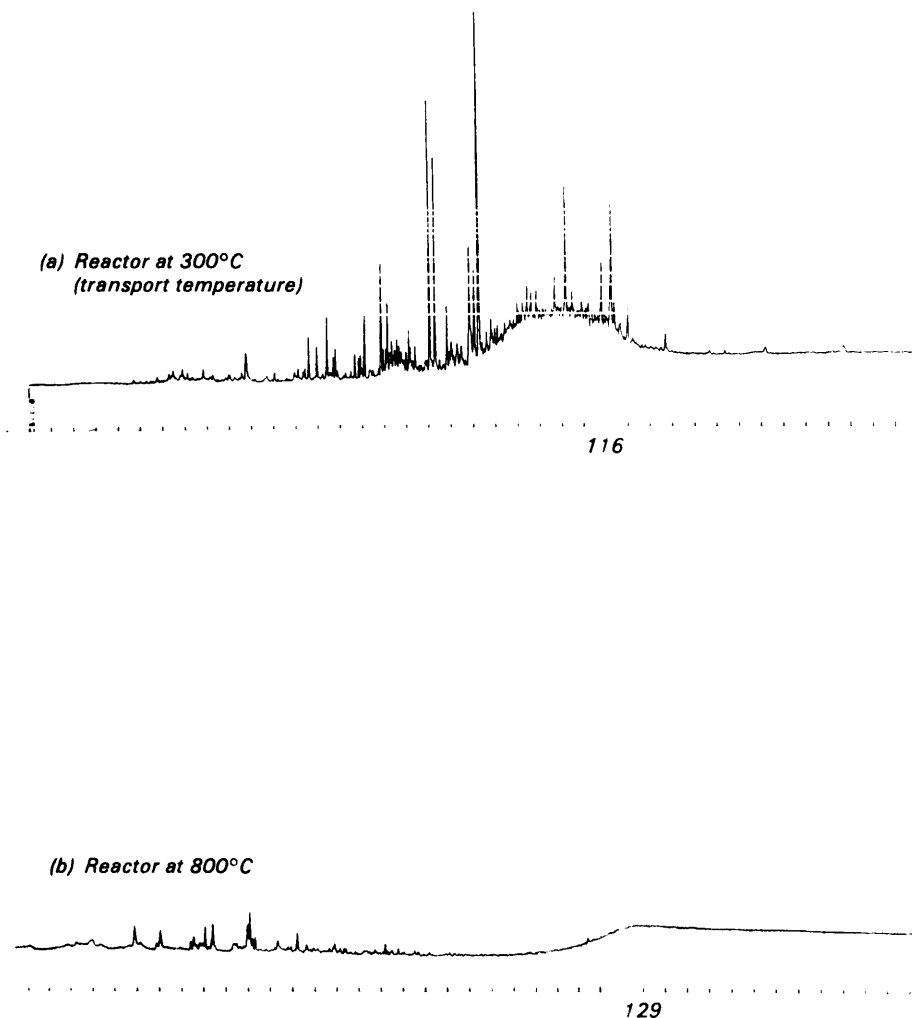


Figure 4. Comparison of potential emissions levels from (a) drying zone of multiple hearth versus (b) fluidized bed incinerator.

the Arrhenius expression:

$$k = A \exp [-E_a/RT]$$

and the three-parameter non-Arrhenius expression:

$$k = BT^n \exp [E/T].$$

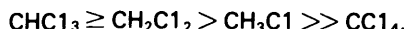
The data analyzed in this manner always exhibited non-Arrhenius kinetics with the results presented in Table 2.

Table 1. Chloromethane-OH Rate Constants as a Function of Temperature (571 to 782 K)

| Reactant | $k(10^{13} \text{cm}^3/\text{molec}\cdot\text{s})$ | $T(K)$ |
|--------------------------|--|--------|
| $\text{CH}_3\text{C1}$ | $8.38 \pm 0.296^*$ | 578 |
| $\text{CH}_3\text{C1}$ | 15.96 ± 1.31 | 687 |
| $\text{CH}_3\text{C1}$ | 24.97 ± 2.25 | 776 |
| $\text{CH}_2\text{C1}_2$ | 11.12 ± 0.590 | 580 |
| $\text{CH}_2\text{C1}_2$ | 19.83 ± 2.94 | 674 |
| $\text{CH}_2\text{C1}_2$ | 33.26 ± 4.09 | 773 |
| CHC1_3 | 14.07 ± 1.60 | 571 |
| CHC1_3 | 20.00 ± 1.46 | 680 |
| CHC1_3 | 31.73 ± 1.81 | 772 |
| CC1_4 | 1.65 ± 0.056 | 614 |
| CC1_4 | 3.54 ± 0.050 | 773 |
| CC1_4 | 5.12 ± 0.800 | 782 |

* Standard deviation in rate constant.

