Control of dioxin, furan, and mercury emissions from municipal waste combustors

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Abstract

There is a significant public and scientific concern over the potential risks of air pollution emissions from municipal waste combustors (MWCs). The primary pollutants of concern are polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDDs/PCDFs), and mercury (Hg). Depending on the composition of the waste and the technologies used, PCDD/PCDF emissions may range from less than 1.0 to more than 20 000 ng/dscm. Hg concentrations in MWC flue gas may range from less than 200 to more than 1000 µg/dscm.

Trace organic emissions are dependent on the combustion and flue gas cleaning technologies employed and the conditions at which they are operated. Good combustion practice and dry scrubbing techniques employing fabric filter (FF) bag houses can be used to reduce average PCDD/PCDF emissions to less than 20 ng/dscm. Dry scrubbers in combination with electrostatic precipitators (ESPs) are less effective, resulting in typical PCDD/PCDF emissions of less than 75 ng/dscm. Powdered activated carbon can be injected into the flue gas to reduce Hg emissions from spray dryer (SD)/FF and SD/ESP systems to less than 0.08 mg/dscm. It can also be used to improve PCDD/PCDF capture in these systems.

This article provides an overview of MWC air pollution control technologies and applicable Federal air emission control requirements. Knowledge concerning PCDD/PCDF formation is summarized, and data are provided on the performance of combustion and flue gas cleaning techniques used to control PCDD/PCDF emissions. The fundamental Hg properties which affect capture in flue gas cleaning equipment are discussed, and the results of carbon injection control tests are summarized.

Keywords: Municipal waste combustors; Dioxin formation and control; Mercury control; MWC air pollution regulations

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1. Introduction

In June 1987, EPA's Office of Air Quality Planning and Standards (OAQPS) announced its intention to develop new air pollution rules for municipal waste combustors (MWCs) [1]. This decision was based, in part, on a study of the risk associated with MWCs [2]. Pollutants posing the highest risks included polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDDs/PCDFs) and hazardous trace metals. On 20 December 1989, EPA proposed new source performance standards (NSPS) for all new MWCs and emission guidelines (EGs) for all existing MWCs [3]. NSPS and EGs for MWCs larger than 225 mg/day in capacity were promulgated in February 1991 [4].

In November 1990, Congress passed amendments to the Clean Air Act [5]. Section 129 of these amendments directed EPA to establish MWC emission limits for particulate matter (PM), hydrogen chloride (HCl), sulfur dioxide (SO_2), nitrogen oxides (NO_x), carbon monoxide (CO), PCDDs/PCDFs, cadmium (Cd), mercury (Hg), and lead (Pb). These emission limits were to be based on the application of maximum achievable control technology (MACT).

This article provides a brief overview of MWC technologies, a summary of EPA's revised air pollution rules for MWC, a review of current knowledge concerning formation and control of PCDDs/PCDFs, a review of knowledge on the control of Hg, and information on the performance of commercial technologies for continuously controlling emissions of PCDDs/PCDFs and Hg. The focus of the article is the control of air pollution emissions as needed to reduce risks from chronic long-term exposures to PCDDs/PCDFs and Hg. The article does not address the requirements for complying with short-term (short averaging time) emission regulations.

2. MWC technologies

Three major types of MWCs are commonly used in the US: mass burn, refuse-derived fuel (RDF), and modular [6]. The best combustion technologies ensure adequate waste burn-out and produce minimal products of incomplete combustion (PICs) in the flue gas. In the US, dry flue gas cleaning technologies are generally used to control air pollution emissions. Wet scrubbing systems are seldom used [7]. PM is collected in devices that depend on electrostatic forces [electrostatic precipitators (ESPs)] or physical filtration [fabric filters (FFs)]. Cd and Pb are solids at flue gas cleaning temperatures and are efficiently collected in ESPs or FFs. Hg is normally a vapor at flue gas cleaning temperatures, and special methods must be used for its control [8].

Acid gases are controlled by dry scrubbers by injecting a calcium-based reagent {limestone ($CaCO_3$), lime (CaO), or hydrated lime [$Ca(OH)_2$]} into the flue gas to convert HCl and SO_2 into solid compounds that can be collected in a PM control device [9]. Several methods may be used to inject and mix the sorbent with flue gas: lime spray dryers (SD), dry sorbent injection into the furnace (FSI), or dry sorbent injection into the flue gas duct (DSI). The most advanced NO_x control technology

being applied in the US uses either ammonia (NH_3) or urea [$CO(NH_2)_2$] as a selective non-catalytic reduction (SNCR) reagent to reduce NO_x to nitrogen [10].

The chemistry involved in acid gas and NO_x control, and the mechanisms involved in PM control are generally well understood. The major problem associated with control of these pollutants (PM, acid gases, and NO_x) is the engineering optimization of flue gas cleaning processes that are also effective in the control of trace metals and trace organics.

The most difficult-to-control MWC pollutants of concern are PCDDs/PCDFs and Hg. PCDDs/PCDFs can be formed in MWCs as a high temperature PIC or they can be formed downstream of the combustor by low temperature synthesis reactions involving fly ash [6, 11, 12]. Hg is typically a vapor at flue gas cleaning temperatures and difficult to collect in flue gas cleaning equipment.

3. Revised federal emission control requirements

On 20 September 1994, EPA proposed revised NSPS and EGs for MWCs. These revised rules require the use of good combustion practice (GCP) and MACT flue gas cleaning techniques to continuously limit emission of PCDDs/PCDFs, CO, PM, Cd, Hg, Pb, HCl, SO_2, and NO_x [13]. The control technologies on which the performance requirements are based are summarized in Table 1. These technologies or technology combinations which give equivalent or better performance with the proposed requirements may be used.

The method of achieving PCDDs/PCDFs control is to use GCP in combination with appropriate flue gas cleaning techniques. The objectives of GCP are to maximize furnace destruction of organics and minimize low-temperature PCDD/PCDF formation reactions [14–16]. Furnace destruction of organics is

Table 1
Basis for proposed MACT performance requirements[a] (20 September 1994)

Proposed requirements	Basis for emission limits[b]
Emission guidelines (EG)	
Small (> 35–225 Mg/day)	GCP + DSI + ESP + CI
Large (> 225 Mg/day)	GCP + SD/ESP (or SD/FF) + CI + SNCR
New source performance standards	
Small (> 35–225 Mg/day)	GCP + SD/FF + CI
Large (> 225 Mg/day)	GCP + SD/FF + CI + SNCR

[a] Technologies which provide equivalent or better performance may also be used.
[b] GCP = Good combustion practice.
ESP = Electrostatic precipitator.
DI = Dry injection of sorbent (FSI = furnace sorbent injection and DSI = duct sorbent injection).
CI = Carbon injection.
SD/ESP = Lime spray dryer absorber and ESP.
SD/FF = Lime spray dryer absorber and fabric filter baghouse.
SNCR = Selective non-catalytic reduction.

Table 2
Proposed GCP requirements for MWCs (20 September 1994)

1. CO requirements	CO emission limits	
Type of combustor	EG limits (ppm) (Avg. time, h)	NSPS limits (ppm) (Avg. time, h)
Mass burn water wall (MBWW)	100 (4)	100 (4)
Mass burn refractory wall (MBRW)	100 (4)	100 (4)
Mass burn rotary water wall (MBRW)	250 (24)	100 (24)
Mass burn rotary wall refractory (RWR)	100 (24)	100 (4)
Refuse-derived fuel stokers (RDF)	200 (24)	150 (24)
Fluidized bed combustors (FBC)	100 (4)	100 (4)
Modular combustion units (MCU)	50 (4)	50 (4)
Coal/RDF mixed fuel-fired (Coal/RDF)	150 (4)	150 (4)

2. Load not to exceed maximum load demonstrated during most recent PCDD/PCDF compliance tests
3. PM control device inlet temperature not to exceed level demonstrated during most recent PCDD/PCDF compliance tests
4. Chief facility operator, shift supervisors, and control room operators must meet training and certification requirements

Table 3
Proposed emission limits for MWCs[a] (September 20, 1994)

Pollutant/measurement	Guideline limits (or % reduction)		NSPS limits (or % reduction)
	Small (≥35 to 225 Mg/day)	Large (>225 Mg/day)	Large and small (≥35 Mg/day)
ng/dscm [ng TEQ/dscm][b]	60 [1.0]	30 [0.5]	13 [0.2]
PM (mg/dscm)	69	27	15
Opacity[c] (%)	10	10	10
Cd (mg/dscm)	0.10	0.04	0.01
Pb (mg/dscm)	1.6	0.50	0.10
Hg (mg/dscm)	0.08 (85)	0.08 (85)	0.08 (85)
HCl (ppmv)	250 (50)	35 (95)	25 (95)
SO$_2$ (ppmv)[d]	80 (50)	35 (75)	30 (80)
NO$_x$ (ppmv)	None	180[e]	180[e]

[a] All emissions corrected to 7% O$_2$.
[b] Average of three stack tests using EPA Method 23. Toxic equivalents based on International Toxic Equivalency factors. Values are weight of total tetra- through octa-congeners. Values in brackets are for [toxic equivalents based on 1989 International Toxic Equivalency (TEQ) factors].
[c] EPA Method 9. Limit for 6 min averages.
[d] 24 h averaging time.
[e] Applies to large plants only. 24 h averaging time.

controlled by establishing technology-based emission limits for CO (see Table 2). Downstream formation and stack emissions are controlled by a limit on steam load in waste-to-energy plants and a limit on PM control device operating temperature.

The load is a surrogate parameter used to limit the relative amount of PM carried out of the combustor with flue gas (PM carryover). The purpose of the inlet temperature limit is to control PCDD/PCDF synthesis reaction rates, and solid- and vapor-phase partitioning of PCCDs/PCDFs in the PM control device. Solid-phase PCDD/PCDF emissions are limited by the use of efficient PM control equipment.

The Hg emission limit is based on the injection of powdered activated carbon in conjunction with dry scrubbing. The activated carbon adsorbs gas-phase Hg and is collected in the PM control device.

Acid gas (HCl and SO_2) and metal (Cd, Hg, and Pb) emission limits require equipment and operating conditions that complement PCDD/PCDF control. Acid gas sorbents may reduce PCDD/PCDF formation rates, and the use of activated carbon for Hg control improves PCDD/PCDF control.

