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# Formation and Destruction of Chlorinated Pollutants during Sewage Sludge Incineration

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The limitations facing land filling and recycling and the planned ban on sea disposal of sludge leads to the expectation that the role of sludge incineration will increase in the future. The expected increase in sludge incineration will also increase scrutiny of the main drawback to sewage sludge incineration—the formation of hazardous air pollutants (HAPs). Despite the extensive body of knowledge available on sewage sludge combustion, very few studies have been conducted on the formation of HAPs during sludge combustion. In this work, the interactions between sewage sludge pyrolysis products and sludge ash were investigated using a dual chamber flow reactor system and a horizontal laboratory scale reactor. The results of this study shows that sludge ash can catalyze oxidation and chlorination of organics. In the absence of HCl in the gas stream, sludge ash acts as an oxidizing catalyst, but in the presence of HCl, sludge ash acts as a chlorination catalyst producing high yields of organochloride compounds.

## Introduction

Wastewater treatment generates a solid residue with high organic matter content called biosolid or sewage sludge. During the past decades after the enactment of the clean water act of 1972, sewage sludge produced annually in the U.S. increased dramatically from 4.6 million dry tons in 1972 to 6.9 million dry tons in 1998 (1). In the European Union (EU) a similar trend was observed. It is estimated that in 2005 around 10 million dry tons of sewage sludge will be generated in EU. In a report by the European Environmental Agency (2), sewage sludge was identified as “a future waste problem”. Management of this quantity of sewage sludge is not an easy task. High contents of water, organic matter, and pathogen agents prohibit the possible uses of this waste.

The best application of sewage sludge is as an agricultural fertilizer. It is a good source of phosphorus and nitrogen and also increases the organic matter of the fertilizer. However, the major limitation in this use is the high concentrations of toxic metals, organic pollutants, and pathogens that can contaminate soil and crops. Environmental laws regulate that sewage sludge should meet a certain metal concentration standard before it can be used for agricultural purposes. Soon, it is expected that this regulation will also include maximum concentrations of some organic pollutants. The EU is

developing a law that will restrict concentrations of polychlorodibenzo-*p*-dioxin/furans (PCDD/F), polyaromatic hydrocarbons (PAHs), diethylhexylphthalate (DEPH), nonylphenols, and lineal alkyl sulfonates (LAS) in sewage sludge (3). A Danish study (4) shows that up to 41% of the sludge exceeds the new limitations and thus cannot be used as fertilizer. If sewage sludge cannot be used as fertilizer, then the only management technique available is land filling. Before land filling, it is desirable to dewater and stabilize the sludge to reduce its pathogen levels, odor, and organic pollutants. The primary stabilization methods include alkali (lime) stabilization, anaerobic and aerobic digestion, composting, and incineration. Incineration is sometimes classified as a disposal method, but in fact is a stabilization method because the final destination of ashes generated in incineration is the landfill.

The major advantages of using incineration as a method of sewage sludge management are the reduction of disposal volume and the total destruction of pathogen agents and organic pollutants. These benefits make incineration an important technique in sewage sludge stabilization. In 1998, around 22% of sewage sludge was incinerated in the U.S. and 21% in the EU. In the EU it is expected that incineration will increase to 40%, due to implementation of new and stricter laws for agricultural sludge use and land filling.

The main drawback of incineration is the formation of hazardous air pollutants (HAPs). Sewage sludge incineration has been identified as an important source of inorganic and organic HAPs (5). Inorganic pollutants from this source are mainly volatile metals present in the sewage sludge like cadmium and mercury. Organic pollutants identified in sludge incinerator stacks could be classified into four different groups according to the chemistry and hazardous properties: (a) partially oxidized compounds such as formaldehyde, acetaldehyde, and phenol; (b) aromatic hydrocarbons such as benzene, toluene, and PAHs; (c) small chlorinated aliphatic hydrocarbons such as chloromethane and dichloroethylene; and (d) dioxin-like compounds. The last group generates the most interest because these compounds have shown a high mutagenic activity. In a recent communication of the U.S. EPA (Toxics Release Inventory program (6)), it is estimated that by 2004 dioxin emissions from sewage sludge incineration will be higher than municipal waste and medical waste incineration. The exhaust gas from a sludge incineration plant has already been shown to have mutagenic activity (7), however, at a lower level than that observed from exhaust gas of a municipal solid waste (MSW) incineration plant.

