Effect of Soot and Copper Combustor Deposits on Dioxin Emissions

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ABSTRACT

An experimental study was conducted to investigate the effects of residual soot and copper combustor deposits on the formation of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) during the combustion of a chlorinated waste. In a bench-scale setup, distillate fuel oil doped with copper compounds was fired under sooting conditions in a quartz reactor heated by a Linberg furnace to 900°C. Soot- and copper-containing aerosols were carried by the hot flue gas and deposited on a separate quartz "deposition" tube connected to the exit of the quartz reactor. Selected experiments were also conducted to deposit either soot or copper on separate quartz deposition tubes. In a separate setup, 1,6-dichlorohexane was injected into a natural-gas-fired furnace reactor to produce a flue gas that contained 6.2% oxygen, 8.6% carbon dioxide, 10–50 ppm carbon monoxide, and 500 ppm hydrogen chloride. The deposition tubes were separately attached to the furnace reactor and a flue gas slip stream was passed through the tubes into a PCDD/F sampling train. The deposition tubes were maintained at 320°C by an electrical heating tape. Sulfur dioxide (SO_2) was injected near the flame zone of the furnace reactor in selected experiments. High levels of PCDD/Fs were measured at the exit of the deposition tubes containing both soot and copper deposits. No PCDD/Fs were found during experiments using a tube with only soot deposits, and trace amounts of PCDD/Fs were found with a deposition tube containing only copper deposits. Repeated experiments with the same deposition tube containing soot and copper deposits resulted in reductions in the amount of PCDD/Fs formed, indicating decreased formation with time. Significantly lower PCDD/F emissions were measured from the experiments with SO_2 injection, indicating that SO_2 is effective in suppressing PCDD/F formation reactions. It was also found that a deposition tube previously exposed to flue gases from 1,6-dichlorohexane incineration exhibited residual PCDD/F formation reactions when exposed to flue gases from the combustion of natural gas. The results demonstrate that the combustor deposits containing copper and soot can cause "memory effects" that can play an important role in the emissions of PCDD/Fs from commercial incinerators.

Key words: Chlorinated waste incineration; dioxin emissions; soot and copper deposits; wall effects; memory effects

INTRODUCTION

POLYCHLORINATED DIBENZO-*P*-DIOXINS (PCDDs) and polychlorinated dibenzofurans (PCDFs), collectively known as dioxins, are of concern because of their persistence and wide distribution in the environment, and the high toxicity of some individual compounds. The emission of PCDD/Fs from waste incineration has been considered the major anthropogenic source of PCDD/Fs (U.S. EPA, 1994). However, there is a major imbalance between the atmospheric deposition of PCDD/Fs and known emission sources that is significantly attributed to poor characterization of PCDD/F sources (Brzuzy and Hites, 1996). PCDD/F emission sources are difficult to characterize as there are many interacting variables, such as the composition of the material combusted, the design and operating conditions of the combustion process, and the design and operating condition of flue gas cleaning equipment—all of which influence PCDD/F emissions (Miles et al., 1987). A complex interaction of surface-induced catalysis, aromatic ring formation, and chlorination countered by destruction and dechlorination reactions occurring in the postcombustion region from components of unburned organics, chlorine, and catalysts can result in dioxin formation (Addink and Olie, 1995). Research would improve the characterization of a wide variety of PCDD/F emission sources, which constitutes an important component in developing strategies for controlling and reducing their emissions.

With the exception of municipal solid waste (MSW) combustion, little is known about the PCDD/F emission characteristics of other sources. Results of characterization studies on MSW combustion in the field indicate that the emissions are strongly associated with high entrainment and carryover of fly ash into the cooler regions of the combustor, including particulate capturing devices such as baghouses and electrostatic precipitators, with fly ash playing a critical role in providing the catalytic surfaces and/or sources of unburned organics required for PCDD/F formation (Kilgroe, 1996). However, in a recent study of characterizing PIC (products of incomplete combustion) emissions from incineration of chlorofluorocarbons (CFCs) using a bench-scale combustor that had been used for incineration of wastes containing many different metals including copper, high PCDD/F emissions were observed from CFC incineration that generated no fly ash (Hassel, 1991). Follow-up tests confirmed that PCDD/F emissions increased significantly when CFC was incinerated in a combustor that had been fired with a copper-containing fuel prior to CFC incineration (Lee et al., 1996). Significantly lower PCDD/F emissions observed from repeated experiments using a pilot scale combustor after refractory replacement, compared to those measured from the original unit under similar operating conditions, suggest that recent facility history has an effect on PCDD/F emissions (Gullett and Raghunathan, 1997). The "memory" effect, i.e., that wall deposits accumulated on the cooler regions of the combustor play a role in promoting dioxin formation, has been suspected of causing PCDD/F emissions from many field units.

A study of the combined effect of combustor deposits containing both soot and trace levels of copper on PCDD/F formation during chlorinated waste incineration is reported in this work. A strong promotional effect, similar to that observed from CFCs, for chlorinated wastes in general will have a significant implication, as large quantities of chlorinated wastes are disposed of by incineration. Commercial incineration facilities are used for treating a wide variety of industrial wastes that often contain metals. Trace levels of copper may be deposited on cooler regions of the combustor when a waste containing copper is incinerated, and soot is the most common deposit found in combustion systems. The strong catalytic effect of copper on dioxin formation is well documented (Hagenmaier et al., 1987; Stieglitz et al., 1989a; Gullett et al., 1990), and soot has also been implicated in dioxin formation (Stieglitz et al., 1989a,b). Sulfur dioxide (SO_2) has been shown to inhibit PCDD/F formation in MSW combustion applications (Raghunathan and Gullett, 1996). Research is needed to better understand the role of combustion-generated wall deposits on the PCDD/F emissions from chlorinated waste incineration and to inhibit their formation.

In this work, copper and soot aerosols, generated by firing a copper-containing fuel under fuel-rich conditions in a bench-scale combustion unit, were passed to and deposited on the inner surface of a clean quartz tube connected to the unit. Incineration experiments on a surrogate chlorinated waste were conducted using a pilot scale combustor. A slip stream of the flue gas produced from the surrogate waste incineration was passed to the quartz tube deposited with soot and copper previously, and PCDD/Fs were sampled at the end of the tube under controlled residence time and temperature conditions. Tests were conducted to evaluate the effects of soot (produced by oil or natural gas firing) and copper (inorganic and organic), and the presence of SO_2 in suppressing PCDD/F formation promoted by the wall deposits. Overall results have been presented elsewhere (Raghunathan, et al., 1977), and detailed discussions are presented in this paper.