The proposed 1994 EPA emission requirements for new and existing sources are summarized in Table 3. The proposed rules have different requirements for new and existing plants, and for small (>35 to $\leqslant 225$ Mg/day) and large (>225 Mg/day) plants. The PCDD/PCDF emission requirements can be met by complying with emission limits for total tetra-through octa-PCDDs/PCDFs or International Toxic Equivalency (TEQ) factors for PCDDs/PCDFs relative to 2,3,7,8-TCDD. The proposed limits are: 60 ng/dscm (or 1.0 ng TEQ/dscm) for small existing plants, 30 ng/dscm (or 0.5 ng TEQ/dscm) for large existing plants, and 13 ng/dscm (or 0.20 ng TEQ/dscm) for large and small new plants[1] [1].

Although PCDD/PCDF emissions cannot be continuously monitored, operating and emission parameters which correlate with PCDD/PCDF emissions will be continuously monitored and controlled. These continuous compliance parameters include CO emission limits, boiler steam load, and PM control device inlet temperatures. Opacity and SO_2 are to be continuously monitored to guarantee proper operation of the flue gas cleaning equipment. Each MWC will also be subject to annual PCDD/PCDF compliance tests. The use of these continuous monitoring and compliance parameters will ensure that each MWC operates at conditions necessary to control formation and emission of PCDDs/PCDFs.

4. PCDD/PCDF formation mechanisms

PCDDs/PCDFs were first discovered in the stack gas of municipal waste incinerators in 1977 [17]. Since then a considerable amount of research has been devoted to identifying PCDD/PCDF emission sources and understanding PCDD/PCDF formation mechanisms.

There are probably three primary routes for PCDD/PCDF formation: gas-phase reactions involving chlorinated precursors such as chlorobenzenes (CBs), chlorophenols (CPs), or polychlorinated biphenyls (PCBs); condensation reactions involving gas-phase precursors and fly ash; and solid-phase reactions on the surface of fly ash

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[1]US EPA emission concentrations for MWCs are expressed in dry standard cubic meters (dscm) corrected to 7% O_2 and standard conditions at 20 °C (68 °F) and 101.3 kPa (14.7 psi).

involving metal chlorides and fly ash carbon [11]. The third route of formation, which involves the reaction of unburned carbon in fly ash to form PCDDs/PCDFs, is called *de Novo* synthesis [12, 18–20].

Based on theoretical and experimental studies, it has been concluded that gas-phase reactions cannot result in amounts of PCDDs/PCDFs found in MWC flue gases and that formation of these compounds must predominantly come from reactions involving solid surfaces (heterogeneous reactions) [21].

Laboratory experiments have shown that CPs and other precursor compounds react with MWC fly ash, metal ion catalysts, and activated carbon to form PCDDs/PCDFs. Metal ions that promote PCDD/PCDF formation include copper chloride ($CuCl_2$), copper oxide (CuO), copper sulfate ($CuSO_4$), ferric oxide (Fe_2O_3), zinc oxide (ZnO), nickel oxide (NiO), and aluminum oxide (Al_2O_3) [22, 23]. The most reactive metal ion catalyst is $CuCl_2$.

Gas-phase precursors can originate as waste thermal decomposition products or as high-temperature PICs. Low-temperature oxidation reactions involving fly ash carbon can also produce CP or other precursor compounds that in turn react to form PCDDs/PCDFs by surface-mediated reactions (condensation, absorption–desorption, etc.) [24, 25].

De Novo synthesis reactions were discovered by heating municipal waste incinerator fly ash in a laboratory furnace [12]. De Novo synthesis consists of low-temperature carbon oxidation reactions which provide the biaryl ring structures for PCDD/PCDF formation and metal ion catalyzed reactions which provide the necessary chlorine (Cl) for PCDD/PCDF formation. Low temperature carbon oxidation reactions may be catalyzed by metal ions or carbon structures similar to activated carbon [24, 25]. The Cl for (oxy)-chlorination reactions can be provided from either metal chlorides in the fly ash or Cl in the flue gas.

The amount of PCDDs/PCDFs formed in laboratory experiments is dependent on the fly ash annealing (heating) temperature, the amount and type of carbon in fly ash, the amounts of Cu and other catalytic metals, and the concentration of H_2O, O_2, and HCl in gases passing through the annealing reactor [18–25].

De Novo synthesis reactions generate a variety of chloro-organic compounds including CPs, chloro-benzonitriles, -thiophenes, -benzofurans, -benzothiophenes, PCDDs, -naphthalenes, PCDFs, and -benzenes (see Fig. 1) [20]. Laboratory experiments show that de Novo reactions occur at temperatures ranging from approximately 250 to 600 °C [12, 18–20]. At temperatures above 600 °C, chloro-organics are rapidly destroyed and at temperatures below 250 °C, reaction rates result in minimal formation.

There are eight congener classes of PCDDs/PCDFs: di-, tri-, tetra-, penta-, hexa-, hepta-, and octa-. The relative synthesis rate of each congener class is dependent on temperature. Laboratory experiments by Schwartz et al. on one MWC fly ash indicated that maximum formation rates of total di- through octa-PCDDs occur near 300 °C and that total di- through octa-PCDFs have maximum formation rates near 470 °C (see Fig. 2). At temperatures of 300 °C and lower more than 50% of the PCDDs/PCDFs were tetra- through octa-congeners. At 350 °C and higher temperatures more than 50% of the PCDDs/PCDFs were di- and tri-congeners. At
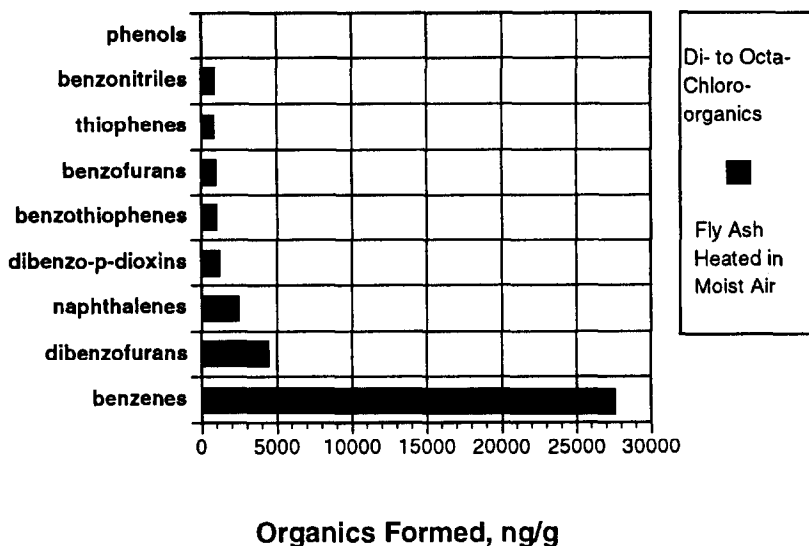
Organics Formed, ng/g

Fig. 1. Chloro-organics formed during de Novo synthesis.
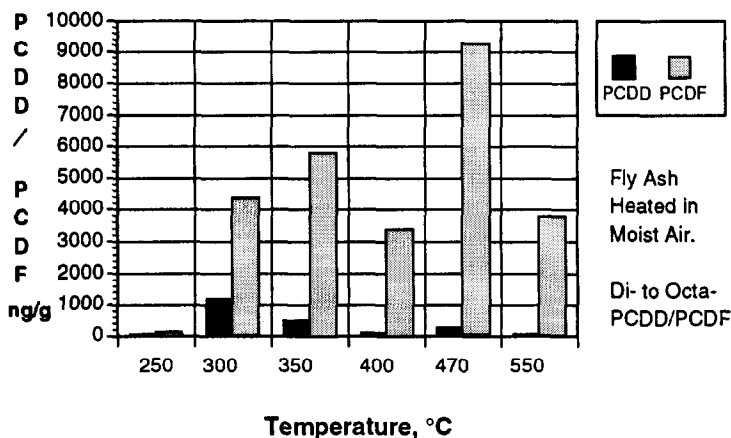

Temperature, °C

Fig. 2. Effect of temperature on de Novo formation rates.

temperatures lower than 250–300 °C, PCDDs/PCDFs were predominantly retained on fly ash. As temperatures increase the proportion of congeners found in the vapor-phase increases; i.e., PCDDs/PCDFs were increasingly partitioned into a vapor phase as temperatures increased [20].

From a risk perspective, the di- and tri-PCDD/PCDF congeners are not considered to be important, and most research on PCDD/PCDF formation has measured only the synthesis rate (or flue gas concentration) of the tetra- through octa-congeners. Laboratory formation experiments have generally shown that rates of the

tetra- through octa-PCDDs/PCDFs reach maximum values at 300 °C [12, 13, 18, 20]. (Hereafter, values given for PCDDs/PCDFs shall be understood to be the total tetra-through octa-congeners of PCDDs/PCDFs unless otherwise noted.) For de Novo synthesis, PCDF formation rates dominate over the entire formation temperature window of 250–600 °C. Relative to PCDFs, PCDD formation rates are only significant at temperatures from 250 to 350 °C. Above 350 °C the net amount of PCDDs formed is less than 10% of the net amount of PCDFs formed [20]. PCDFs have been shown to have a maximum (tetra- through octa-) de Novo synthesis rate near 300 °C with a lower local formation peak near 470 °C [20].

5. PCDD/PCDF formation and emission at MWCs

Factors affecting the formation and subsequent emission of PCDDs/PCDFs from MWCs include:
(1) Composition and properties of waste,
(2) combustion conditions,
(3) composition of flue gas,
(4) amount of entrained PM,
(5) flue gas time/temperature profile,
(6) PM control device operating temperature, and
(7) method of acid gas and PM control.

5.1. Composition and properties of waste

Rapid changes in waste composition or properties may cause combustion upsets and lead to PCDD/PCDF formation. Although PCDDs/PCDFs are formed during steady-state combustion conditions, the amounts formed are believed to increase substantially during combustion upsets associated with improper feed conditions. It is important to blend or mix waste prior to combustion to reduce variations in heating content, volatility, and moisture content [15].

While waste composition probably affects the amounts of specific organics formed during combustion, there is no conclusive scientific evidence that specific solid waste components, such as polyvinyl chloride (PVC), are primarily responsible for the formation and emission of PCDDs/PCDFs [10].

5.2. Combustion conditions

Any PCDDs/PCDFs contained in the waste are believed to be destroyed in active flame zones or the high-temperature regions of MWCs [15]. However, the fuel composition and combustion conditions determine the specific PICs that are necessary precursors for PCDD/PCDF formation. These precursor compounds are formed by the oxidation and thermal destruction processes which occur in the burning waste bed, the active flame region above the bed, and the high-temperature regions of the

furnace. PICs which have been implicated in PCDD/PCDF formation include: CBs, CPs, PCBs, and the carbon in fly ash [11, 12, 18, 24–26].