Several researchers have investigated the formation of HAPs from sewage sludge combustion (8, 9) in laboratory furnaces. These investigations show that combustion of sewage sludge generates a considerable amount of chloroaliphatics, chlorobenzenes, phenols, and nitrogenated compounds. Fullana et al. studied sewage sludge emissions under pyrolytic conditions and observed similar classes of compounds (10). In all studies formation of organics was investigated at high temperatures, and the pollutant formation due to interactions between products of incomplete combustion and sludge ash were ignored. Heterogeneous catalysis in the postcombustion zone is considered one of the most important factors in pollutants formation. Ashes present in this zone can catalyze reactions such as partial oxygenation, chlorination, and condensation that are necessary for the formation of most of the HAPs. PCDD/Fs are a typical pollutant formed due to heterogeneous reactions in the postcombustion zone. The major pathways of PCDD/F formation are condensation of chlorophenols, partial oxida-

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TABLE 1. Chemical Composition of Sewage Sludge<sup>a</sup>

component	wt%, dry fuel (free of ash)	component	wt%, dry fuel (free of ash)
H <sup>b</sup>	9.8	N <sup>b</sup>	1.6
C <sup>b</sup>	59.8	S <sup>b</sup>	<1
component	ppm, dry sewage sludge	component	ppm, dry sewage sludge
B <sup>b</sup>	260	Ba <sup>c</sup>	370
Na <sup>c</sup>	600	Pb <sup>c</sup>	1100
Se <sup>d</sup>	200	V <sup>d</sup>	100
Sn <sup>d</sup>	500	Mn <sup>c</sup>	300
component	wt%, ash (calculated)	component	wt%, ash (calculated)
Si <sup>d</sup>	10.6	Ni <sup>c</sup>	0.95
Al <sup>c</sup>	1.51	Mg <sup>c</sup>	0.43
Ca <sup>c</sup>	15.3	Zn <sup>c</sup>	1.73
Pd <sup>d</sup>	10.4	Sr <sup>c</sup>	0.61
Cu <sup>c</sup>	2.81	K <sup>c</sup>	0.22
Cr <sup>c</sup>	0.65	Ti <sup>d</sup>	0.47
Fe <sup>c</sup>	10.2	Cl <sup>d</sup>	0.39

<sup>a</sup> Ash content = 46.2%. <sup>b</sup> Analyzed by elemental analysis. <sup>c</sup> Analyzed by ICP previous digestion with HNO<sub>3</sub>. <sup>d</sup> Analyzed by X-ray fluorescence.

tion of carbon (de novo), and ash catalyzed chlorination of precursors (11). Gas–solid interactions do not always lead to pollutant formation; under certain conditions, metals present in ashes can also act as oxidation catalysts and therefore destroy pollutants. Weber et al. (12) studied this destructive effect of fly ash (from MWI) and concluded that when fly ash has a high concentration of metals and chlorine content of waste is low, fly ash can destroy PCDD/Fs. In sewage sludge incinerators such as the multiple-hearth furnaces and fluidized bed combustors, there is a strong interaction between gases and solids, which can lead to the formation and destruction of organic pollutants in sewage sludge. However, no studies have been conducted to investigate the impact of these gas–solid interactions on pollutant emissions. The present study attempts to address this question by investigating the catalytic activity of sewage sludge ash.

## Material and Experimental Apparatus

The sewage sludge used in this study was obtained from an urban wastewater plant located in Alicante (Spain). This plant works with a physical-chemical method, and the sludge was treated with chemical softening and mechanical dehydration. As shown in Table 1, this sewage sludge contains a high concentration of metals. As a result, it cannot be used as fertilizer; the easiest method of disposal is incineration. The sewage sludge used in this study was dried and ground into fine particles before it was used in experiments.

The majority of the experiments in this study were conducted using a dual chamber flow reactor assembly. The experimental design of this system is based on the fact that most organics pollutants (also called products of incomplete combustion) that take part in postcombustion gas–surface reactions are formed in “pyrolytic pockets” in the main combustion chamber (10). The schematic diagram of the experimental apparatus used is given in Figure 1a. The first chamber was operated at high temperature under pyrolytic conditions, and the second chamber was operated at postcombustion zone conditions (temperatures ranged from 300 to 500 °C). During an experiment, sludge was introduced in the first chamber and pyrolyzed in helium atmosphere by increasing the chamber temperature from ambient to 725 °C at a heating rate of 50 °C/min. The effluent from the first chamber then entered the second chamber (0.7 cm i.d. quartz