EXPERIMENTAL

The experiments conducted in this study involved two separate steps: (1) a deposit generation step in which soot,

copper, or a combination of soot and copper from a small quartz laboratory reactor was deposited on the interior of a clean quartz tube; and (2) a formation step in which flue gas from a pilot scale combustor was passed through each of the deposition tubes and collected in a PCDD/F sampling train for subsequent analysis.

Preparation of Tube Deposits

The deposit generation system (Fig. 1) consists of a quartz reactor constucted of two concentric tubes, 1 m in length. The inside diameters (ID) of the outer and inner tubes are 25 and 5 mm, respectively. The reactor is contained in a Linberg electrical furnace and maintained at 900°C. Air is introduced in one end of the outer tube and is preheated as it flows through the Linberg furnace. Deposit substances are introduced into the entrance of the inner tube where it mixes and reacts with the preheated air as it passes through the Linberg furnace in a direction opposite to the outer air flow. In the deposition step, a clean quartz tube (150 cm in length and 25 mm ID) was connected to the exit of the reactor. The tube was wrapped with electric heating tape and maintained at 120°C to prevent moisture condensation. The deposition step for each test was carried out for about 45 min, and a thin layer of the deposition substance was coated on the inside of each of the deposition tubes.

Baseline tube deposits were prepared by injecting an aqueous solution of $Cu(NO_3)_2$ into the reactor maintained at a temperature of 900°C. Thermodynamic equilibrium calculations predict that the $Cu(NO_3)_2$ will be decomposed and converted to oxides of copper that can be deposited on the walls of the downstream deposition tube. A suspension containing Cu_2O powder in no. 2 fuel oil was prepared for the first series of combustion deposi-

tion tests. The Cu_2O/fuel oil mixture was stirred continuously to keep the particles in suspension. The mixture was metered by a peristaltic pump, sprayed with the aid of nitrogen, and injected into the inner tube of the reactor at a rate of 0.8 ml/min. During deposition the burner was run under fuel-rich combustion conditions with and without the addition of Cu_2O.

A third deposition method was used with the combustion of natural gas. In this method, CH_3OH was used as a suspension agent for CuO. CH_3OH was used for the suspension agent because the combustion of CH_3OH does not generally produce soot. Natural gas was used as the sooting fuel. CuO was used instead of Cu_2O because it forms a better suspension in CH_3OH. The natural gas was introduced through the annular space formed by an additional outer concentric tube placed around the CH_3OH atomizer. The fourth method used to generate deposits was to burn a solution of CuNph, an organic copper compound, in no. 2 fuel oil. The solution was prepared by dissolving CuNph (8% copper by weight) in no. 2 fuel oil to make up a solution containing 0.5% copper by weight. During the deposition step the solution was injected into the reactor at a rate of 0.8 ml/min for 45 min.

PCDD/F Formation Experiments

The formation portion of the experiments was conducted with EPA's pilot scale innovative furnace reactor (IFR). The IFR, shown in Figure 2, is a down-fired, refractory-lined, cylindrical unit that is 3 ml long with an ID of 20.3 cm. It can be fired with natural gas, fuel oil, or coal at a nominal capacity of 49 kW. A detailed description of the facility can be found elsewhere (Raghunathan and Gullett, 1996). For this study the IFR was fired with natural gas at a constant firing rate of 29 kW.
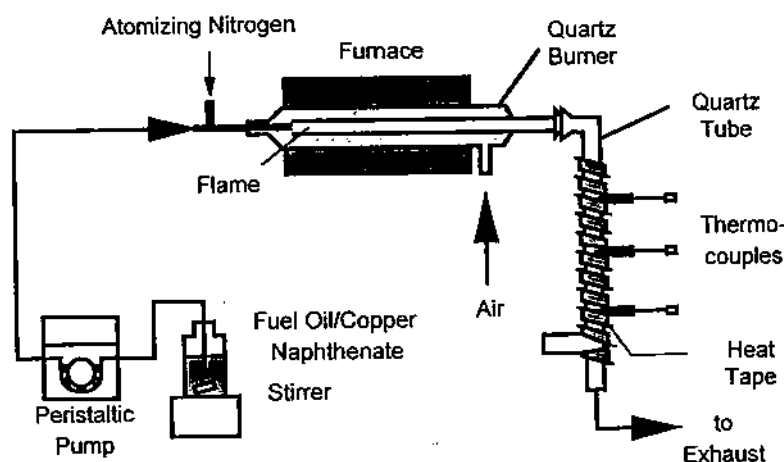

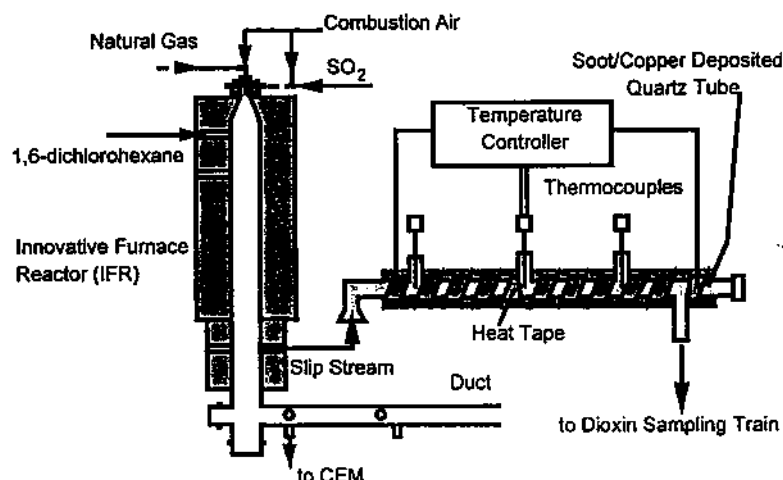FIG. 1. Experimental setup for conducting the deposition experiments.

FIG. 2. Experimental setup for conducting the PCDD/PCDF formation experiments.

During tests simulating the combustion of chlorinated wastes, 1,6-dichlorohexane (DCH) was injected into the IFR just below the burner. The rate of DCH injection, 1.0 ml/min, was controlled by a Perkin-Elmer Series 10 liquid chromatography pump to provide a hydrogen chloride (HCl) concentration of 500 ppmv in the flue gas. Two test were conducted to study the effect of SO_2 in inhibiting PCDD/F formation. During these tests gaseous SO_2 was injected near the burner at a rate needed to yield SO_2 flue gas concentrations of 600 ppmv.

During each of the formation tests, a deposit-coated tube was connected to the last port in the vertical section of the IFR and a slip stream was drawn through the tube port in a PCDD/P sampling train (see Fig. 2). The temperature at the last port is approximately 600°C. The tube was maintained at 320°C by a temperature controlled electrical heating element. An EPA Method 23 (1991) train was connected to the end of the tube for PCDD/F sampling. The flue gas was monitored during each test for oxygen (O_2), carbon dioxide (CO_2), and carbon monoxide (CO) concentrations using continuous emission monitors (CEMs). Input flows of natural gas, combustion air, and SO_2 were monitored using rotameters.