GCP can be used to maximize the furnace destruction of organics and minimize the downstream formation of PCDDs/PCDFs by controlling the amounts of PM carried out of the furnace with flue gas. Furnace destruction of organics must include destruction of both gas- and condensed-phase organics. Field test experiments have shown that PCDD/PCDF formation correlates with the CO and total hydrocarbon (THC) concentrations in flue gas and the amounts of PM carried out of the combustor with flue gases [15, 16].

Combustion-related variables that affect the destruction, formation, and furnace emissions include combustion temperatures and residence times, the amount and distribution of combustion air, and mixing.

Waste and its associated thermal decomposition products must be exposed to elevated temperatures for a sufficient time to destroy completely their organic components. Time scales required for destruction are typically measured in milliseconds for gaseous compounds in active flame zones. Combustion reaction times in the order of seconds-to-minutes may be required for the complete destruction of small solid particles. Combustion temperatures and residence times of 980 °C (1800 °F) and 1–2 s, respectively, are generally believed sufficient to destroy thermally gas-phase compounds [15, 16]. However, even at temperatures of 980 °C or higher, residence times needed for the complete combustion of entrained solid particles may be insufficient, and residual unburned carbon in fly ash may lead to heterogeneous reactions which form PCDDs/PCDFs.

The amount of excess air used for combustion must be sufficiently high to minimize the existence of fuel-rich pockets and sufficiently low to avoid quenching of combustion reactions. The distribution of combustion air is also important. Burning refuse beds contain drying, devolatization, combustion, and burn-out zones. Each zone requires a different amount of combustion air. State-of-the-art MWCs often use zoned underfire air supplies to provide proper air distribution to the refuse bed and overfire air to complete combustion of pyrolysis products leaving the bed.

Poor mixing increases the amount of organic material available for the formation of PCDDs/PCDFs. It may result in local stoichiometries that are insufficient for the complete oxidization of gas- and solid-phase organics. Poor mixing may also lead to the formation of difficult-to-destroy soot particles. Methods of achieving good mixing include the use of furnace configuration and overfire air jets.

5.3. Composition of flue gas

The effects of flue gas composition on PCDDs/PCDFs are complex [21, 26–28]. Oxygen is required for the low-temperature carbon oxidation reactions that are associated with de Novo synthesis. Oxygen and H_2O are also required for the Deacon process reaction which provides Cl for the chlorination of PCDDs/PCDFs or their precursor compounds. The Cl for the Deacon process reaction may come from either the inorganic chlorides in fly ash or the Cl in flue gas. PCDD/PCDF formation increases with increasing level of HCl or Cl_2 in combustion gases [27, 28]. Although

the flue gas concentrations of O_2 and H_2O affect the rate of PCDD/PCDF formation, the waste moisture content and excess air levels determine the concentrations of these two constituents. It is generally not practical to control the moisture or water content of wastes and the amount of excess air must be fixed at levels needed to obtain good combustion.

5.4. Entrained particulate matter

The entrainment and carryover of fly ash into the cooler regions of MWCs may lead to the formation of PCDDs/PCDFs and other trace organics. Metal ions or fly ash carbon can catalyze condensation formation reactions, and fly ash carbon can serve as the source of organics for the de Novo synthesis of PCDDs/PCDFs. PM carryover is determined by the aerodynamic properties of particles, the method of waste combustion, and combustor gas flow characteristics. Methods of limiting PM carryover include the proper furnace design, the control of the under-to-overfire-air ratio, the amount of excess air, and load (refuse burn rate) [15, 16].

5.5. Time/temperature profile

Laboratory combustor experiments have shown that the concentration of PCDDs/PCDFs in downstream flue gas depends on the time/temperature profile in the cooling sections of combustion systems [29, 30]. The time/temperature profile is determined by the time required by flue gas and suspended PM to pass through the heat extraction regions of boilers, superheaters, and economizers. High flue gas temperature quench rates reduce the time that entrained particles spend in the temperature range associated with high PCDD/PCDF formation rates.

5.6. PM control device operating temperature

ESPs and FFs can function as chemical reactors that generate and emit PCDDs/PCDFs [15, 16, 31]. A large fraction of the PCDDs/PCDFs entering PM control devices is commonly associated with collectible fly ash. However, the large mass of particles within the device can serve as a source for the synthesis of PCDDs/PCDFs. Limiting the temperature at which PM control devices are operated is important in controlling the formation and emission of PCDDs/PCDFs [14–16].

Maximum de Novo synthesis reaction rates occur at temperatures ranging from 300 to 470 °C [20]. Lowering PM control device operating temperatures to less than 250 °C results in a major reduction in PCDD/PCDF formation rates and alters the partitioning of vapor- and solid-phase PCDDs/PCDFs [31].

5.7. Method of acid gas and PM control

FSI and DSI can be used to reduce acid gases and allow for lower PM control device operating temperatures. Pilot scale experiments have shown that injection of $Ca(OH)_2$ into the flue gas at temperatures greater than 800 °C significantly reduces

the formation of PCDDs/PCDFs [28]. The reduction in PCDD/PCDF yield appears to result from both a reduction in the HCl content of flue gas and an inhibitory effect on fly ash surface reactions. DSI can also be used to remove HCl and reduce heterogeneous formation rates in the PM control device, but substantial amounts of PCCDs/PCDFs may be formed upstream of the sorbent injection point. Most of these PCDDs/PCDFs will be retained in the PM control device if the PM control device operating temperatures are low enough.

SD systems combine the advantages inherent in high flue gas quench rates, sorbents which probably modify PCDD/PCDF synthesis reactions, and low PM control device operating temperatures.

Solid-phase PCDDs/PCDFs can be captured in PM control devices. The amount captured will depend on the PM collection efficiency of the device. In FFs some vapor-phase PCDDs/PCDFs may also be captured by fly ash carbon as the flue gas passes through the filter cake.

Flue gas concentrations of PCDDs/PCDFs can either decrease or increase across an ESP [14, 31]. Increases are associated with high rates of PCDD/PCDF synthesis within a PM control device. PM control devices containing collected fly ash can serve as reactors for formation of PCDDs/PCDFs [32, 33]. The amount formed will depend on the temperature, the mass of PM within the control device, the composition of the fly ash, the composition of the flue gas, and the residence time of PM within the device.

Previously collected or newly formed PCDDs/PCDFs can remain within the PM control device or it can be desorbed into the flue gas. Alternatively, solid-phase PCDDs/PCDFs can be re-entrained in ESPs or escape capture by defective FF baghouses. FFs are more effective than ESPs in controlling PCDDs/PCDFs because of their higher PM control efficiency. Any PM not collected by the control devices may contain PCCDs/PCDFs.

PM control device collection efficiencies > 99% are probably necessary to control adequately PCDD/PCDF emissions.

6. PCDD/PCDF control at commercial MWCs

Stack emission of PCDDs/PCDFs from commercial MWCs has been found to range from <0.01 to 400 ng TEQ/dscm (<1.0 to 20 000 ng/dscm), depending on combustion and flue gas cleaning conditions (see Fig. 3) [31, 34–36]. Although the stack emissions are dependent on combustion conditions, the lowest emissions are generally obtained with MWCs equipped with SD/FF, followed in order by DSI/FF, SD/ESP, DSI/ESP, and ESP.

6.1. Combustion technology effects

Combustion conditions and the time/temperature profile in the cooling zones downstream of the combustor determine the amounts of PCDDs/PCDFs entering flue gas cleaning devices and the potential for formation within the devices.
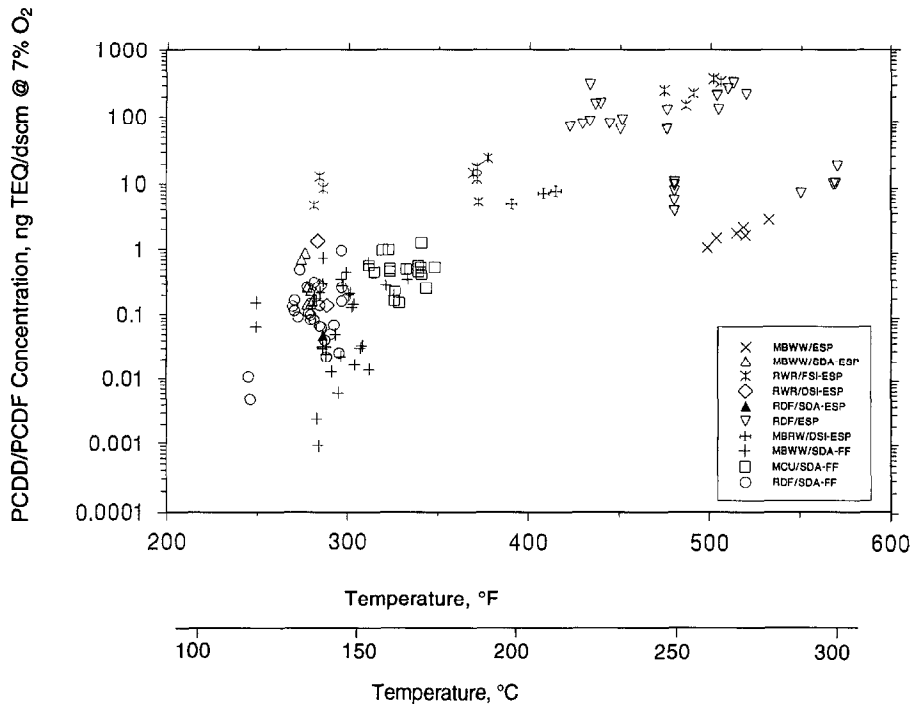
Fig. 3. Dependency of PCDD/PCDF emissions on technology and PM control device operating temperature [36].

The relationship of combustion conditions to the formation and emission of chloroorganics is especially acute for MWCs which do not have acid gas controls and which use an ESP to capture PM. This was shown by the results of Environment Canada's National Incinerator Testing and Evaluation Program (NITEP) project on the environmental characterization of mass burn technology at Quebec City [37, 38]. The Quebec City project consisted of 13 comprehensive tests at 6 different combustion conditions ranging from good to poor. Trace organics measured during the test included PCDDs, PCDFs, CBs, CPs, PCBs, and polycyclic aromatic hydrocarbons (PAHs). Combustion conditions evaluated included effects of waste firing rate (low, normal, and high) at good combustion conditions; low combustion temperatures; and poor combustion air distribution. Selected results of these tests are summarized in Table 4.

The lowest trace organic emissions were measured for good combustion conditions at normal waste burn rates (normal steam load). Combustion systems are typically designed for optimum performance at normal "full load" conditions. The increase in PCDDs/PCDFs and other trace organics at other combustion conditions was the result of a number of factors including lower combustion efficiencies, higher rates of PM carryover, higher ESP operating temperatures, and higher PM emission rates.