The rate data indicated relative OH reactivities for the chloromethanes to be:



The high temperature relative reactivities for $\text{CH}_3\text{C1}$, $\text{CH}_2\text{C1}_2$, and CHC1_3 are in accord with their gas-phase thermal stabilities under oxidative conditions. In other words, OH reactivity increases with increasing C1 substitution for the chloromethanes. This indicates that OH reactivity is more sensitive to the ease of hydrogen atom abstraction (which increases as the C1 atom substitution increases) than to the total number of abstractable H atoms present. If we extend this hypothesis to the limit of perchlorinated compounds, these results indicate a much smaller OH reactivity as compared to any of the hydrogen-containing chloromethanes. Although the C-C1 bond in CC1_4 is weaker than any C-H bond in the remaining chloromethanes, the

endothermicity of this reaction due to the low stability of HOC1 formation results in a relatively high-energy reaction pathway.

Extrapolating these results to the types of PIC's produced in the oxidative degradation of contaminated sewage sludge, perchlorinated hydrocarbons such as $\text{C}_2\text{C1}_2$, $\text{C}_2\text{C1}_4$, $\text{C}_3\text{C1}_4$, and $\text{C}_4\text{C1}_4\text{O}$, should prove more difficult to incinerate than their hydrogen containing analogs (i.e., $\text{C}_2\text{HC1}$, $\text{C}_2\text{HC1}_3$) due to the lack of abstractable hydrogen atoms. Additional PIC's believed to form from the sludge matrix, such as simple aromatics (i.e., benzene, toluene, styrene), should prove more difficult to incinerate than their chlorinated analogs because of the larger C-H bond energies.

Conclusions

Based on laboratory studies of the thermal decomposition of hazardous organic mixtures and sewage sludge spiked with various hazardous organic compounds, the following conclusions are proposed:

- Some common hazardous organic contaminants are relatively fragile and easily destroyed, but their products of incomplete combustion pose a greater incineration challenge.
- Contaminants of moderate-to-high thermal stability may be volatilized in the drying zone of multiple hearth incinerators and emitted with great efficiency.
- The thermal decomposition behavior of common hazardous sludge contaminants differed when these principal organic hazardous constituents (POHC's) were decomposed as mixtures in a sludge matrix versus as mixtures of pure compounds. The following trends were observed for the eight POHC's tested:
 - For very fragile POHC's, the sludge exerted no effect on the incinerability of the POHC.
 - For POHC's of intermediate thermal stability (most of the compounds tested), the sludge appeared to decrease the incinerability of the POHC (i.e., compound was more stable in sludge).

- For very stable POHC's the sludge increased the incinerability of the POHC (i.e., POHC was more readily destroyed in presence of sludge).
- Thermal decomposition products from the biomass itself included potentially hazardous PIC's which are on EPA's Appendix VIII list.
- Total mass emissions from the biomass are expected to be much greater than from trace contaminants.
- Interactions between the sludge and chlorinated contaminants may pose additional health risks in incineration of sludge from industrial sites.

Recommendations

The results of this study have answered some very basic questions; however, some very important questions have been raised. The following additional research is recommended:

- Conduct additional laboratory studies to explain the sludge stabilization effect on hazardous organics.
- Extend laboratory testing to other sludges and contaminants.
- Extend the laboratory analysis to include identification of volatile emissions.
- Conduct laboratory analysis of the uncombusted sludge residue to determine the chemical composition of full-scale particulate emissions.
- Conduct additional laboratory studies on the effects of sludge heating rate in both multiple hearth and fluidized bed systems.
- Utilize laboratory test data to guide future full-scale emissions testing and derive correlations between predicted versus observed emissions.
- Based on laboratory data, establish a "hit list" of suspected major incinerator emissions that would be the subject of full-scale compliance testing.
- Determine health effects of these emissions to compare with other sources for the establishment of a mass emissions regulatory standard.

The full report was submitted in fulfillment of Cooperative Agreement No. CR-811777 by the University of Dayton Research Institute under sponsorship of the U.S. Environmental Protection Agency.

Table 2. Non-Arrhenius Parameters for Chloromethane-OH Reactions

| Reactant | $B(\text{cm}^3/\text{molec}\cdot\text{s})$ | n | $E(\text{cal}/\text{mole})$ | $T \text{ Range (K)}$ |
|--------------------------|--|-----|-----------------------------|-----------------------|
| $\text{CH}_3\text{C1}$ | $5.89 \pm 1.22 \times 10^{-21}$ | 3.0 | $-145 \pm 59^*$ | 296 - 776 |
| $\text{CH}_2\text{C1}_2$ | $5.14 \pm 0.98 \times 10^{-21}$ | 3.0 | 75 ± 59 | 298 - 773 |
| CHC1_3 | $8.38 \pm 0.45 \times 10^{-21}$ | 3.0 | -70 ± 21 | 298 - 772 |
| CC1_4 | $4.56 \pm 0.80 \times 10^{-22}$ | 3.0 | 331 ± 67 | 296 - 782 |

* One standard deviation in data.

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Richard A. Dobbs is the EPA Project Officer (see below).

The complete report entitled "Potential Emissions of Hazardous Organic Compounds from Sewage Sludge Incineration," (Order No. PB 87-199 626/AS; Cost: \$18.95, subject to change)

will be available only from:

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