At the beginning of each formation test involving DCH injection, the IFR was fired with natural gas only, whereas the tube coated with deposits was connected to the IFR and flushed with the chlorine-free flue gas for about 1 h. Then, the flue gas flow through the tube was shut off and DCH was introduced into the IFR. After 45 min of DCH injection, the IFR slip stream was allowed to pass through the tube into the Method 23 sampling train. Sampling runs were typically 1 h in duration. The residence time of slip stream flue gas in the tube was approximately 2 s.

The collected PCDD/F samples were analyzed by high-resolution gas chromatography/low-resolution mass spectrometry (HRGC/LRMS) using a modification of EPA Method 23 (1991). This modified method differs from the Method 23 in that LRMS is used instead of high-resolution MS, and only the total amount of each homolog group is reported. In addition, the samples were analyzed for the mono- to tri-congeners as well as the tetra through octa congeners that are specified in Method 23. Selected isotopically labeled internal standards were used to aid in quantification of each of the homolog groups. The mono- to tri-congeners were included in the analyses to provide interprefative information to PCDD/F formation mechanisms.

RESULTS AND DISCUSSION

The deposition and IFR test conditions for each of the PCDD/F formation tests are summarized in Table 1. Good combustion conditions were achieved during all the tests as indicated by the low CO emissions, which ranged betwen 9 and 41 ppmv. Results of PCDD/F analyses for each of the formation tests are presented in Table 2. It should be noted that some of the PCDD/F congener concentrations were over the calibration range of the analytical method; therefore the values reported are considered semiquantitative, but they are sufficient for comparison between different tests. The data in Table 2 include values for: total tetra- to octa- PCDD; total tetra- to octa-PCDF; the sum of total tetra- to octa-PCDD and PCDF; total mono- to octa-PCDD; total mono- to octa-PCDF; and the sum of total mono- to octa-PCDD and PCDF. In general, the mono- to tri-congeners accounted for a small fraction of the total PCDD and PCDF yields. Unless otherwise noted, numerical values used in de-

scribing the formation experiments will refer to the values for the total of the mono- to octa-congeners.

The term not detected (ND) is used in Tests 1–3 to describe test results where the PCDDs, PCDFs, or PCDD/Fs were below instrument detection limits (i.e., with a signal-to-noise ratio <2.5). Sample-specific method detection limits were not determined. Estimated total PCDD/F concentrations at the detection limit were determined based on a theoretical instrument detection limit for a single isomer in each congener. These estimated concentations were at least several orders of magnitude below those concentrations presented in Tests 4–12. Numerical values are not presented for tests where PCDD/Fs were not detected. According to Method 23, nondetects are reported as zeroes.

Test 1 was performed with a clean quartz tube without deposits. A quartz tube with only copper deposits from the thermal decomposition of $Cu(NO_3)_2$ was used for Test 2. (A thin layer of dark red deposit, presumably copper oxides, was found on the inner surface of the quartz tube after the deposition step.) A quartz tube with soot deposits from the combustion of no. 2 fuel oil was used for Test 3 (no copper compound was added to the fuel oil). The results, shown in Table 2, indicate that a clean tube (Test 1) or a tube coated with soot alone (Test 3) produced no PCDD/Fs when flue gas generated from DCH incineration was passed through the tube. The tube coated with copper alone (Test 2) produced no PCDDs and only negligible quantities of PCDFs (5 ng/dcm total PCDFs). A preliminary test was conducted prior to Test 1 to sample for PCDD/Fs at the same port where a slip stream of the flue gas generated from the IFR was diverted to the quartz tube. The test was conducted without a quartz tube connecting to the IFR, and under the combustion conditions and DCH feed rate identical to those of other tests conducted later. PCDD/Fs were not detected in the test, confirming that no PCDD/Fs were formed in the flue gas before it entered the quartz tube at about 600°C.

Tests 4 and 5 were conducted with quartz tubes containing deposits from the sooting combustion of oil-containing suspensions of Cu_2O particles. Both tests gave relatively high levels of PCDD/F formation: 6700 ng/dcm in Test 4 and 21,000 ng/dcm in Test 5. While neither soot nor copper promoted dioxin formation by itself, they exhibited significant activity when they were both present. The greater amounts of PCDD/Fs formed during Test 5 may have resulted from increased copper in the soot deposits, increased levels of chlorine in the flue gas, or both.

The congener distributions of the PCDD/Fs obtained in Tests 4 and 5 are shown in Figures 3 and 4, respectively. The effect of increased copper and/or chlorine levels was to shift the congener distribution to the more chlo-

rinated species. For Test 4, the PCDD and PCDF distribution peaks corresponded with the HxCDD and TrCDF congeners, respectively. For Test 5, the PCDD distribution peak corresponded with the OCDD congener and the PCDF peak at the HpCDF congener. Figures 3 and 4 also show that Test 5 produced relatively more PCDDs to PCDFs than Test 4. The ratios of the total PCDD to PCDF congeners increased from about 1:5 in Test 4 to about 1:2 in Test 5. The deposits and chlorine levels in Test 5 not only produced more total PCDD/Fs; they resulted in a higher degree of chlorination and increased the formation of PCDDs relative to PCDFs. It should be noted that the low-resolution mass spectrometer employed for this study was not capable of resolving individual isomers within a congener group. Therefore comparison on isomeric pattern of the PCDD/F samples generated from different tests cannot be made.

A second series of formation tests (Tests 6–9) were performed using a quartz tube with deposits from the sooting combustion of a suspension of CuO in CH_3OH and natural gas. Results of the initial test (Test 6) indicated higher levels of PCDD/F formation (48,000 ng/dcm) than previous tests (see Table 2). Although the exact causes of the higher formation rate are unknown, there are several probable causes. The use of higher amounts of copper in the deposition step may have provided a greater number of active sites for PCDD/F formation.

The PCDD/F formation is much higher in this series of tests, which used a tube with more copper injection (2.53 g), than that from Test 5 (21,000 ng/dcm) using a tube with less copper injected (1.79 g). The use of CuO in CH_3OH suspension in this series of tests is also suspected to increase catalytic PCDD/F formation. CH_3OH is less viscous compared to No. 2 oil. Better atomization and finer droplets were produced from the injection of CuO in CH_3OH suspension compared to that from the Cu_2O/no. 2 oil method used during the tube deposition step. The dispersion of finer copper species on the tube surfaces resulting from improved atomization during the deposition step may have enhanced the catalytic activity of the deposited copper species leading to more PCDD/F emissions during the formation step.