CO concentrations, which can be used to characterize combustion efficiency, ranged from 17 ppm during the low load good combustion tests to 173 ppm during

one of the poor air distribution tests. CO and average trace organic concentrations for the six different test conditions are shown in Table 4.

PM carryover rates can be estimated from the rate of fly ash collection since fly ash removal in the ESP should exceed 98%. ESP ash rates ranged from 45 to 130 kg/h (see Table 4). The correlation between PM carryover and PCDD/PCDF emission rates is shown in Fig. 4. Changes in PM carryover rate can be attributed primarily to changes in the flue gas flow rate and the ratio of underfire to overfire air. At higher loads, increased gas flow rates increase entrainment and carryover of PM. Higher underfire air flow rates also increase PM entrainment.

During the low combustion temperature tests at Quebec City, excess air rates were increased to lower the combustion temperature. This had the effect of increasing volumetric flow rates and particle entrainment. During the poor combustion air distribution tests, the underfire to overfire air ratio was increased, thereby increasing PM carryover.

Although the ESP operating temperature was not measured during the Quebec City tests, stack temperatures, which are probably about 10–15 °C lower, are given. The 16–30 °C higher stack temperatures, measured during the high-load, low-combustion temperature, and poor air distribution tests are reflective of higher ESP operating temperatures; hence, higher chloro-organic formation rates.

Average stack emissions of PM during each of the six different test conditions were low load, $26 \, mg/Sm^{3}$[2]; normal load, $22 \, mg/Sm^{3}$; high load, $36 \, mg/Sm^{3}$; high
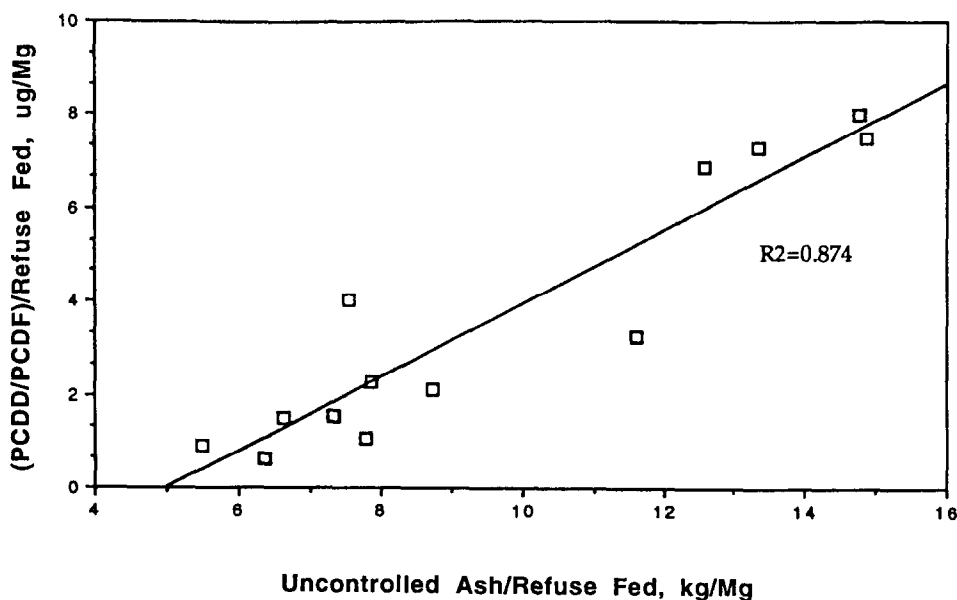

Fig. 4. Relationship of PM carryover to PCDD/PCDF emissions, Quebec City MWC.

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[2] mg/Sm^{3} denotes the tetra- through octa-PCDD/PCDF concentration on a dry basis corrected to 12% CO_2 and standard conditions at 25 °C (77 °F) and 101.3 kPa (14.7 psi).

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Table 4
Effect of combustion on trace organics in stack gas and collected ESP fly ash, Quebec City mass burn MWC[a]

Combustion conditions	Good comb. low load	Good comb. normal load	Good comb. high load	Marginal comb. high load	Low comb. temp.	Poor air distrib.
Parameter						
Test number, PT-	02, 10, 11	05, 06, 12	07, 09	13	03, 04	14, 15
CO, range (ppm) (Avg.)	17–30 (23)	20–37 (28)	43–43	77	76–80 (78)	153–173 (160)
Stack temp (°C)	210	210	226	240	230	230
PM emission (mg/Sm³)	26	22	36	54	55	62
ESP ash rate (kg/h) (% combustibles)	45 (6.9)	57 (7.6)[b]	79 (10.6)	128 (7.4)	130 (6.1)	116 (8.3)
Organics	*Stack conc. (ng/Sm³) (fly ash conc., ng/g)*					
PCDD	53 (760)	19 (580)	55 (620)	164 (590)	300 (600)	2100 (950)
PCDF	114 (220)	44 (190)	100 (260)	118 (180)	300 (230)	310 (260)
CB	3500 (960)	3300 (890)	4320 (1600)	6400 (1600)	9920 (1380)	9520 (1520)
CP	9490 (1240)	5080 (1820)	7990 (1700)	10 000 (1200)	22 500 (1290)	23 700 (2970)
PCB	4280 (5)	3020 (ND)	4840 (ND)	1600 (ND)	7000 (12)	1630 (24)
PAH	7090 (100)	4030 (110)	5380 (100)	3200 (46)	21 800 (120)	3150 (330)
Total organics	24 500 (3300)	15 500 (3600)	26 700 (4300)	21 500 (3100)	61 800 (3600)	38 500 (6100)

[a] All values are test condition averages unless otherwise noted. Flue gas concentrations corrected to 25 °C, 101.3 kPa, and 12% CO_2.
[b] Average for PT-05 and PT-12. PT-06 test result of 36.9% excluded.

load marginal combustion, 54 mg/Sm^3; low combustion temperature, 55 mg/Sm^3; and poor air distribution, 62 mg/Sm^3. The higher PM emissions can be attributed to higher PM loadings at the ESP inlet and higher flue gas flow rates. Some or all of the increase in PCDD/PCDF emissions can be attributed to increases in the emission of solid-phase PCDDs/PCDFs.

RDF spreader stoker combustors burn shredded wastes in a semi-suspension firing mode [6, 15]. They have inherently higher PM carryover rates and a higher percentage of carbon in their fly ash than fly ash from modern mass burn combustors. These factors result in a higher potential for PCDD/PCDF formation in RDF combustors. Older RDF units which do not employ acid gas scrubbers have exhibited PCDD/PCDF emissions in excess of 10 000 ng/dscm [34].

The Mid-Connecticut project was conducted by EPA and Environment Canada to evaluate the effects of combustion and SD/FF process conditions on air pollution emissions and residue characteristics from a modern RDF spreader stoker combustor [39–43]. The project consisted of 13 performance tests. Combustion tests were conducted at low, intermediate, normal, and high loads. The amount and distribution of combustion air were varied to provide good, poor, and very poor combustion conditions as determined by flue gas concentrations of CO [39].
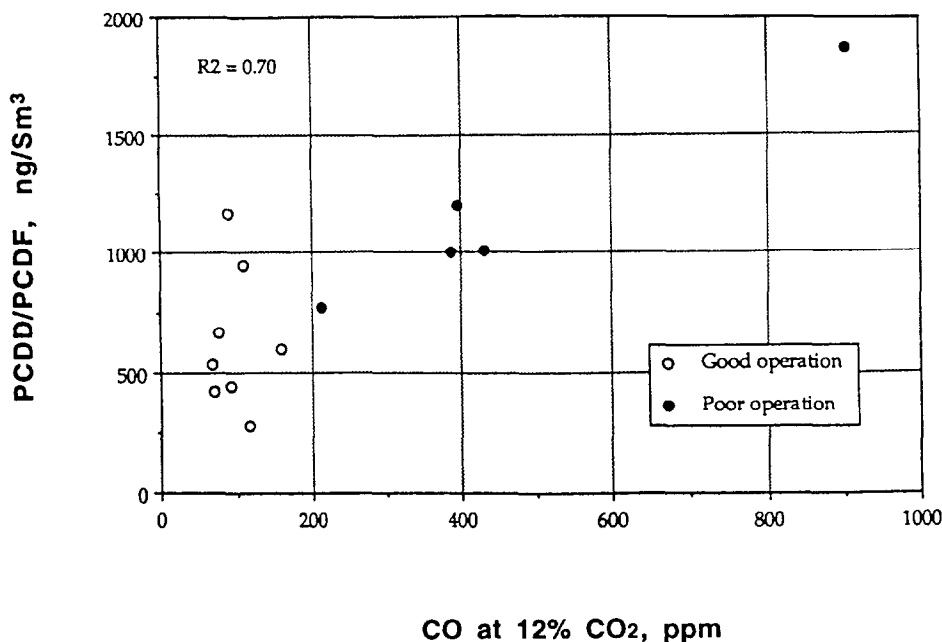

Fig. 5. Relationship between CO and PCDD/PCDF concentrations at SD inlet, Mid-Connecticut MWC.

Table 5
Organic concentrations at spray dryer inlet, Mid-Connecticut test program

Combustion conditions	Good combustion (Inter. load)	Very poor combustion (Inter. load)	Good combustion (Normal load)	Poor combustion (Normal load)
Test numbers	2, 10	5	8, 9, 11	3, 4, 7
SD Inlet				
Temp. (°C)	192	189	194	199
CO (ppm)	93	903	83	344
THC (ppm)	2.5	52	3	14
HCl (ppm)	450	469	461	430
SO_2 (ppm)	186	169	179	189
NO_x (ppm)	185	149	185	168
PM (mg/Sm^3)	4990	4460	4210	4050
Organics (ng/Sm^3)				
PCDD	228	580	125	196
PCDF	579	1280	591	732
CB	6050	15 800	5480	6940
CP	14 300	114 000	14 300	24 100
PCB	20	20	33	11
PAH	7330	112 000	16 500	53 900
Total organics	28 500	242 000	37 000	85 900
FF Outlet				
Temp (°C)	224	220	271	264
HCl (ppm)	19	21	54	19
SO_2 (ppm)	92	132	112	19
PM (mg/Sm^3)	4.9	3.9	5.1	5.8
Organics (ng/Sm^3)				
PCDD	0.13	0.37	0.33	0.37
PCDF	0.11	1.12	0.39	0.34
CB	53	754	228	110
PCB	ND	ND	19	12
CP	64	3240	3310	1882
PAH	2280	7730	3310	1882
Total organics	2400	14 000	3800	2200
VOC (ng/Sm^3)	102 000	3 370 000	16 000	632 000

Fig. 5 illustrates the relationship between CO and PCDD/PCDF concentrations at the SD inlet. CO and THC were found to be the two best single parameters for predicting PCDDs, PCDFs, CBs, CPs, and PAHs at the SD inlet [39].