reactor), which was held at a fixed temperature to study the interaction between organic compounds generated by pyrolyzing sludge in the first chamber and the sludge ash particles. A 2 cm long fixed bed of catalytic particles was held in place by quartz wool plugs inside the second chamber; the residence time of gases in the fixed bed was in the range of 2–3 s. Approximately 150 mg of sewage sludge was pyrolyzed in the first chamber, and the pyrolysis products passed through a fixed bed composed of 50 mg of catalytic material in the second reactor chamber. The effluent from the first chamber was mixed with air to create 4% O<sub>2</sub> in the reaction environment of the second reactor chamber. All transfer lines in the reactor system were maintained at 250 °C.

Selected experiments were conducted on a horizontal laboratory scale reactor (Figure 1b). In this reactor system the sample (sludge) is introduced into the reactor at 850 °C in a quartz boat into an air atmosphere. Gases evolved go through a catalyst that has been placed in the post-combustion zone where temperature is between 300 and 500 °C. Figure 1b shows a schematic diagram of a reactor with the temperature profile.

Interactions between solid (catalyst) and gaseous sludge pyrolysis products were investigated using four different catalytic materials. The first catalyst was the ash from sewage sludge combustion. Ash is combusted to destroy all organic carbon that may be able to form pollutants. This ash was generated by combusting the sludge at 600 °C for 12 h. The second catalyst used was ash with CuCl<sub>2</sub>, which was generated by mixing combusted ash with CuCl<sub>2</sub> to 4 wt % in Cu. The third catalyst was ash with CuO. This material was generated by combusting sewage sludge at 600 °C for 12 h with Cu(NO<sub>3</sub>)<sub>2</sub> in such a way that the resultant ash contained 4% (by weight) CuO. The fourth catalyst was CuCl<sub>2</sub> impregnated in quartz wool.

In both systems, dual chamber reactor and horizontal reactor, the effluent was trapped on an adsorbent trap (Amberlite XAD-2). After each experiment, the adsorbent trap was extracted (Soxhlet Extraction) with methylene chloride for 18 h, then concentrated, and analyzed using GC-MS. In dual chamber reactor experiments chlorophenols, chlorobenzenes, polychlorobiphenyls (PCB), and polychloronaphthalenes (PCN) were quantified in selected ion mode. Analytical standard calibration curves were used to obtain quantitative response factors for each congener.

In the runs performed on the horizontal laboratory scale reactor, semiquantitative analysis of the same compounds was done in scan mode. Identification of compounds was done using library NIST, and the quantification was done using a response factor of deuterated internal standards spiked before extraction (EPA Method 8270). A high-resolution gas chromatograph and mass spectrometer (HRGC–HRMS

AutoSpec NT) apparatus equipped with a Hewlett-Packard GC was used for dioxin and furan analysis. The spectrometer was operated in the electron impact ionization mode at 10 000 resolving power. For PCDD/F analysis, <sup>13</sup>C-labeled PCDD/F standards (Wellington Labs, Canada) were used. Quantitative determination was performed by the isotope dilution method based on the relative response factors previously obtained from three standard solutions (EPA1613-CS1, CS2, and CS3).

## Results and Discussion

In the preliminary stages of this research, two runs were made in the horizontal reactor gas comparing the effluent from sludge combustion with and without ash interaction. Ashes from sewage sludge have high concentrations of transition metals, which are known chlorination catalysts, and their presence was expected to increase the yield of chloro-organic compounds in the effluent gas. However, GC/

TABLE 2. Experiment Performed in Dual Chamber Reactor

series	run name	catalyst	temperature furnace	HCl in gas stream
first and second	C0-300	none	300	no
first	C1-300	ash	300	no
first	C1-400	ash	400	no
first	C1-500	ash	500	no
second	C2-300	ash+CuCl <sub>2</sub>	300	no
second	C2-400	ash+CuCl <sub>2</sub>	400	no
third and fourth	C2-500	ash+CuCl <sub>2</sub>	500	no
third	C0-300HCl	none	300	yes
third	C1-300HCl	ash	300	yes
third	C1-400HCl	ash	400	yes
third	C1-500HCl	ash	500	yes
fourth	C3-300HCl	ash+CuO	300	yes
fourth	C3-400HCl	ash+CuO	400	yes
fourth	C3-500HCl	ash+CuO	500	yes