The PCDD/F analysis results from Test 6 were obtained 13 days after the incineration test was completed due to the time-consuming PCDD/F analyses. After the high PCDD/F formation results were confirmed, the remaining three tests in the series (Tests 7–9) were performed consecutively, using the same tube that had been used in Test 6, on the same day. Test 7 was performed without DCH injection; flue gas produced from natural gas combustion was passed through the tube that had been used in Test 6 and stored in a cabinet since the test was

completed. Test 8 was performed after Test 7 was completed, with DCH incineration resumed at a feed rate (1.0 ml/min) to produce 500 ppmv HCl in the flue gas. For the last test (Test 9), SO_2 was injected into the IFR at a rate to produce 600 ppmv SO_2 in the flue gas during the DCH incineration.

Much lower levels of PCDD/Fs (1200 ng/dcm) were formed in Test 7 when input of chlorine into the IFR was stopped. However, the significant levels of PCDD/F, PCDFs in particular, measured in Test 7 indicate that there was still residual activity from previous tests for PCDD/F formation. It is possible that prior exposure of the tube deposited with trace levels of a copper species to chlorine during Test 6 led to the formation of copper chlorides, which remained as the source of chlorine for PCDD/F formation during the subsequent test (Test 7). The PCDD/F congener distribution patterns for Tests 6 and 7 are shown in Figures 5 and 6, respectively. Comparison of the two figures shows a shift to the less chlorinated species when the input of chlorine was stopped. Once the injection of DCH was resumed in Test 8, the levels of PCDD/F were restored to a certain extent (13,700 ng/dcm), although they are still far from comparable to those high levels (48,000 ng/dcm) observed for the initial test (Test 6). The lower PCDD/F formation observed in Test 8 may possibly be due to the fact that reactivity of the soot/copper deposits decays gradually

with reaction time. The PCDD/F congener distribution pattern for Test 8 is shown in Figure 7; it also shows a shift to the less chlorinated species when compared to those shown (Fig. 5) for the initial test (Test 6).

The injection of SO_2 during the incineration of DCH in Test 9 at a sulfur-to-chlorine ratio of 1.2 reduces PCDD/F emissions (4500 ng/dcm) significantly. The congener distribution pattern for Test 9 is shown in Figure 8. The ratios of PCDD to PCDF congeners decrease significantly from about 1:3 for the previous three tests to about 1:5 for Test 9 when SO_2 was injected. The reductions in total PCDD/F yields are 78% and 63%, respectively, from Tests 8 to 9. It appears that SO_2 injection has a stronger inhibition effect on the formation of PCDD than that of PCDF. Similar reduction in PCDD/F emissions from SO_2 injection has been observed for MSW combustion applications (Raghunathan and Gullett, 1996). An attempt was made to conduct an additional DCH incineration test without SO_2 injection subsequent to Test 9 in order to examine whether the inhibition effect of SO_2 on PCDD/F formation still remained with the deposited tube once it had been exposed to SO_2. The recoveries of internal standards required for the PCDD/F analyses failed to achieve the acceptable levels specified by Method 23, and results for this test are therefore not reported.

The last series of tests (Tests 10–12) were conducted

TABLE 1. SUMMARY OF TEST CONDITIONS FOR DEPOSITION AND FORMATION EXPERIMENTS

| | | | | | 1,6-Dichlorohexane incineration conditions | | |
| | | | | | | Flue gas composition | |
Test no.	Quartz tube deposits deposition method[a]	Cu injected[b] (g)	Chlorine input[c] (ppmv)	SO_2 input[d] (ppmv)	O_2 (vol % dry)	CO_2 (vol % dry)	CO (ppmv dry)
1	None (clean tube)	0	500	0	6.4	8.5	11
2	Aqueous Cu(NO₃)₂ solution	1.02	500	0	6.4	8.5	11
3	Oil sooting (no copper)	0	500	0	6.1	8.6	9
4	Cu₂O suspension, oil sooting	0.96	500	0	6.2	8.5	40
5	Cu₂O suspension, oil sooting	1.79	1000	0	6.1	8.6	16
6	CuO in methanol, NG sooting	2.53	500	0	6.2	8.5	40
7	CuO in methanol, NG sooting	2.53	0	0	6.3	8.5	21
8	CuO in methanol, NG sooting	2.53	500	0	6.4	8.5	21
9	CuO in methanol, NG sooting	2.53	500	600	6.4	8.4	41
10	Copper naphthenate, oil sooting	0.21	500	0	6.2	8.6	26
11	Copper naphthenate, oil sooting	0.21	500	0	6.2	8.6	26
12	Copper naphthenate, oil sooting	0.21	500	600	6.2	8.6	26

[a]All oil soots generated with no. 2 fuel oil; NG, natural gas.

[b]Total amount of copper injected during deposition step.

[c]HCl concentration in the IFR flue gas as calculated from the 1,6-dichlorohexane input (1.0 ml/min for 500 ppmv HCl, 2.0 ml/min for 1000 ppmv HCl).

[d]Measured as the SO_2 concentration in the IFR flue gas.

TABLE 2. PCDD AND PCDF RESULTS FROM FORMATION EXPERIMENTS (NG/DCM)

Test no.	PCDD tetra-octa	PCDF tetra-octa	PCDD/PCDF tetra-octa	PCDD mono-octa	PCDF mono-octa	PCDD/PCDF mono-octa
1	ND[a]	ND	ND	ND	ND	ND
2	ND	5	5	ND	5	5
3	ND	ND	ND	ND	ND	ND
4	1,100	3,300	4,400	1,160	5,500	6,700
5	6,000	13,200	19,200	6,000	14,900	21,000
6	11,400	34,900	46,300	11,400	36,500	48,000
7	300	800	1,100	300	900	1,200
8	3,600	9,500	13,100	3,600	10,200	13,700
9	800	3,600	4,400	800	3,700	4,500
10	34,100	98,700	132,800	34,500	120,300	155,000
11	23,300	82,400	105,700	23,400	91,200	115,000
12	4,800	10,800	15,600	4,800	12,700	17,500

[a]ND, not detected.