Selected combustion test results showing flue gas concentrations of pollutants at the SD inlet are shown in Table 5. The concentration of all trace organics, except PCBs, increased as combustion conditions deteriorated. PCDD/PCDF concentrations increased from 716 ng/Sm^3 for good combustion at normal load (CO = 83 ppm) to 1860 ng/Sm^3 for very poor combustion at intermediate load (CO = 903 ppm). Total measured organics at the SD inlet (PCDDs, PCDFs, CBs, CPs, PCBs, and PAHs) increased from 28 500 ng/Sm^3 for good combustion at intermediate

load (CO = 93 ppm) to 242 000 ng/Sm^3 for very poor combustion at intermediate load [43].

Average flue gas temperatures ranged from 189 to 194 °C at the SD inlet and 120–165 °C at the SD outlet. Laboratory de Novo synthesis experiments have shown that little fly ash reactivity below 250 °C and further chloro-organic synthesis reaction in the FF were unlikely.

The pollutant concentrations at the SD inlet represent both vapor-phase organics and particle-bound organics. Most of the solid-phase organics will be collected as PM in the SD/FF system. Some fine PM and volatile compounds will escape capture. Table 5 also contains the results of volatile organic compound (VOC) measurements made at the FF outlet using EPA Method 0030 (VOC measurements were not made at the SD inlet). The concentration of VOCs increased from 102 000 ng/Sm^3 for good combustion at intermediate load to 3 370 000 ng/Sm^3 for very poor combustion.

Combustion conditions have a big effect on high-temperature destruction of organics, low-temperature chloro-organic synthesis, and the ultimate emission of semi-volatile compounds and VOCs. The design and operation of the air pollution control equipment will determine whether further organics are formed and whether they are collected or emitted to the atmosphere.

6.2. ESPs without acid gas control

In the 1970s and early 1980s, large MWCs constructed in the US normally used only ESPs for emissions control; scrubbers were seldom used. Most of the ESPs on these MWCs were designed to operate at temperatures in the range 175–315 °C to avoid acid gas corrosion. ESPs hold large amounts of PM and, at temperatures near 300 °C, de Novo synthesis reactions can produce large quantities of PCDDs/PCDFs.

The ESP operating temperature is perhaps the most important variable affecting the formation and emission of chloro-organics in ESP systems. At PM control device operating temperatures above 250 °C, de Novo synthesis reaction rates become significant and the partitioning of PCDDs/PCDFs into a vapor-phase increases with increasing temperature.

The results of tests to evaluate the effects of ESP operating temperature on the formation and emission of PCDDs/PCDFs are depicted in Fig. 6. These tests were conducted on a mass burn refractory MWC with a water spray flue gas quench chamber and an ESP, located in Montgomery County, Ohio [32]. Quench water flow rates were adjusted to obtain nominal ESP inlet temperatures of 300, 200, and 150 °C. The test conditions included: normal and poor combustion (low-temperature) tests at 300 °C inlet temperature; normal combustion with and without furnace injection of CaCO$_3$ at 200 °C inlet temperature; and normal combustion with furnace injection of CaCO$_3$ and duct injection of Ca(OH)$_2$ at 150 °C ESP inlet temperature.

The flue gas concentrations of PCDDs/PCDFs were higher at the ESP outlet than at the inlet for all tests, indicating PCDD/PCDF formation within the ESP. Under normal combustion conditions at the high ESP inlet temperature (300 °C), ESP inlet concentrations of PCDDs/PCDFs averaged 200 ng/dscm while stack concentrations
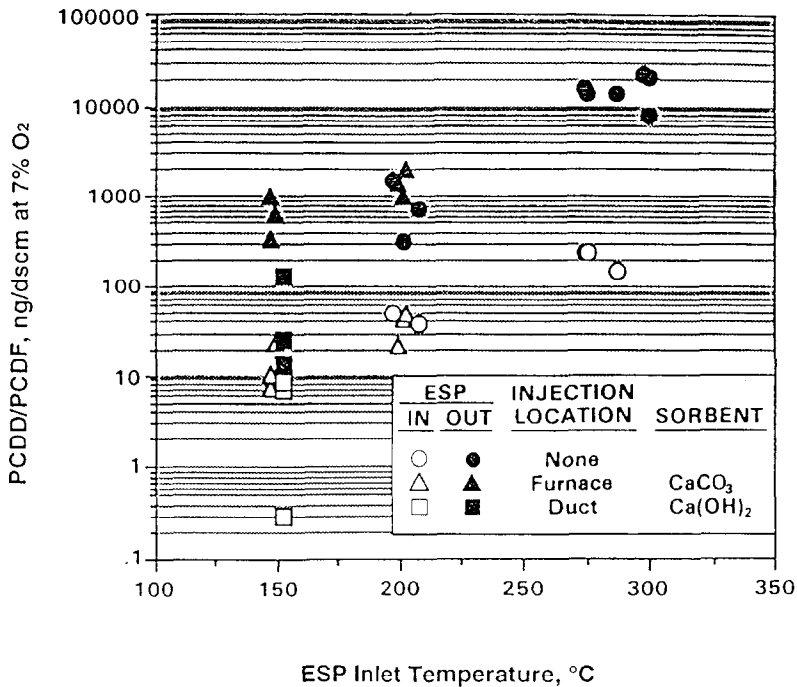
Fig. 6. Effect of ESP inlet temperature on PCDD/PCDF formation, Montgomery County MWC.

averaged 17 000 ng/dscm. Reducing the ESP inlet temperature to 200 °C without sorbent injection reduced average stack emissions to 870 ng/dscm. For tests with furnace injection of $CaCO_3$, stack emissions of PCDDs/PCDFs averaged 1480 ng/dscm at an ESP inlet temperature of 200 °C and 670 ng/dscm at 150 °C inlet temperature. The lowest emissions (57 ng/dscm) were obtained using duct injection of $Ca(OH)_2$. Operating at the lowest practical ESP operating temperature is critically important in minimizing PCDD/PCDF emissions.

Control of PCDDs/PCDFs in MWCs equipped with ESPs is dependent on the combustion conditions, the operating temperature of the ESP, and the ESP collection efficiency. The ESP operating temperature is critical, and it may be necessary to scrub acid gases for the flue gas to permit lowering the PM control device temperature to levels where acid gas corrosion is not a problem.

6.3. Dry scrubbers with ESPs

At the lower PM control inlet device temperatures typically employed by dry scrubbing systems, formation rates are greatly reduced and PCDDs/PCDFs are predominantly retained on captured fly ash. Although substantial quantities of trace organics may be formed during the combustion process, most of the semi-volatile organics are effectively collected in dry scrubbing systems. This is especially true of SD/FF systems.

MWCs equipped with SD/ESP systems are less efficient in controlling PCDD/PCDF emissions than similar MWCs equipped with SD/FF [31, 35]. The latter devices have better PM control efficiencies, and the flue gas is passed through a filter cake where PCDDs/PCDFs can be adsorbed on carbon particles. A review of data from eight different combustion units equipped with SD/ESPs indicated PCDD/PCDF emissions ranging from 9 to 173 ng/dscm. All but one of these units had emissions of less than 75 ng/dscm, and the average for the range of typical emissions was 38.1 ng/dscm [35].

The performance of SD/ESP systems in controlling PCDDs/PCDFs can also be improved by the injection of powdered activated carbon into the flue gas at the entrance to the SD system [44–46]. During three EPA-sponsored tests at the Camden County MWC, stack concentrations of PCDDs/PCDFs without activated carbon averaged 46.8 ng/dscm. During three tests in which 360 mg/dscm of dry activated carbon was injected into the flue gas upstream of the SD/ESP, stack concentration of PCDD/PCDF averaged 5.6 ng/dscm [45, 46]. Tests in Europe on MWCs equipped with SD/FF and SD/ESP systems have also shown the effectiveness of carbon injection for reducing PCDD/PCDF emissions [44].

6.4. Dry scrubbers with FFs

A review of data from 20 different combustion units equipped with SD/FF systems indicated PCDD/PCDF emissions ranging from 1 to 22 ng/dscm. Nineteen units had emissions less than 12 ng/dscm, and the average for these units was 6.6 ng/dscm. Two large MWCs with DSI/FF systems had PCDD/PCDF emissions of 5 and 18 ng/dscm, respectively [35].

MWCs with SD/FF are capable of controlling PCDD/PCDF emissions to levels below 10 ng/dscm as illustrated by performance tests on an RDF combustor at the Mid-Connecticut Resource Recovery Facility in Hartford, Connecticut [40–43]. During 13 tests under varying combustion and flue gas cleaning conditions, stack emissions of PCDDs/PCDFs ranged from 0.03 to 1.5 ng/Sm^3 and averaged 0.56 ng/Sm^3. SD/FF inlet and outlet data for these tests as a function of different SD/FF test conditions are shown in Table 6.

The nine test conditions given in Table 6 were combinations of SD outlet temperatures (120, 140, and 165 °C) and SO$_2$ concentrations at the FF outlet (low, medium, and high). Lime feed rates to the SD were controlled to achieve the targeted SO$_2$ outlet concentrations. PCDD removal efficiencies exceeded 99.7% except for one test at 99.2%, and PCDF removal efficiencies exceeded 99.9% for all tests. Because removal efficiencies were so high, it was difficult to determine whether SD operating parameters or sampling and analysis precision limits were responsible for results at different test conditions.

Removal efficiencies for CBs and CPs exceeded 94%. Stack concentrations of PCBs were generally below detection limits at SD outlet temperatures of 120 and 140 °C. PAH removal efficiencies averaged 94%. Although trace organic emissions appeared to decrease with decreasing SD outlet temperature, this trend was obscured by changes in trace organics concentrations during poor and very poor combustion tests.