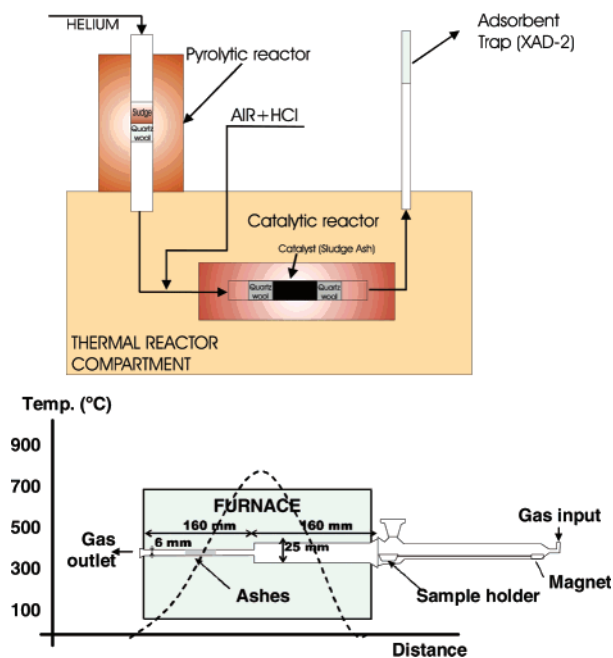


FIGURE 1. Schematic of experimental systems: (a) dual chamber reactor and (b) horizontal laboratory scale reactor.

MS scan analysis was unable to identify any significant differences between both runs. Even more unexpected were the PCDD/F analyses, which showed a decrease in PCDD/Fs yield as consequence of gas/solid interaction. The run catalyzed with sludge ash had two times fewer PCDDs and twenty times fewer PCDFs. To explain these unexpected results, the experiments listed in Table 2 were designed and conducted in the dual chamber reactor. These experiments were divided into four series. In the first series, the effect of ash was investigated at 300, 400, and 500 °C. In the second series, ash with CuCl<sub>2</sub> was used as a catalyst. The reason for adding CuCl<sub>2</sub> was to increase the copper and chlorine content of the ash to create additional C-Cl bonds. For the third series, we used the ash from the first series of experiments, but the reaction gas in the second chamber contained 1500 ppm of HCl. HCl as a source of chlorine was also included in the air stream of the fourth series of experiments. In the fourth series, ash with CuO was used as a catalyst.

In all of the experiments, only chlorinated and non-chlorinated phenol, biphenyl, and naphthalene were analyzed using the selective ion mode. Only chlorinated benzenes were analyzed, since non-chlorinated benzene was too volatile to be trapped in the XAD-2 resin. Results from the

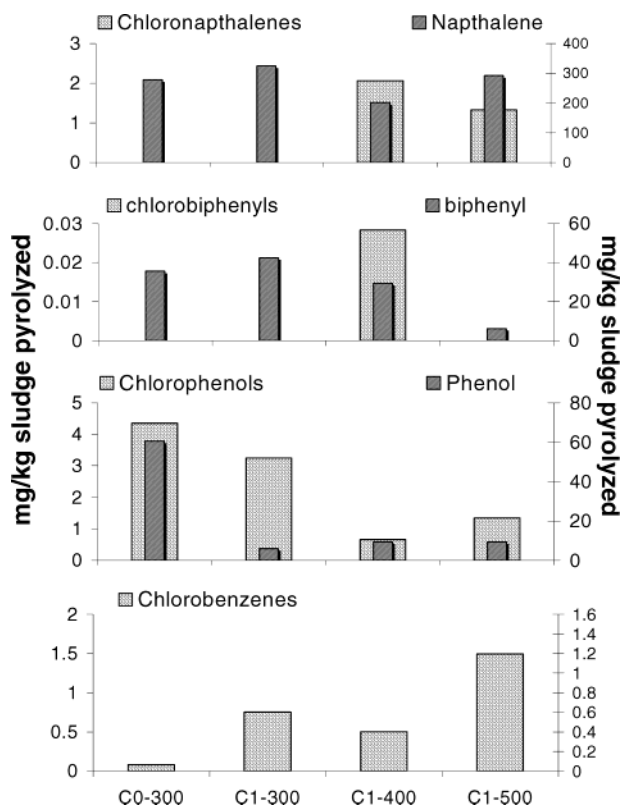


FIGURE 2. Yield of analyzed compounds in the first series of experiments. Left axis is for chlorinated compounds and right axis for non-chlorinated.