using a tube that was coated with deposits generated by burning a solution of copper(II) naphthanate (CuNph) dissolved in no. 2 oil under sooting conditions. CuNph, an organometallic compound completely soluble in no. 2 oil, produced a spray in the quartz burner much better than those produced either by Cu_2O/no. 2 oil suspension or CuO in CH_3OH suspension used in the previous tests. A significantly smaller amount of copper was injected

for preparing the deposits used for this series of tests. Initial tests using a quartz tube coated with deposits generated by the CuNph/no. 2 oil solution with 1 g of the total amount of copper injected produced such high PCDD/F levels that they exceeded the calibration ranges of the GC/MS used for PCDD/F analyses. Another quartz tube prepared with less copper injected (0.21 g) was used for the tests.
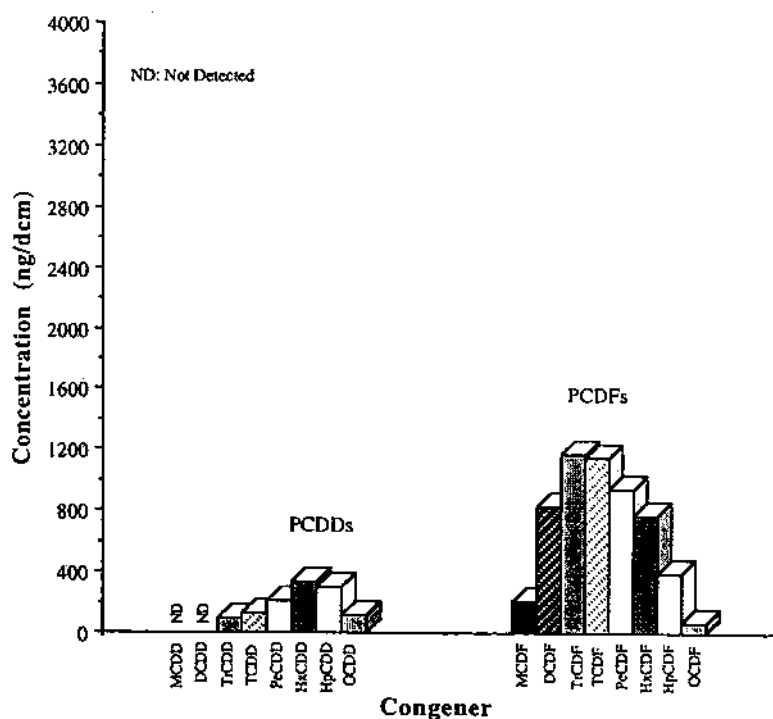

FIG. 3. Distribution of PCDD/PCDF congeners from test 4 (0.96 g Cu as Cu_2O in no. 2 fuel oil, 500 ppmv HCl from 1,6-dichlorohexane incineration).
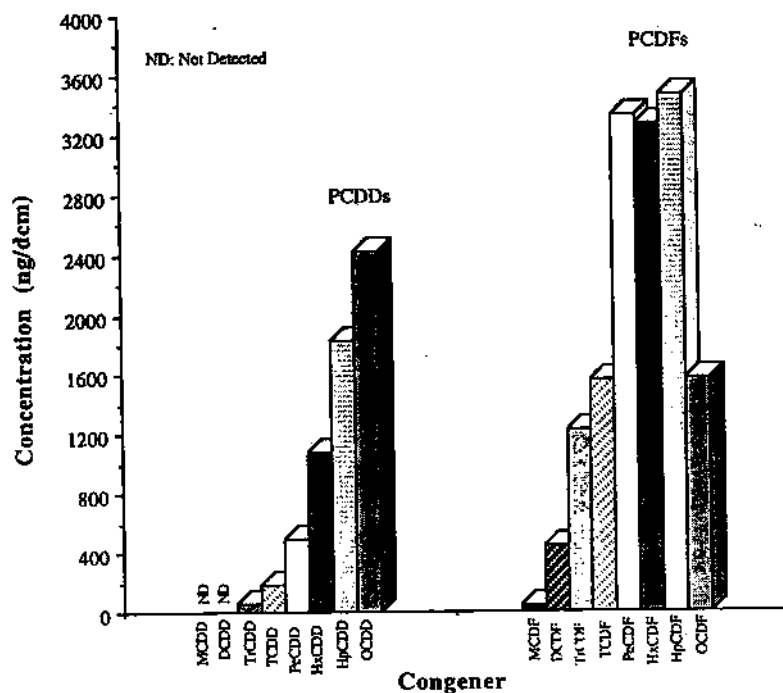
FIG. 4. Distribution of PCDD/PCDF congeners from test 5 (1.79 g Cu as Cu$_2$O in no. 2 fuel oil, 1000 ppmv HCl from 1,6-dichlorohexane incineration).

