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Optimizing the Elimination of Dioxin-Like Compounds (PCDD/Fs and PCBs) Through Effective Combustion Practices in the Flue Gas in the Medical Waste Incineration Facility

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ABSTRACT

Polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs) are considered the most toxic and most concerning volatile organic compounds in the industrial flue gases. They are formed in various processes involving the combustion of organic materials in the presence of chlorine compounds, including modern and domestic coal burning, waste incinerators, sinter plants, cement industry, and metallurgical processes. The primary objective of this study was to investigate the destruction of PCDD/Fs and polychlorinated biphenyl (PCBs) using effective combustion practices. Flue gas samples were collected from the medical waste incineration plant to analyze PCDD/Fs and PCBs destruction under different temperature intervals, O_2 content, residence time, and exhaust gas recirculation. It has been found that, relying solely on good combustion practices is not sufficient to completely destruct PCDD/Fs and PCBs emissions. Even with the implementation of optimal combustion techniques, certain congeners such as 2,3,4,7,8-PeCDF and 1,2,3,7,8-PeCDD were still measured in high concentrations. Consequently, additional techniques such as dry sorbent injections, should be explored to meet the new stringent requirements of 0.1 ng I-TEQ/m^3.

1. INTRODUCTION

Polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs) are considered the most toxic and most worrying volatile organic compounds in the industrial flue gases [1]. PCDD/Fs and dioxin like polychlorinated biphenyl (dl-PCBs) are known contaminants belonging to the group of compounds classified as Persistent Organic Pollutants (POPs). PCDD/Fs compounds are created in all processes associated with the combustion of organics within the presence of different chlorine compounds (modern and domestic coal burning, waste incinerators, sinter plants, cement industry, ferrous and non-ferrous metallurgy, engine transport) [2-4]. Due to their lipophilic nature, they are known to bio accumulate, are carcinogenic and pose a significant health risk even at low concentrations [5]. Early life exposure to PCBs have been linked to attention deficit hyperactivity disorder (ADHD), autism spectrum disorders (ASD), or learning problems [6]. Dioxin congeners have many properties, but only a few are cancer-causing due to their ability to attach to a receptor in the body, which controls cell division. As a result, United States Environmental Protection Agency (USEPA) requires the emission into the environment and food chain to be strictly controlled. A Global Monitoring Plan (GMP) on Persistent Organic Pollutants (POPs) calls for monitoring of semi-volatile chemicals in ambient air and stack emissions [7].

Various studies such as Liu et al. [8], Li et al. [9], Gerasimov [10], Rao et al. [11] have studied the formation of PCDD/Fs during combustion processes. These studies provide valuable insights into the formation mechanisms of PCDD/Fs, highlighting both advantages and shortcomings in formation of PCDD/Fs. One advantage is the comprehensive investigation of combustion conditions such as temperature, oxygen content, and residence time, shedding light on their roles in PCDD/Fs formation. However, a significant shortcoming lies in the indistinct impact of these parameters during waste combustion, leading to confounded interrelationships and complicating the optimization of combustion practices. Combustion conditions have been investigated for the formation of PCDD/Fs, yet the impact of these operating parameters during waste combustion is indistinct, bringing about confounded interrelationships [12]. The role of chlorine on the formation of PCDD/Fs is debatable, some studies showed correlation between chlorine sources and PCDD/Fs formation [13, 14] while others show minimal correlation [15, 16]. Wang et al. [17] found that the amounts of highly chlorinated PCDD/Fs (i.e., octa-PCDD/Fs) does not necessary formed from high chlorine input, but they may form from presence of precursors such as chlorobenzenes (CBzs), chlorophenols (CPhs) and polycyclic aromatic hydrocarbon (PAHs) as they share similar formation mechanisms.