Table 6
Effect of SD/FF operating conditions on control of PM, Hg, HCl, SO₂, and trace organics, Mid-Connecticut RDF combustor

	Target SD outlet temperature, (°C)								
	120°			140°			165°		
SO₂ target level	Low	Medium	High	Low	Medium	High	Low	Medium	High
Test number	7	10	2, 5	6	12, 13, 14	8	3, 11	4	9
Spray dryer inlet									
PM (mg/Sm³)	4230	4530	4950	3310	3430	4750	4310	3270	3890
Hg (µg/Sm³)	584	718	680	583	568	646	622	614	644
HCl (ppm)	399	429	470	404	445	538	416	471	432
SO₂ (ppm)	183	194	173	192	187	184	187	186	178
Organics (ng/Sm³)									
PCDD	207	243	396	317	95	211	161	151	71
PCDF	796	424	1007	885	341	951	611	623	378
PCB	17	13	23	12	ND	24	42	ND	6
CB	7100	6200	10 900	9400	4600	7100	6200	6000	4800
CP	25 200	16 200	62 900	41 600	14 400	20 200	20 800	17 000	11 300
PAH	51 800	6300	60 200	88 600	7700	10 300	47 100	22 500	32 400
Total organics	85 100	29 400	135 000	141 000	27 100	38 800	74 900	46 300	49 000
Fabric filter outlet									
PM (mg/Sm³)	4.4	4.1	4.8	2.7	5.5	3.9	5.6	7.6	5.8
Hg (µg/Sm³)	7.4	8.4	6.6	11.5	9.2	4.2	19.6	13.4	14.1
HCl (ppm)	8	19	20	10	18	41	21	31	96
SO₂ (ppm)	17	74	112	9	59	126	17	44	189
Organics (ng/Sm³)									
PCDD	0.17	0.18	0.23	0.35	0.06	0.29	0.35	0.37	0.58
PCDF	0.15	1.10	0.62	0.16	0.12	0.47	0.29	0.49	0.50
PCB	ND	ND	ND	ND	ND	7	27	19	14
CB	110	42	400	540	ND	110	290	90	110
CP	230	80	1600	1300	90	190	190	170	390
PAH	1400	2600	4800	2000	2900	2400	3700	2000	2400
Total organics	1740	2720	6860	3840	2990	2710	4210	2280	2920
VOC (ng/Sm³)	984 000	151 000	1 710 000	174 000	280 000	253 000	333 000	307 000	416 000

6.5. Continuous control of PCDDs/PCDFs

There is currently no feasible method for continuously measuring PCDD/PCDF emissions. Continuous control of PCDDs/PCDFs is of concern from regulatory and risk assessment perspectives. EPA's strategy to ensure continuous compliance with PCDD/PCDF emission limits is to place limits on CO concentrations, steam load, PM control device operating temperature, and opacity. The first three parameters limit formation and partitioning of PCDDs/PCDFs and the final parameter (opacity) will ensure proper operation of the PM control device in collecting solid-phase PCDDs/PCDFs. The effectiveness of the limiting parameters for continuously controlling PCDD/PCDF emissions is verified by periodic compliance tests on each MWC that is subject to regulation.

The manner in which the four continuous compliance parameters function to limit PCDD/PCDF emissions can be illustrated using the results of the Quebec City and Mid-Connecticut research projects on the formation and control of PCDD/PCDF emissions. PCDD/PCDF emissions for the four poor and one marginal combustion tests at Quebec City averaged 505 ng/Sm^3 [37]. Average PCDD/PCDF emissions for the eight good combustion tests averaged 132 ng/Sm^3. If the two good combustion tests with high loads (average = 154 ng/dscm) are excluded because of a requirement to comply with a GCP load limitation, then the average PCDD/PCDF emission for the remaining six tests is 113 ng/dscm.

While the opacity measurement cannot be used to quantify PM concentrations, it provides an indication of relative PM emissions. During the 13 Quebec City mass burn tests, the correlation coefficient, r^2, between PM and stack emission of PCDDs and PCDFs was 0.64 and 0.63, respectively. The average PM emission and opacity for the six good combustion tests at normal and low loads were 22 mg/Sm^3 and 31%, respectively. The average PM emission and opacity for the seven tests at high load and poor combustion were 51 mg/Sm^3 and 35%, respectively. The proposed EPA opacity limit of 10% guards against failures of the PM control equipment which would lead to excessive emission of particulate-bound PCDDs/PCDFs.

All tests on the Mid-Connecticut project met the proposed EPA NSPS emission limits for PM (15 mg/dscm) and PCDDs/PCDFs (13 ng/dscm). Only the tests at the low SO$_2$ target levels met the proposed NSPS limit of 30 ppm for SO$_2$. The average PCDD/PCDF emission for the four tests meeting this criterion was 0.51 ng/dscm. The continuous monitoring and compliance requirements for SD/FF flue gas cleaning systems appear to satisfactorily control PCDD/PCDF emissions to levels required by the proposed NSPS.

PCDD/PCDF emissions can also be expected to vary over time and from unit to unit. Most of the MWC field test data collected in the US and Canada have been reported in terms of total (tetra- through octa-congeners) PCDDs/PCDFs. EPA's proposed PCDD/PCDF emission limits are based on total tetra- to octa-PCDDs/PCDFs or PCDD/PCDF-TEQs, and variation in total and TEQ emissions is of interest.

PCDD/PCDF compliance test data for three units at the York County, PA, Resource Recovery Facility are summarized in Table 7 [47]. Each of the units is a

Table 7
PCDD/PCDF compliance test data,[a] York County Resource Recovery Facility (Mass burn rotary water wall MWCs with SD/FF)

Year	PCDD/PCDF (ng/dscm)				
Unit	Total	Avg.	TEQ	Avg.	Total/TEQ
1990					
1	4.00		0.063		83.5
	3.41		0.055		82.0
	5.40	4.3	0.086	0.068	62.8
2	9.13		0.144		63.4
	4.49		0.059		65.1
	3.21	5.6	0.045	0.09	71.3
3	3.05		0.056		54.5
	4.94		0.067	0.06	73.7
	2.75	3.6	0.045		61.1
1991					
1	16.20		0.125		129.5
	7.93		0.083		125.9
	17.10	13.8	0.098	0.10	174.7
2	2.80		0.028		100.0
	772.41		9.921		77.9
	96.07	290.4	0.831	3.59	115.6
3	5.78		0.028		206.4
	24.0		0.109		220.3
	7.28	12.4	0.050	0.06	145.6
1992					
1	1.26		0.067		18.8
	2.44		0.130		18.9
	1.36	1.69	0.074	0.09	18.4
2	8.17		0.391		20.9
	3.95		0.251		15.7
	3.22	5.11	0.217	0.29	14.8
3	3.25		0.188		17.3
	3.17		0.188		16.9
	6.56	4.33	0.393	0.26	16.7
1993					
1	5.10		0.090		56.7
	11.09		0.156		71.1
	0.00	5.40	0.000	0.08	
2	11.87		0.173		68.6
	5.20		0.084		61.9
	5.46	7.51	0.073	0.11	74.8
3	9.32		0.113		82.5
	6.61		0.076		87.0
	8.09	8.01	0.109	0.10	74.2

[a] Tests by EPA Method 23 during January, February, or early March of each year.

mass burn rotary water wall combustor equipped with a SD/FF system. Compliance test data (average of three runs for each year) are provided for each unit for 1990–1993. Except for one extreme value (290 ng/dscm), the total PCCD/PCDF compliance values of all three units ranged from 1.7 to 13.8 ng/dscm, averaging 6.5 ng/dscm. Excluding the extreme value, the TEQ values ranged from 0.06 to 0.29 ng TEQ/dscm, averaging 0.13 ng TEQ/dscm. On an individual test basis, the Total/TEQ values ranged from 14.8 to 220. The results of the compliance tests also indicate that average long-term PCDD/PCDF emissions can be adequately controlled by the continuous emission monitoring methods required by EPA.

6.6. Control of other organics

During many field tests, PCDDs/PCDFs have been the only trace organic pollutants measured. However, a number of field tests conducted to evaluate PCDD/PCDF control have measured other trace organic compounds. These measurements were made to more fully characterize formation and control of trace organics and to determine the concentration of organic compounds thought to be PCDD/PCDF precursors. These field test results confirm laboratory research showing that the complex of chloro-organic synthesis reactions that form PCDDs/PCDFs also lead to the formation of CBs and CPs [20]. In addition, the poor combustion conditions which increase PCDDs/PCDFs are generally found to increase the emission of PAHs and VOCs.

The Quebec City Mass Burn test project results showed good correlations between the concentrations of CO, THCs, PCDDs, PCDFs, CBs, and CPs in the stack gas [37, 38]. As indicated in Table 4, stack concentrations of PCDDs, PCDFs, CBs, and CPs were higher for the low combustion temperature and poor air distribution combustion tests than for the good combustion tests. Average stack concentrations of PCBs and PAHs were also higher for the low combustion temperature tests than for the good combustion tests. The average stack concentrations of PAHs and PCBs were lower for the poor air distribution tests than for the good combustion condition tests – an unexpected result. The total measured stack concentrations of trace organics were nearly four times higher for the low combustion temperature tests than the good combustion tests while the total measured stack concentration of trace organics was nearly 250% higher for the poor air distribution tests than for the good combustion tests.

Measurements on the Mid-Connecticut unit indicated that the concentration of trace organics at the SD inlet increased as combustion conditions deteriorated (see Table 5). Stack concentrations of PCDDs, PCDFs, CBs, CPs, PCBs, and PAHs appeared to be independent of combustion conditions, except for the very poor combustion condition test. Stack concentrations of VOCs were dependent on load and combustion conditions. VOC emissions increased with increasing load and decreasing combustion efficiency.

While PCDD/PCDF emissions have been of primary concern, MWCs emit a wide variety of trace organic pollutants. Semi-volatile organic compounds that condense or are adsorbed onto fly ash are easily removed in ESPs and FFs. In contrast, VOCs

are not effectively removed by ESP, DSI/ESP, SD/ESP, DSI/FF, or SD/FF systems. GCP is currently the best technique for controlling VOC emissions.

7. Mercury control in MWCs

The capture of Hg in flue gas cleaning devices depends on:
(1) waste composition,
(2) flue gas properties (temperature, gas composition, etc.),
(3) Hg form [speciation and phase (vapor or solid)],
(4) fly ash and sorbent properties,
(5) type of control device.

The waste composition and the relative amounts of Hg in each component determine the concentration of Hg in the MSW flue gas. Hg mass balances from the Quebec City test project indicated that more than 96% of Hg in the MWC output streams was in either the collected ESP ash or the flue gas [38]. Thermochemical calculations indicate that Hg is converted to elemental mercury (Hg^0) in the high temperature regions of the combustor. As the flue gas cools, Hg^0 is converted to other Hg species [48, 49].

7.1. Mercury speciation and control mechanisms

The form of Hg in flue gas depends on the flue gas composition and temperature. For combustion systems containing substantial amounts of Cl in the waste (or fuel), the two predominant forms of Hg at flue gas cleaning temperatures ($<300\,°C$) are believed to be ionic mercury (Hg^{2+}) and elemental mercury (Hg^0) [48–51]. Thermochemical equilibrium calculations indicate that the Hg^{2+} will be predominantly mercuric chloride ($HgCl_2$) [49].