first series of experiments conducted in the dual chamber reactor are shown in Figure 2. Despite the low concentration, phenol and chlorophenols exhibit different behavior than other pollutants. Chlorophenol yields at 400 and 500 °C are lower than those at 300 °C and lower than those without ash. Also, the non-chlorinated phenol shows a decrease in yield in the presence of ash, while the other pollutants analyzed (except naphthalene at 500 °C) do not exhibit this behavior under the conditions of this study. A possible explanation for the behavior of chlorophenols is the dual activity of ash as oxidizing and chlorinating catalyst. Chlorophenols adsorb strongly to the ash surface due to the presence of hydroxyl-groups that react through the elimination of water to form surface-bound phenoxylates (13). These phenoxylates are intermediates in oxidative catalytic reactions that result in the destruction of chlorinated and non-chlorinated phenols. The structure of the other pollutants prevents them from strongly adsorbing on the ash surface and consequent destruction by catalytic oxidation. For these compounds, the dominant catalytic reaction is chlorination.

This difference in the reactivity of phenols and other pollutants on the catalytic surface was also observed by Born et al. (14). They conclude that in the presence of fly ash at 400 °C, phenol is oxidized mainly to CO<sub>2</sub>, whereas benzene is quasi inert under these conditions. In the second series of experiments, when CuCl<sub>2</sub> was added to the ash, a significant increase in yield of chlorinated compounds was observed (see Figure 3). These results were expected because CuCl<sub>2</sub> is a strong chlorinating agent. From these data, it is important to note that the chlorination effect is less important in the case of phenol, as its yields are only three times higher than experiments without the catalyst, and they further decrease at 400 and 500 °C. This shows an important effect of the catalytic oxidation of ash even when CuCl<sub>2</sub> is present, especially at high temperatures when copper will mainly be present as an oxide. Another interesting result in this series



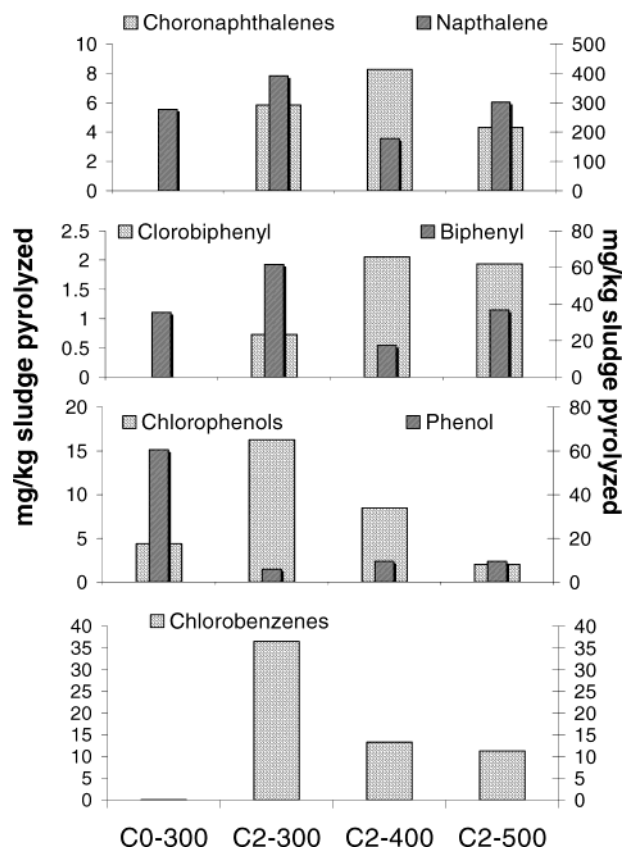


FIGURE 3. Yield of analyzed compounds in the second series. Left axis is for chlorinated compounds and right axis for non-chlorinated.