Additionally, the debate surrounding the role of chlorine in PCDD/Fs formation highlights the need for further research to elucidate its influence conclusively. Parameters which show the effectiveness of the combustion process, such as CO, have been displayed to correlate with PCDD/Fs destruction [1]. The reaction of chlorinated precursors, CPhs and CBzs in the gas phase under high-temperature homogeneous reactions, in the temperature range of 500 - 800°C has also shown to favor the formation of PCDD/Fs. The other mechanism is their formation at low-temperature heterogeneous reactions in the presence of metal catalysts, in the temperature range of 200 - 400°C [17]. Moreover, the findings by Wang et al. [17] that highly chlorinated PCDD/Fs may not necessarily form from high chlorine input but instead from the presence of precursors such as chlorobenzenes, chlorophenols, and polycyclic aromatic hydrocarbons suggest a need for a nuanced understanding of precursor pathways. Despite these challenges, parameters indicating combustion process effectiveness, such as CO levels, show promise in correlating with PCDD/Fs destruction, offering a potential avenue for optimizing combustion practices. Further research into the mechanisms governing PCDD/Fs formation, including both homogeneous and heterogeneous reactions, particularly in varying temperature ranges, is essential for developing targeted strategies to mitigate their formation and emission effectively.

The current study aims to investigate the influence of key combustion parameters such as temperature, oxygen levels, residence time, and exhaust gas recirculation on the formation and destruction of PCDD/Fs and PCBs in the flue gas of medical waste incinerators. By understanding how these parameters impact the PCDD/Fs compounds, the study seeks to identify optimal operating conditions that minimize their release into the environment. Additionally, the study aims to estimate the total load of PCDD/Fs in the atmospheric environment surrounding the incineration facility, providing valuable insights for risk assessment and management. Furthermore, the study aims to contribute to the development of effective combustion practices and technologies for mitigating the emissions of PCDD/Fs and PCBs, thereby ensuring regulatory compliance and safeguarding public health and environmental quality. The current study also addresses several gaps in the current understanding of PCDD/Fs formation and mitigation in medical waste incineration facilities. Firstly, it seeks to provide clarity on the interrelationships between key combustion parameters which have been identified as influential but remain poorly understood. By systematically investigating these factors, the study aims to fill the gap in knowledge regarding their specific impacts on PCDD/Fs formation and destruction during combustion processes. Furthermore, the study will explore the pathways and mechanisms through which PCDD/Fs are formed from precursor compounds such as chlorobenzenes, chlorophenols, and polycyclic aromatic hydrocarbons. This will help elucidate the complex formation pathways of PCDD/Fs and fill gaps in knowledge regarding the contributions of different precursor compounds to PCDD/Fs emissions in medical waste incineration facilities.

The study found that higher temperatures, particularly above 600°C, led to increased concentrations of PCDD/Fs and PCBs, with PCDFs being more dominant overall. Oxygen concentration exhibited a significant influence on PCDD/Fs and PCBs formation, with optimal yields observed at 8% oxygen content. Residence time also played a crucial role, with an optimal duration identified for minimizing PCDD/F and PCB concentrations. Furthermore, the study highlighted the distribution of these compounds in both gas and solid phases, with PCDFs predominantly emitted in the gas phase at higher temperatures. Additionally, analysis of PCDD/F congener profiles revealed distinct patterns under different combustion conditions, emphasizing the importance of understanding and controlling these parameters for effective PCDD/F and PCB mitigation. The findings highlighted the complexity of PCDD/F and PCB formation and destruction mechanisms, suggesting the need for a comprehensive approach combining combustion practices with additional measures for complete destruction and environmental risk reduction.

2. MATERIALS AND METHODS

2.1 Materials

Calibration solutions of the seventeen regulated 2,3,7,8-chloro-substituted PCDD/Fs (CSL-CS4), EPA-1613, and twelve PCBs (CS1-CS6), WP-CVS, containing the corresponding $^{13}C_{12}$-labelled compounds in nonane, were obtained from AfriFusion (Pty) Ltd (Midrand) for quantification purposes. The calibration solutions of PCDD/Fs and PCBs covered a concentration range from 0.1 to 400 ng mL^{-1} and between 0.1 and 200 ng mL^{-1}, respectively. The $^{13}C_{12}$-labelled surrogate standard solutions, EPA-1613 LCS and WP-LCS, injection standard solutions, EPA-1613 ISS and WP-ISS, for PCDD/Fs and PCBs were also supplied by AfriFusion (Pty) Ltd. Standards and calibration solutions were stored at 4°C until their analyses. Dichloromethane, toluene, cyclohexane, isooctane, and n-hexane for organic trace analysis were purchased from Chemspeed Technologies (USA) together with ethyl acetate and nonane. Silica gel was obtained from AfriFusion (Pty) Ltd (Midrand), basic Alumina ICN from MP Biomedicals (Germany), while Carbopack C 80/100 was obtained from Fluka (Switzerland). Benzene (grade reagent for analysis, purity $\geq$ 99.7%), and diethyl ether (EMSURE® for analysis, purity $\geq$ 99.7%) from Merck South Africa, and tetrahydrofuran (Photrex™ reagent, purity at 99%) supplied by AfriFusion (Pty) Ltd (Midrand), were used as potential dopants. Helium Alphagaz™ 1 (purity $\geq$ 99.999%), supplied by Air Liquide (Madrid, Spain), was used as the GC carrier gas, whereas nitrogen (purity > 99.995%), from Linde (Barcelona, Spain), was employed as the make-up gas for the GC-APPI source.