Most metals condense to form solid particles as flue gas is cooled so that they can be collected as PM. However, both Hg^0 and $HgCl_2$ are vapors [Hg(v)] at typical flue gas cleaning control device operating temperatures ($300–140\,°C$), and special methods must be devised for their capture [8].

Hg in MWC flue gases can be captured if it is in the solid phase [Hg(s)] or is absorbed on fly ash or special sorbents such as powdered activated carbon. Hg(v) capture without the use of special sorbents depends on the amount of carbon in the fly ash. Well-designed and operated mass burn combustors have little carbon in their fly ash and, even when equipped with SD/FFs or SD/ESPs, they exhibit Hg control levels below 50%. Conversely, RDF combustors contain relatively high amounts of carbon in the fly ash ($>2\%$). And, they commonly exhibit control efficiencies above 80% and 90% when equipped with SD/ESPs and SD/FFs, respectively. Fig. 7 shows the distribution of Hg stack concentrations for RDF and non-RDF MWCs equipped with SD/FF and SD/ESP systems [35].

Two techniques employed for Hg capture in dry flue gas cleaning systems are the use of activated carbon and sodium sulfide (Na_2S) [8, 52]. Na_2S, a crystalline solid, is dissolved in water and injected upstream of the flue gas cleaning equipment. Hg^0(v)
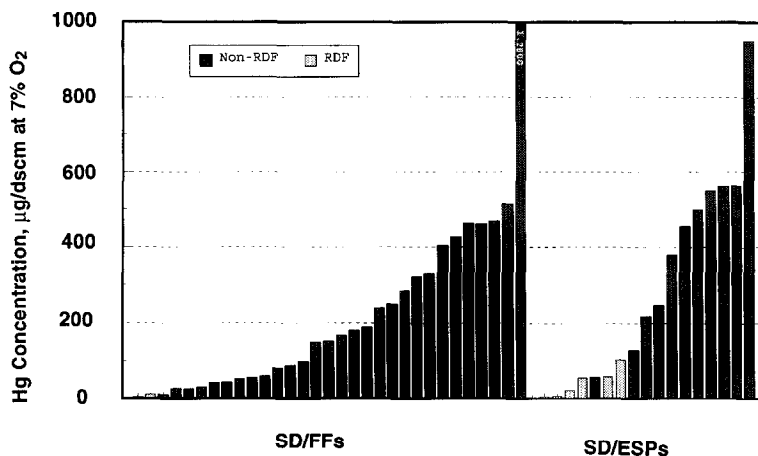
Fig. 7. Hg capture in MWCs with SD/FFs and SD/ESPs, large plants (> 225 Mg/day).

and Hg^{2+}(v) are converted to a solid form of Hg [mercury sulfide (HgS)] that can be collected in a PM control device. Na_2S has been used at MWC facilities in Europe and Canada for Hg control. Na_2S test results from European facilities show Hg emissions ranging from 40 to 70 µg/dscm and removal efficiencies from 65% to 90% [52].

Activated carbon has been used in two ways to control Hg(v) emissions [8, 52]. It can be injected as a powder into the flue gas where it absorbs Hg (v) and is then collected in a PM control device. Flue gas can also be filtered through a carbon bed filter which removes Hg(v) and other air pollutants. Carbon bed filters are currently being applied to European MWCs where they are primarily used to improve emission control of PCDDs/PCDFs, Hg, and other trace metals [53]. EPA has sponsored two major field tests on the injection of powdered activated carbon for Hg control and has selected this technology as the basis for Hg emission control requirements on MWCs [45, 46, 54–56].

7.2. Performance of powdered activated carbon systems

The performance of powdered activated carbon systems depends primarily on the carbon injection rate, carbon injection method, carbon properties, flue gas temperature, and PM control method. Performance tests in the US and Europe have primarily been limited to the application of carbon injection to mass burn MWCs equipped with SD/FF or SD/ESP systems [44–46, 52].

Two major test projects have been conducted in the US to evaluate the use of carbon injection on mass burn MWCs. The first was conducted on an MWC in Stanislaus County, CA, equipped with a SD/FF system. The second was conducted on two MWCs in Camden County, NJ, equipped with SD/ESP systems. These tests show that stack concentrations of Hg depend on the Hg concentration in the flue gas (SD inlet concentration), the carbon content of fly ash, and the operating conditions of the carbon injection system.
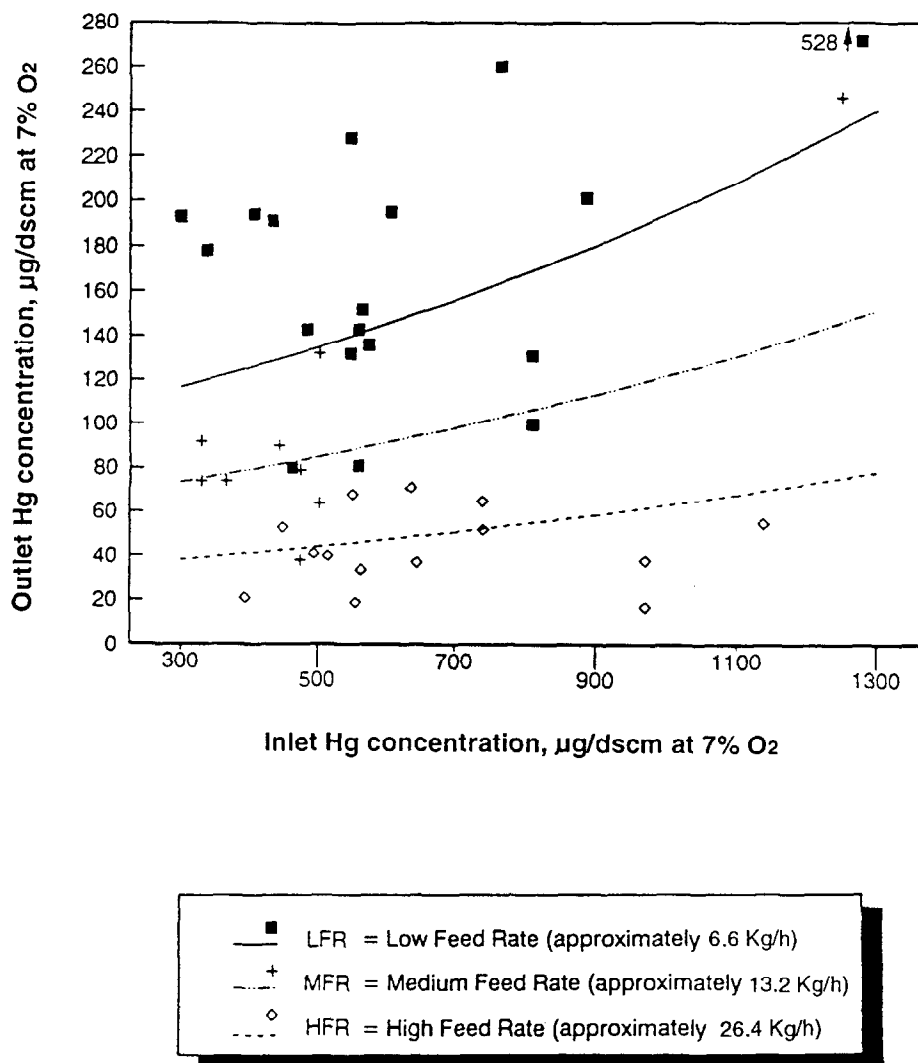
Fig. 8. Performance of activated carbon in SD/FF system, Stanislaus County MWC.

Mercury concentrations in MWC flue gas are highly variable with time. In MWCs the total solid-phase flue gas carbon (carbon in fly ash plus the carbon injection rate) appears to be the key determinant of Hg capture. In the absence of carbon injection, the amount of Hg captured depends on the amount of carbon in the fly ash. When the fly ash carbon content is low or when Hg concentrations are high, poor removal efficiencies are obtained. When the fly ash carbon content is high and the Hg concentration is low, high removal efficiencies are obtained.
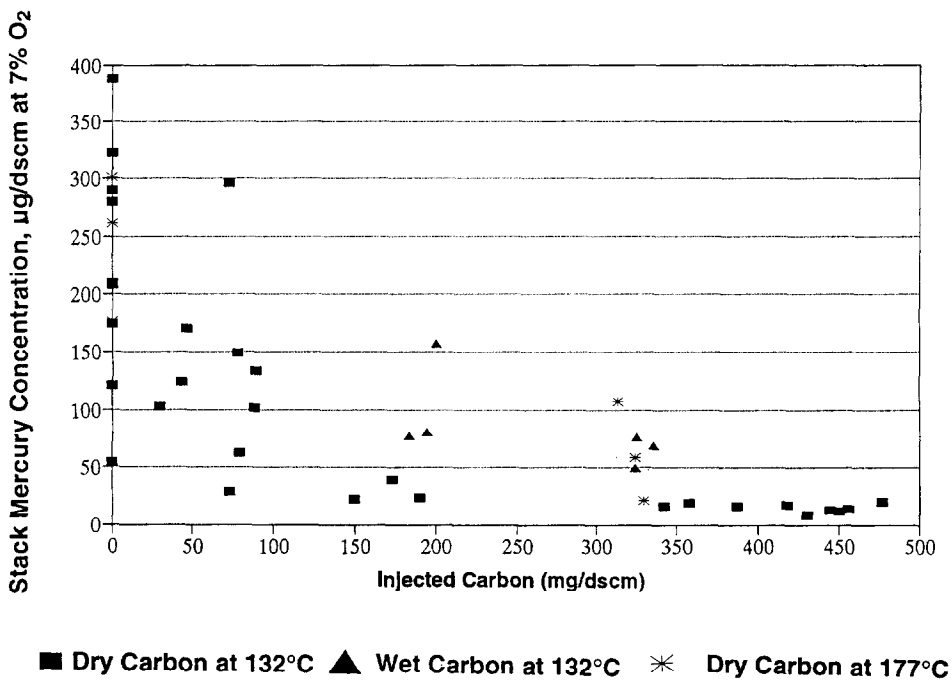
Fig. 9. Effect of injected carbon on mercury control in SD/ESP, Camden County MWC.

Injection of powdered activated carbon into the flue gas can be used to increase solid-phase carbon concentration. Increasing the carbon injection rate reduces both the average and variability of emissions. At high carbon injection rates, there is generally sufficient carbon to capture low or high levels of Hg. The amount of excess carbon needed for continuously high levels of capture will depend on the variation of Hg concentration in the flue. Highly variable Hg inlet concentrations will require high excess carbon injection rates to ensure continuous Hg capture.