is the behavior of chlorobenzenes with temperature. The yield of chlorobenzenes decreases with increases in temperature, exhibiting a trend similar to chlorophenols. But this behavior is not observed in chloronaphthalenes and chlorobiphenyls. This change in the behavior of chlorobenzenes is probably due to the presence of chlorine from the decomposition of  $\text{CuCl}_2$ . It has been shown that in the presence of chlorine, benzene can be converted to phenol (15), and the phenol formed is easily oxidized by the ash. The effect of HCl on the formation of chlorinated pollutants was investigated in the third series of experiments. HCl by itself is not a good chlorinating agent, but in the presence of a catalyst and oxygen, HCl can oxidize through the Deacon reaction to  $\text{Cl}_2$ , which is a strong chlorinating agent. HCl can also chlorinate metals and metal chlorides can chlorinate organics. The results of the third series of experiments (in Figure 4) show that the addition of HCl increases the yields of chlorinated compounds. This shows that ash metal is getting chlorinated and also perhaps catalyzing the formation of  $\text{Cl}_2$  via the Deacon process. In this series, chlorination increased with temperature for all compounds; this result agrees with the Deacon process, which shows an increase in oxidation of HCl with temperature. In this series, the phenol yield remains almost constant at all temperatures, which is indicative of the low phenol oxidation rate. This is an interesting result because it shows that the presence of HCl decreases the oxidation activity of ash probably by chlorine occupying all active sites. To further investigate the role of copper in chlorination/oxidation phenomena, ash with CuO was used in the fourth series of experiments. In these experiments, the yield of chlorinated compounds was lower than those observed in the experiments with ash + HCl only. The results of the fourth series (Figure 5) shows that Cu is destroying phenol at 400 and 500 °C and is also destroying chlorobenzenes at 500 °C. The yield of choronaphthalene at 500 °C is also lower in this fourth series when compared to

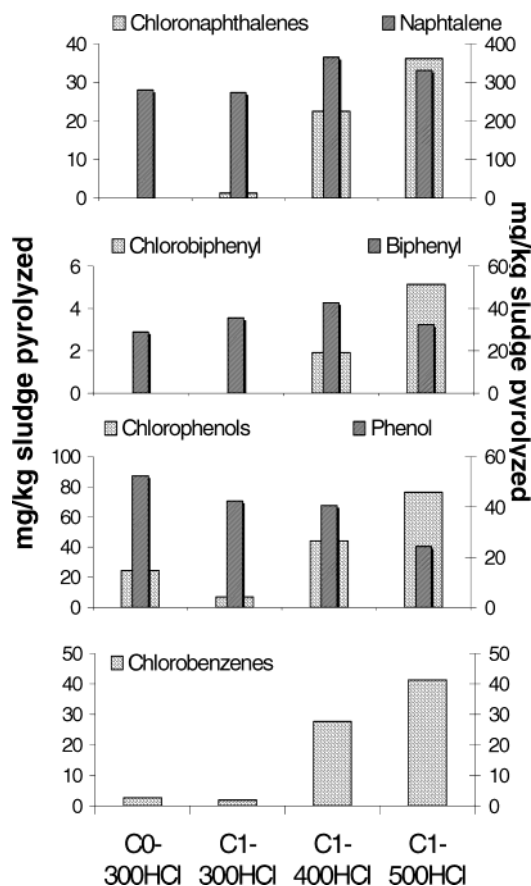


FIGURE 4. Yield of analyzed compounds in the third series. Left axis is for chlorinated compounds and right axis for non-chlorinated.

the third series of experiments. The yield of chlorobiphenyls is quite similar in both the third and the fourth series at 500 °C. These results indicate that Cu acts as an oxidation catalyst at higher temperatures (400–500 °C). However, the extent of oxidation is dependent on the structure of the pollutant. To better understand the formation mechanism of chlorinated pollutants, the isomer patterns of chlorobenzenes and chlorophenols were also analyzed. In all sets of experiments, chlorobenzenes with adjacent chlorine groups had the highest yield. Figure 6 shows a typical distribution for both chlorobenzenes and chlorophenols. The chlorobenzene and chlorophenol patterns observed in our experiments are very similar to those obtained by Froese and Hutzinger when they passed ethylene/HCl mix over fly ash (16, 17). This is consistent with the hypothesis that sludge organics that are evolved during pyrolysis are mainly small aliphatic compounds such as ethylene, and in the presence of HCl and sludge ash in the second chamber these aliphatic compounds chlorinate and condense to form chlorinated pollutants. The chlorobenzene pattern obtained by Milligan (and Altwicker) for de-novo synthesis is different than the ones observed in our experiments (18). In de-novo synthesis, low concentration of hexachlorobenzene and pentachlorobenzene was obtained, whereas in our experiments, the major chlorobenzene product is hexachlorobenzene. Zimmerman et al. have also observed chlorobenzene patterns similar to ours in incinerator flue gas after the incinerator was operated under fuel-rich conditions (19).