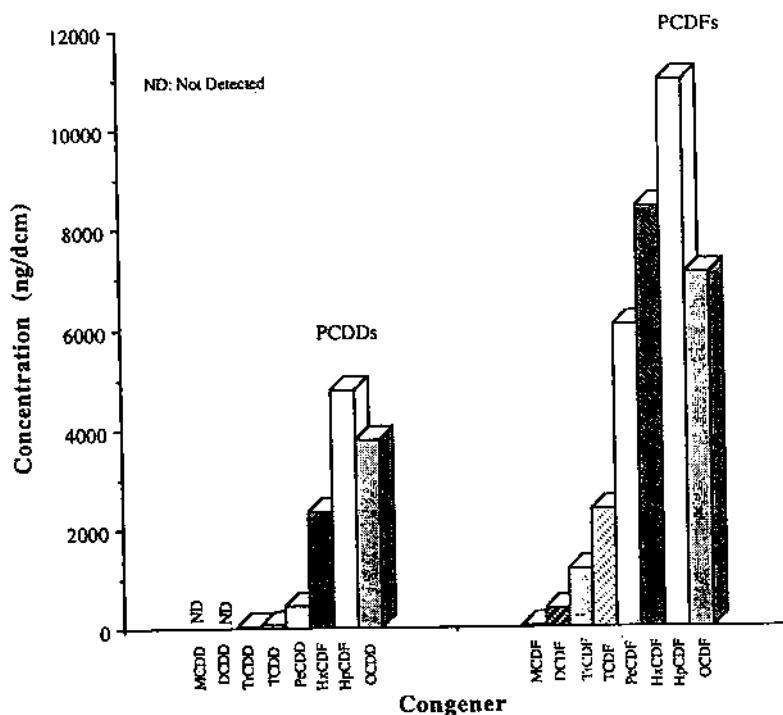**FIG. 5.** Distribution of PCDD/PCDF congeners from test 6 (2.53 g Cu as CuO in methanol, 500 ppmv HCl from 1,6-dichlorohexane incineration).
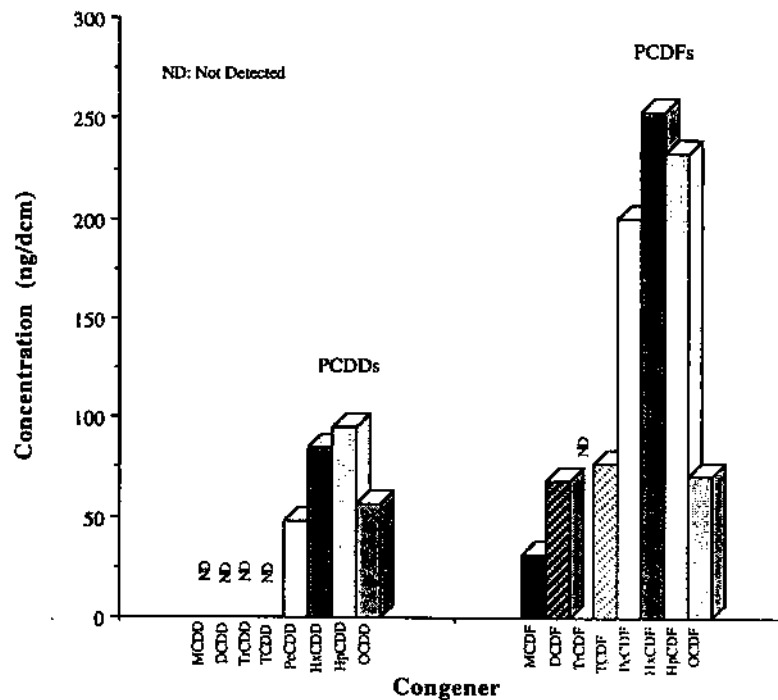
FIG. 6. Distribution of PCDD/PCDF congeners from test 7 (2.53 g Cu as CuO in methanol, 0 ppmv HCl from natural gas combustion).
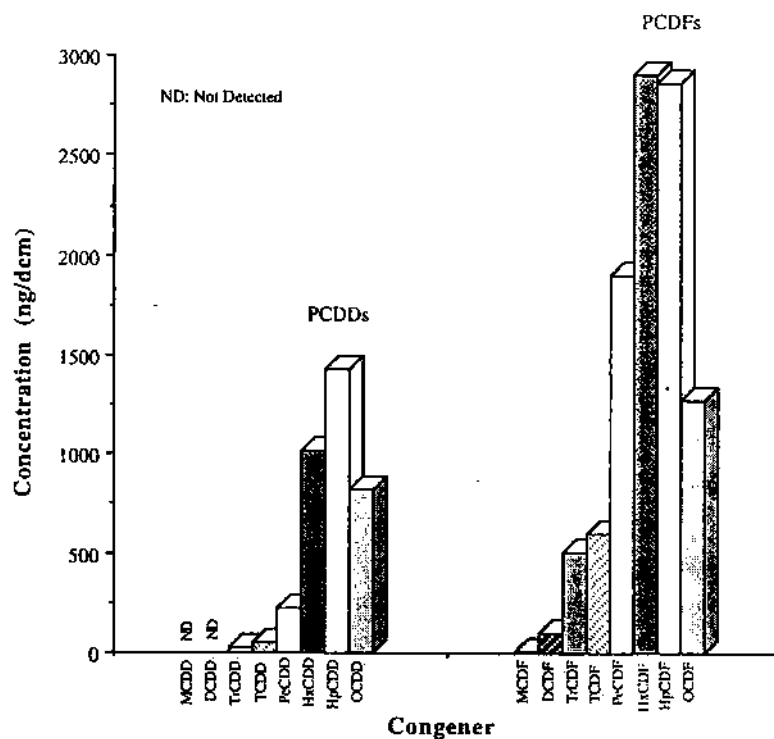

FIG. 7. Distribution of PCDD/PCDF congeners from test 8 (2.53 g Cu as·CuO in methanol, 500 ppmv HCl from 1,6-dichlorohexane incineration).
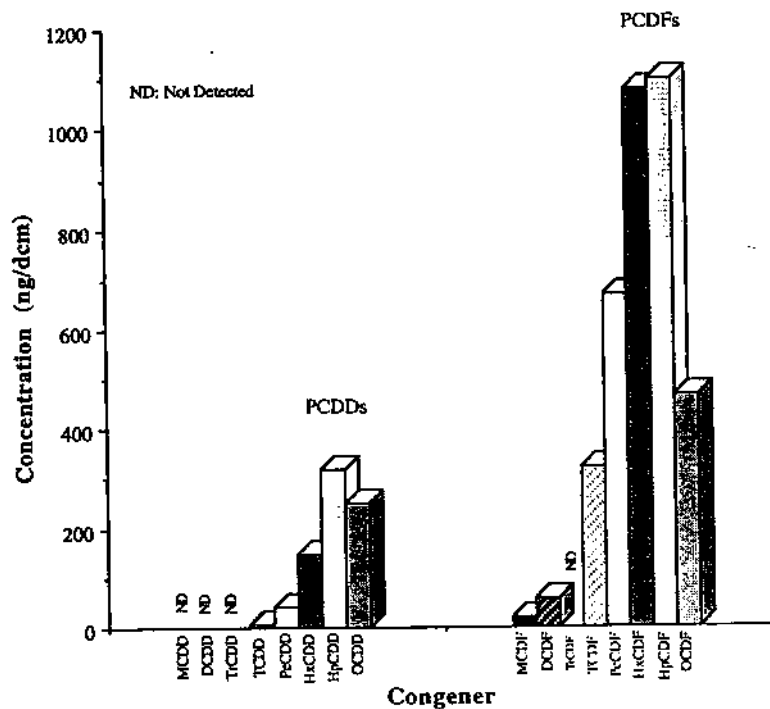
FIG. 8. Distribution of PCDD/PCDF congeners from test 9 (2.53 g Cu as CuO in methanol, 500 ppmv HCl from 1,6-dichloro-hexane incineration, 600 ppmv SO₂ injection).
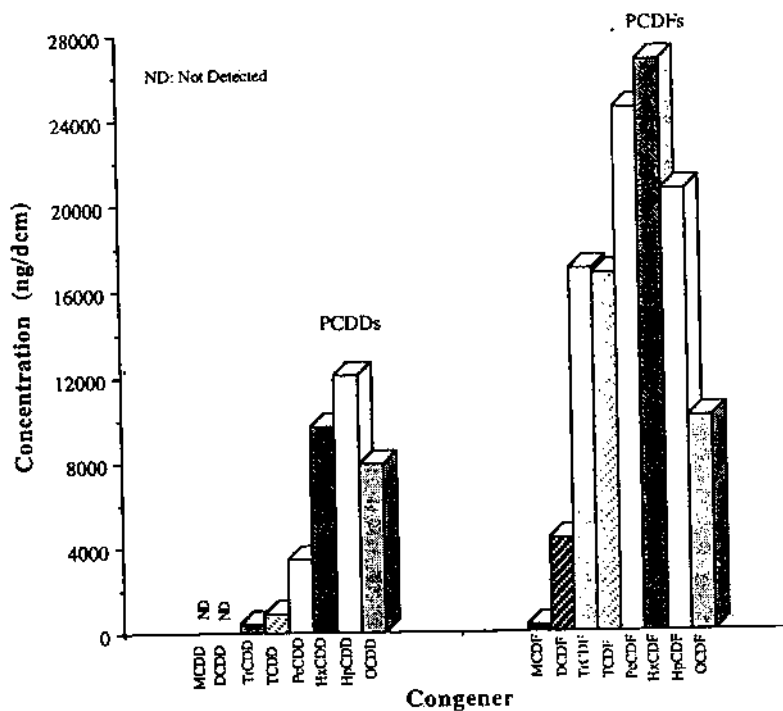
FIG. 9. Distribution of PCDD/PCDF congeners from test 10 (0.21 g Cu as copper (II) naphthanate in no. 2 fuel oil, 500 ppmv HCl from 1,6-dichlorohexane incineration).