In SD/FF tests at the Stanislaus County MWC, Hg capture without carbon injection ranged from 16% to 46%. Outlet Hg concentrations for these tests ranged from 311 to 538 μg/dscm. Hg capture increased with increasing carbon injection rates and, at the highest injection rates of approximately 70–100 mg/dscm, Hg outlet concentrations ranged from 17 to 77 μg/dscm (see Fig. 8) [53–55]. SD outlet temperatures at Stanislaus normally ranged between 136 °C and 145 °C.

During the Camden County SD/ESP carbon injection test project, Hg capture without carbon injection ranged from 18% to 92%. When dry carbon injection rates exceeded 150 mg/dscm and ESP inlet temperature was 132 °C, stack emissions of Hg were generally less than 80 μg/dscm (see Fig. 9) [45, 46]. The dependency of Hg reduction efficiency on the total solid carbon concentration in the flue gas during the Camden County tests is shown in Fig. 10.

The performance of activated carbon in absorbing Hg is dependent on temperature. The temperature at the inlet to the PM control device is normally used as a

■ Dry Carbon at 132°C   ▲ Wet Carbon at 132°C   ✳ Dry Carbon at 177°C
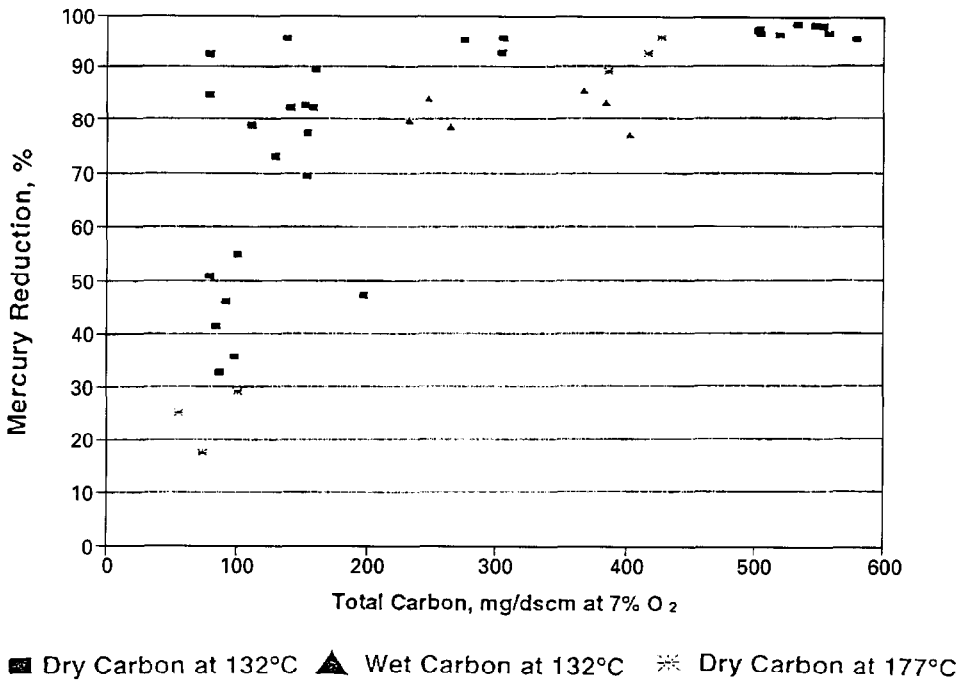
Fig. 10. Effect of total carbon on mercury control in SD/ESP, Camden County MWC.
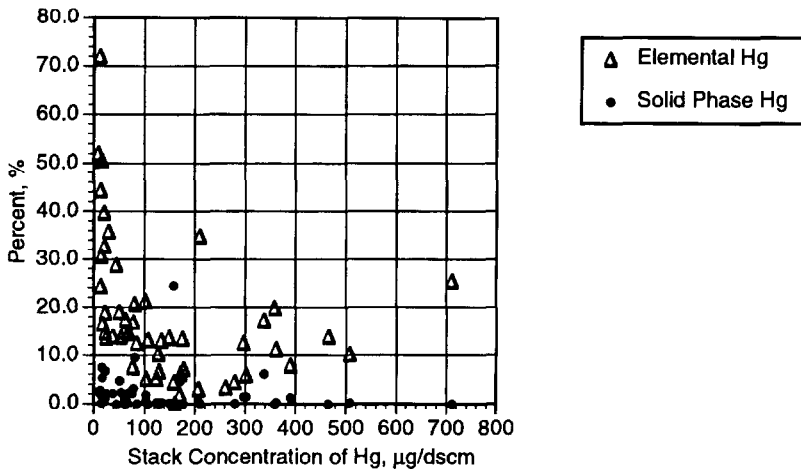

Fig. 11. Distribution of Hg in EPA method 29 sampling train, Camden County and Stanislaus County carbon injection projects.

parameter in evaluating the performance of the device in collecting condensed or absorbed pollutants. The PM control device inlet temperature for SD/FF and SD/ESP systems on MWCs is normally between 135 °C and 145 °C. Tests on the Camden County SD/ESP system at 177 °C indicated only moderate reduction in Hg capture relative to similar tests at 132°C (see Fig. 10) [45, 46]. Temperature variations over the normal operating range of SD/FFs and SD/ESPs can be expected to have only minor effects on Hg capture.

Similar tests on European MWCs have shown that carbon injection can be used to reduce Hg emissions in SD/FF and SD/ESP systems to less than 80 μg/dscm [44].

ESPs and wet scrubbers are commonly used to control emissions from European MWCs. Some European plants have installed activated carbon beds downstream of the primary air pollution control devices to act as polishing filters for the control of metals, dioxins, and acid gases. The use of activated carbon filter beds in combination with conventional control equipment has demonstrated Hg reductions exceeding 99% and Hg outlet concentrations of less than 1 μg/dscm [53].

7.3. Form of mercury emissions

In conducting risk assessments, it is important to estimate the form and speciation of Hg emitted from stacks. The transport, deposition, and environmental uptake of Hg are dependent on the form and speciation of Hg. Several studies estimate the speciation of Hg in MWC flue gases. Metzger and Braun estimate that nearly all Hg in MWCs at flue gas cleaning temperatures is in the form of mercury chlorides [51]. Lindqvist estimates that the speciation of Hg in raw flue gases is approximately 20% Hg^0, 60% Hg^{2+}, and 20% Hg(s) [50]. Pacyna estimates that Hg emissions from European waste incinerators consist of 10% Hg^0, 85% Hg^{2+}, and 5% Hg(s) [57].

There is currently no validated US method for determining the speciation of Hg in stack gas. However, information on the chemical behavior of Hg and the distribution of Hg in EPA's multi-metal sampling train (Method 29) can be used to estimate the form and speciation of Hg in MWC stack gas. Hg found in the probe and filter can be assumed to have been vapor-phase Hg absorbed onto PM or be a solid-phase compound. Both are associated with PM as designated by Hg(PM). $HgCl_2$ is soluble in water and Hg found in the $KMnO_4/H_2SO_4$ impingers was probably $Hg^0(v)$. The distribution of multi-metal train samples collected during the activated carbon injection tests at the Camden County MWC and Stanislaus County tests is shown in Fig. 11.

Tests with stack concentrations of Hg >100 μg/dscm represent no carbon injection or low carbon injection feed rates. For these tests, Hg^0 ranges from 2% to 26% of total Hg. As carbon injection rates and Hg capture increase, the percentage of Hg^0 as a fraction of total Hg increases. This implies that Hg^{2+} is more easily captured by activated carbon than Hg^0. For stack concentrations of Hg < 50 μg/dscm, the fraction of Hg^0 ranges from approximately 14% to 72%. The fraction of Hg (PM) was generally below 5% and exceeded 10% for only one test.

From the results of these tests it can generally be concluded that, for MWCs equipped with SD/ESPs and SD/FFs, the stack emission of Hg(PM) is negligible

unless further Hg is absorbed on the surface of PM between the stack sampling location and the stack exit.

At low levels of control, the stack concentration of Hg is probably 15–30% $Hg^0(v)$ and the rest is $Hg^{2+}(v)$ and Hg(PM). In MWCs with SD/FF or SD/ESP systems, stack concentrations of Hg(PM) are probably less than 5%. At high levels of control, $Hg^{2+}(v)$ is selectively removed, increasing the relative concentration of $Hg^0(v)$, and the relative concentration of $Hg^0(v)$ may be 50% or higher.

8. Conclusions

(1) Dioxin formation is predominantly associated with heterogeneous reactions involving fly ash. These low-temperature synthesis reactions can occur downstream of the combustor at temperatures ranging from approximately 250 °C to 600 °C.

(2) The flue gas cleaning systems most commonly employed on MWCs in the US include ESPs, DSI/FFs, SD/ESPs, and SD/FFs.

(3) Spray dryers and FFs can be used to continuously reduce PCDD/PCDF emissions to less than 20 ng/dscm. Powdered activated carbon, which is needed for Hg control in many MWCs, will provide additional PCDD/PCDF control.

(4) Spray dryers and ESPs can be used to reduce typical PCDD/PCDF emissions from mass burn combustors to less than 75 ng/dscm. Injection of activated carbon, to control Hg emissions, can be used to reduce further PCDD/PCDF emissions to less than 30 ng/dscm (about 0.5 ng TEQ/dscm).

(5) The Hg in MSW is volatilized during combustion and converted to $Hg^0(v)$ or $Hg^{2+}(v)$. Hg in MWC flue gas is believed to be predominantly $HgCl_2(v)$ and $Hg^0(v)$. Both are predicted to be in a vapor phase at stack gas temperatures.

(6) In dry flue gas cleaning systems, Hg(v) can be absorbed onto the surface of particles for collection in PM control devices. Hg(v) can be absorbed either on the residual carbon in fly ash or on activated carbon which has been injected into the flue gas.

(7) RDF combustors have relatively high amounts of carbon in their fly ash (> 2%) and those equipped with SD/FFs may attain Hg removal efficiencies of > 90% due to adsorption of Hg(v) onto the residual fly ash carbon. Other types of MWCs, such as water wall mass burn combustors, may require the injection of activated carbon to obtain efficient Hg(v) control.

(8) Nearly all of the uncontrolled Hg in MWC stack gas is in a vapor form. Method 29 sampling train data suggest that carbon absorption methods collect $Hg^{2+}(v)$ more efficiently than $Hg^0(v)$. As Hg removal efficiencies increase, $HgCl_2(v)$ is selectively removed and the proportion of Hg(v), i.e. $Hg^0(v)$ increases. In MWCs equipped with SD/FFs and SD/ESPs, the relative amount of Hg(PM) in stack gas will generally be less than 5%.

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