To conclude this study, two experiments were conducted in the horizontal reactor. In the first experiment, ash in the presence of HCl was used as a catalyst. In the second experiment, the catalyst used was  $\text{CuCl}_2$  impregnated on glass wool. Table 3 shows yields of chlorinated and non-chlorinated products in these runs. A high yield of chlorinated products

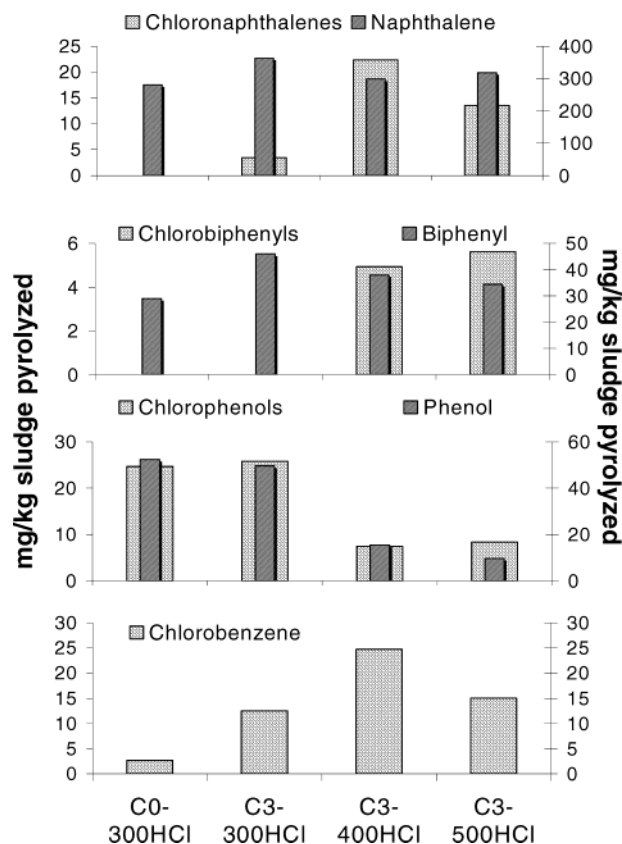


FIGURE 5. Yield of analyzed compounds in the fourth series. Left axis is for chlorinated compounds and right axis for non-chlorinated.

was observed in both experiments, but there were also some differences: with only  $\text{CuCl}_2$  no chlorophenols were observed, but 85 ppm of chlorophenols were observed in the runs performed with ash + HCl. This result agrees with the behavior described in the discussion of dual chamber reactor results; i.e., the presence of Cu increases oxidation of phenols and chlorophenols. PCDD/F yields were also analyzed for these experiments. Figure 7 illustrates the yields of PCDD/F from the four experiments conducted on the horizontal reactor. Ash in the postcombustion zone reduces yields of PCDD/F, but the presence of HCl enhances formation of PCDD/F. It is interesting to note that in the experiments with ash + HCl, the amount of PCDD is higher than PCDF (PCDF/PCDD=0.03), whereas for the  $\text{CuCl}_2$  experiment, the reverse is true. A possible explanation for these results is in the behavior of chlorophenols. Condensation of chlorophenol on ash leads to the formation of more PCDD than PCDF. In experiments with  $\text{CuCl}_2$ , Cu catalyzes the oxidation of chlorophenols and not condensation that leads to formation of PCDD. In the case of ash+HCl, however, the presence of HCl and absence of extra Cu decreases the chances of

TABLE 3. Yields<sup>a</sup> of Chlorinated and Nonchlorinated Compounds in Horizontal Reactor Runs

	no catalyst	Ash+HCl	$\text{CuCl}_2$
non-chlorinated compounds	12000	2100	400
phenol	190	5	nd
naphthalene	2900	440	10
biphenyl	120	240	nd
other	11400	1400	390
chlorinated compounds	nd	1800	1300
chlorobenzenes	nd	44	97
chlorophenols	nd	86	nd
chloronaphthalenes	nd	410	890
clorobiphenyls	nd	160	77
others chlorinated compounds	nd	1100	250

<sup>a</sup> mg/kg sludge pyrolyzed.

chlorophenol oxidation, making chlorophenol condensation an important process. It is difficult to pinpoint the exact reason for the increase of PCDF in  $\text{CuCl}_2$  experiments, but it is possible that chlorine from the decomposition of  $\text{CuCl}_2$  directly chlorinated non-chlorinated dibenzofuran (20).