The levels of PCDD/F (155,000 ng/dcm) measured for the first test (Test 10) in this series are much higher than those found in the previous series of tests. It appears that the soot/copper deposits generated by the CuNph/no. 2 oil solution have the highest reactivity for PCDD/F formation compared to those produced by Cu_2O/no. 2 oil suspension and CuO in CH_3OH suspension. It is possible that the combustion of an organometallic copper compound soluble in the fuel produces very fine copper oxide particles that are deopsited on the quartz tube as the flue gas passed through the tube. The catalytic reactivity of these deposits is expected to be significantly enhanced due to the higher surface areas provided by the finer particles and better dispersion of the copper in the fine particulate deposits.

A test (Test 11) was repeated immediately after Test 10 was completed in order to assess the reduction in PCDD/F formation as a result of decay in the reactivity of the deposits with reaction time. Significantly lower levels of PCDD/F (115,000 ng/dcm) were measured in Test 11 compared to those measured in Test 10, indicating that the reduction in reactivity of the deposits with reaction time is substantial. The reductions in total PCDD/F yields are 33% and 24%, respectively, from Tests 10 and 11. Another test (Test 12), with experimental conditions similar to those for the two previous tests, was repeated after Test 11 was completed. SO_2 was injected at a level of 600 ppmv in the flue gas for this test. The

PCDD/F were reduced to significantly lower levels (17,500 ng/dcm) as a result of SO_2 injection. The reductions in total PCDD/F yields are 80% and 86%, respectively. The reductions are slightly higher than those also caused by SO_2 injection measured in Tests 8 and 9. It appears that injection of SO_2 has a stronger inhibition effect in PCDD/F formation on the soot/copper deposits produced by the CuNph/no. 2 oil solution, which have higher reactivity. Although it is expected that the decrease in PCDD/F formation may be due to repeated testing with the same tube as its recativity for PCDD/F formation decays with reaction time, it appears that the reduction in PCDD/F formation due to SO_2 injection is the predominant factor as suggested by its significantly higher reduction in PCDD/F yields compared to that caused by the decrease in reactivity with reaction time.

The congener distributions measured during Tests 10–12 are shown in Figures 9–11, respectively. The distributions of PCDD congeners are quite similar for these tests. Relatively small quantities of tri- and tetra-congeners were formed; PCDD formation increased rapidly with the extent of chlorination and reached a maximum at the hepta-congener. The change in PCDF congener distribution pattern is noticeable from Tests 10 to 11. Comparison of Figures 9 and 10 indicates that the decay in reactivity of the deposits reduces the formation of the tri- and tetra-PCDF congeners in greater proportions relative to other congeners. However, injection of SO_2 causes
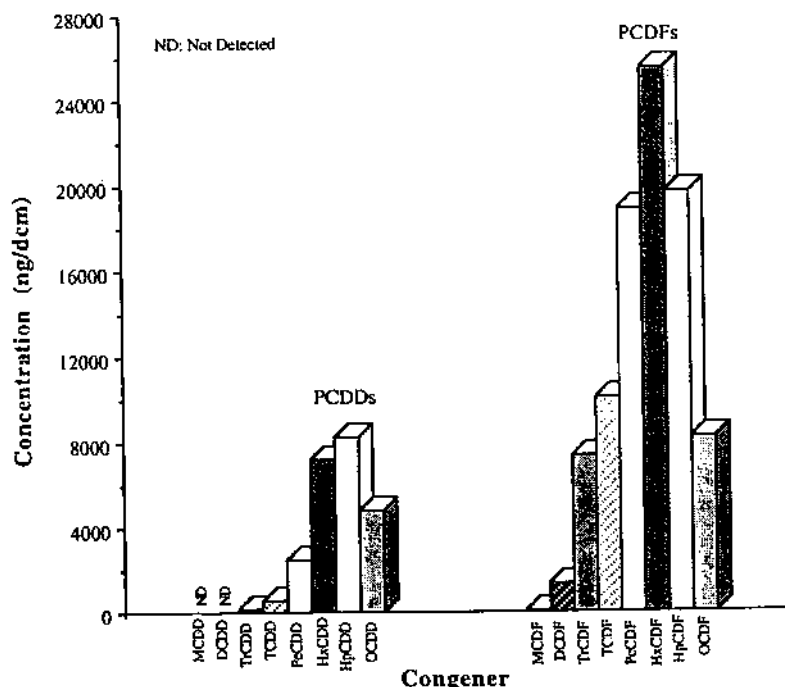

FIG. 10. Distribution of PCDD/PCDF congeners from test 11 (0.21 g Cu as copper (II) naphthanate in no. 2 fuel oil, 500 ppmv HCl from 1,6-dichlorohexane incineration).

very little change in PCDF congener distribution when comparing Figures 10 and 11. The ratios of PCDD to PCDF congeners measured in Tests 10 and 11 are about 1:3.5–3.9, and the ratios increase to about 1:2.6 in Test 12.

Most of the research on dioxin formation mechanisms has been concentrated on the heterogeneous catalytic reactions occurring in the postcombustion region through two possible pathways: de novo synthesis which involved particulate carbon, and catalytic condensation reactions of gaseous organic precursor compounds (Addink and Olie, 1995). Froese and Hutzinger (1996) suggested that the precursor route is accountable for the high PCDD/F formation rates (1–2 s residence time) observed for some combustion systems prior to, or without, the particulate collection equipment. The de novo synthesis, proposed by Vogg and Stieglitz (1986), involves the slow direct chlorination and oxidative breakdown of the aromatic ring structures in the carbon matrix of the particulate carbon, which accounted for the long residence times (5–30 min) required for PCDD/F formation observed in particulate collection equipment. The observed high PCDD/F formation that occurred in short residence times (2 s) in the present study seems to suggest that the strong memory effect of soot and copper deposits on PCDD/F formation proceeds possibly through the precursor route. The de novo route is also possible, as the gas residence

time is short (2 s); however, the high PCDD/F yields were formed over a sampling period of about 60 min by passing a chlorine-containing flue gas over the reactive deposits. High yields of PCDD/F formation are also possible through the de novo route when the flue gas serves as the chlorine source and the deposits provide both the organics and the catalyst needed for the synthesis. Both the de novo synthesis and the precursor routes involve surface-mediated catalytic reactions that occur over a solid surface with the presence of a catalyst, and fly ash and copper compounds are the most extensively studied surface materials and catalysts, respectively (Addink and Olie, 1995).

The strong promotional effect on PCDD/F emissions was observed only on the tubes deposited with both soot and copper; no such effect was observed with either a soot or copper deposit alone in the present study. In the initial CFC study, an old bench-scale combustor that had been used for testing metal-containing wastes was used to burn CFCs. This combustor generated total PCDD/F emissions as high as 23,800 ng/dcm (Hassel, 1991), which are close to the levels measured in the present study. Soot deposit was also found in that combustion unit prior to the CFC tests. Much lower, but still significant, levels of total PCDD/F emissions (up to about 500 ng/dcm) were measured in the follow-up study when a CFC was incinerated in the same combustor that had been
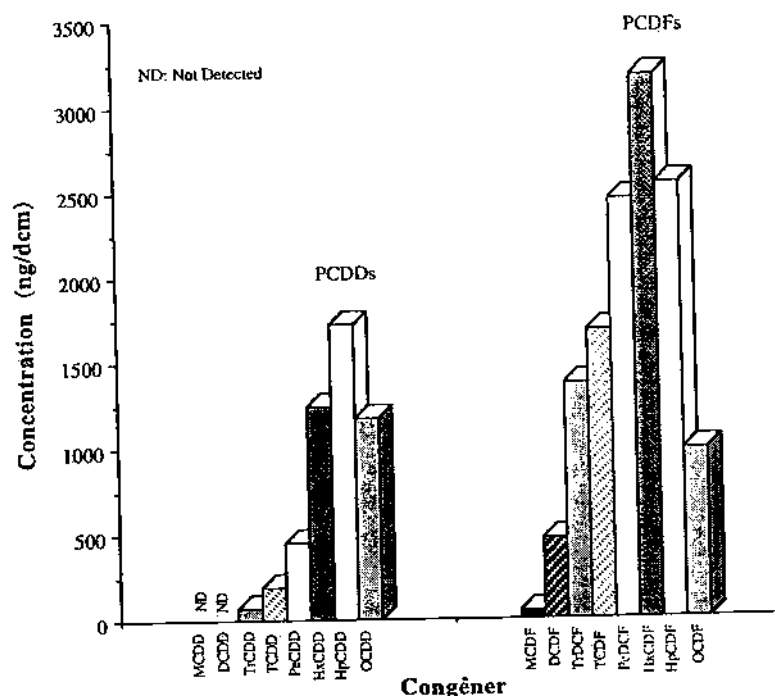

FIG. 11.   Distribution of PCDD/PCDF congeners from test 12 (0.21 g Cu as copper (II) naphthanate in no. 2 fuel oil, 500 ppmv HCl from 1,6-dichlorohexane incineration, 600 ppmv SO₂ injection).

fired with a copper-containing fuel prior to CFC incineration (Lee et al., 1996). The combustor had not been used since the completion of the initial CFC study in September 1991, and the refractory of the combustor was replaced in August 1994 prior to the folow-up CFC study. The much lower levels of PCDD/F emissions observed from the follow-up CFC study compared to those observed in the initial study could be due to very little soot deposit present in the combustor with the newly replaced refractory. A lowering of PCDD/F emissions resulting from refractory replacement has been reported (Gullett and Raghunathan, 1997). All of these observations suggest that soot is important to the observed memory effect on PCDD/F emissions from combustor deposits. It is not known as to whether the role soot plays to promote PCDD/F formation in the combined soot and copper deposits is purely catalytic and/or if it also serves as the source of the aromatic precursors necessary for subsequent PCDD/F formation. Further research could help identify the role soot deposit plays in PCDD/F formation. Soot is the most commonly found deposit on all combustion systems, and it is very important to understand its influence on promoting PCDD/F formation.

CONCLUSIONS

A strong promotional effect on PCDD/F emissions from chlorinated waste incineration has been observed resulting from soot and copper deposited together prior to the waste incineration. Such effect has not been observed on either soot or copper deposit alone. Copper deposits formed by passing either an organic or inorganic copper compound through the combustion environment can produce the memory effect to promote PCDD/F emissions in the presence of soot. The chlorinated waste incineration system "remembers" the presence of soot and copper deposits by producing high-dioxin emissions, once they are deposited in the system. The soot and copper deposits formed by burning an oil-soluble organometallic copper compound in no. 2 oil under sooting conditions exhibited the strongest combined promotional effect. The promotional effect decays gradually with time. It was also observed that that soot and copper deposits are capable of retaining chlorine during chlorinated waste incineration, which served as the source of chlorine to form PCDD/Fs later when the input of chlorinate waste into the combustor stops. Injection of SO_2 is very effective to suppress the combined promotional effect of soot and copper deposits. The soot deposit, formed by combustion of either gaseous or liquid fuel appears to be very important to the memory effect observed. It is unclear as to whether the role of soot in the memory effect is purely catalytic and/or if it also serves as the source of organic precursors needed for PCDD/F formation. Further research would help elucidate the role of soot in the memory effect.

GLOSSARY

CuNph	Copper (II) naphthanate
DCDD	Dichlorodibenzodioxin
DCDF	Dichlorodibenzofuran
DCH	1,6-dichlorohexane
HpCDD	Heptachlorodibenzodioxin
HpCDF	Heptachlorodibenzofuran
HxCDD	Hexachlorodibenzodioxin
HxCDF	Hexachlorodibenzofuran
IFR	Innovative furnace reactor
MCDD	Monochlorodibenzodioxin
MCDF	Monochlorodibenzofuran
OCDD	Octachlorodibenzodioxin
OCDF	Octachlorodibenzofuran
PCDDs	Polychlorinated dibenzo-p-dioxins
PCDD/Fs	Polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans
PCDFs	Polychlorinated dibenzofurans
PeCDD	Pentachlorodibenzodioxin
PeCDF	Pentachlorodibenzofuran
TCDD	Tetrachlorodibenzodioxin
TCDF	Tetrachlorodibenzofuran
TrCDD	Trichlorodibenzodioxin
TrCDF	Trichlorodibenzofuran

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