Even though there are several differences between the two reactor systems used in this study, the experiments in the dual chamber reactor system are able to explain the results from the horizontal reactor system. The first series of experiments in the dual chamber reactor shows the oxidative catalytic effect of ash on phenols, which is perhaps responsible for the reduction in PCDD/F yields observed in horizontal reactor system. The second series of experiments shows that  $\text{CuCl}_2$  can chlorinate the pyrolytic products, which suggest that the increase of PCDFs in the horizontal reactor could be due to chlorination of dibenzofuran. The third and fourth series of experiments in the dual reactor system shows how HCl can increase the survival of phenols (and chlorophenols), thus increasing PCDD formation, which explains the variation of PCDD/F ratio in the horizontal reactor.

**Industrial Implications.** The results of this study show that when the concentration of HCl in the incinerator is low, ash from sewage sludge combustion catalyzes the destruction of phenols and thus decreases the formation of PCDD/Fs in the postcombustion zone. Therefore, in cases where the chlorine content of the sludge is low, combustor designs that increase contact between ash and flue gas are desired. However, when HCl is present, ash becomes more dominant as a chlorination catalyst. In this case, a combustor should be designed to minimize contact between flue gas and ash. It is important to consider the results of this study when discussing coincineration of sewage sludge with municipal waste. Coincineration has been considered a possible solution to reduce the cost of sewage sludge because municipal waste can generate sufficient energy for drying sludge, thus avoiding the expense involved in using fossil fuels. Addition of sludge to municipal waste will not only change the fuel composition

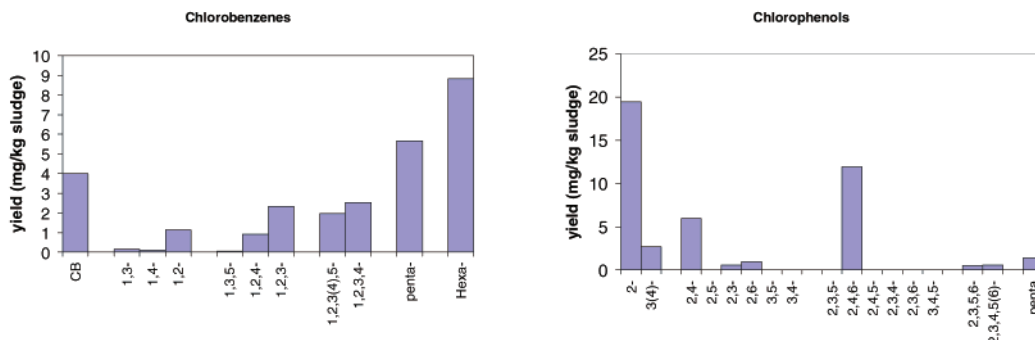


FIGURE 6. Isomer patterns for the ash/HCl experiments at 400 °C: (a) chlorobenzenes and (b) chlorophenols.

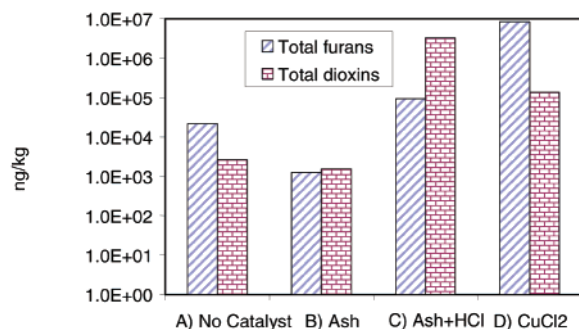


FIGURE 7. PCDD/F yields in experiments in the horizontal laboratory scale reactor.

(S/Cl ratio) but will also change reaction conditions (higher particle loading). An increase of S/Cl ratio due to sulfur present in sewage sludge can inhibit formation of chlorinated pollutants by generating  $\text{SO}_2$  which can convert the chlorine formed via the Deacon reaction back to HCl. This will slow chlorination process as HCl is a much poorer chlorination agent than chlorine. The sulfur oxides can also react with transition metals to form transition metal sulfates thus competing with the formation of transition metal chlorides which are known catalysts for chlorination reactions. Werther and Ogada (21) suggest that the relative lower PCDD/F concentration (in comparison with municipal waste incineration) in sewage sludge was perhaps due to the high concentration of sulfur in sewage sludge. However, the addition of sludge will also lead to an increase in particle (ash) loading in the postcombustion zone which can lead to higher pollutant emissions. Both of these opposing effects due to sludge additions should be considered before a decision is made to coincinerate sludge and municipal waste.

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