2.2 Sampling

2.2.1 Sampling and preparation

PCDD/Fs measurements survey was conducted to determine the formation of PCDD/Fs and PCBs during the incineration of medical waste (MWI) under good combustion practices. The following was understood prior to the commencement of the survey, the staff would ensure that all plant operations were to their satisfaction, including the correct operation of all relevant pollution abatement equipment. PCDD/Fs measurements were determined using sampling and testing procedures as described in US EPA Method 23 "Determination of Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans from Municipal Waste Combustors". The facility utilizes a dry scrubber as pollution abatement equipment. The ISO 9096: 2003 requirements were generally fulfilled in sections of duct with at least 5 hydraulic diameters of straight duct upstream of the sampling plane, and 2 hydraulic diameters downstream of the sampling plane (5 hydraulic diameters from the top of a stack). The height of the stack was 25 m above the ground with 0.66 m dimensions. The distance of sampling ports from nearest duct obstruction downstream was 7 m and the distance of sampling ports upstream from stack exit was 4 m. There were 2 sampling ports of 70 mm each at 90° angle.

The PCDD/Fs measurements survey aimed to comprehensively assess the formation of PCDD/Fs and PCBs during the incineration of MWI under optimized combustion practices. The survey was meticulously designed to capture key parameters influencing the formation and destruction of these compounds. Waste was systematically fed into the incinerator to maintain a consistent burning process, ensuring representative sampling. The temperature settings were carefully controlled, with the primary chamber maintained at 850℃ and the secondary chamber at 1150℃, aligning with optimal combustion conditions. Continuous Emission Monitoring System (CEMS) was used to measure parameters such as oxygen (O_2), particulate matter (PM), temperature profiles, and residence time, providing essential data for understanding the combustion dynamics. This involved careful calibration and setup of the incineration system, including precise control of waste feeding rates to maintain consistent burning conditions. Additionally, sampling points were strategically chosen to capture emissions at various stages of the incineration process, enabling a comprehensive analysis of PCDD/Fs and PCBs formation and distribution. This meticulous design ensured robust data collection and facilitated accurate insights into the complex mechanisms governing pollutant formation in MWI systems operating under optimal conditions.

During the study, rigorous managerial implication measures were implemented to ensure the accurate measurement and control of critical parameters within the medical waste incineration facility. Calibration, routine inspection and cleaning was conduct on the CEMs to ensure the accuracy of the results. Thermocouples were meticulously calibrated and regularly checked to maintain accuracy and reliability in temperature measurements. Additionally, scrubbers and bag filters were carefully maintained and monitored to ensure their optimal performance in capturing and removing pollutants from the flue gas stream. Routine inspections and maintenance activities were conducted on these systems to prevent any malfunctions or leaks that could compromise their efficiency. Instruments were calibrated according to standard procedures, and their functionality was verified before each measurement session to guarantee accurate readings. Similarly, residence time in the combustion chambers was closely monitored and adjusted as necessary to optimize pollutant destruction efficiency. Overall, stringent quality assurance protocols were implemented throughout the study to ensure the reliability and integrity of the data collected, enabling robust conclusions to be drawn regarding the impact of combustion practices on PCDD/Fs and PCBs emissions.

2.2.2 Sample collection

The samples were collected using a PS-1 sampler (Graseby Anderson, GA, USA) following the revised EPA-1613 method. A quartz fiber filter and a glass cartridge with polyurethane foam (PUF) were used for collecting particle phase and gas-phase compounds, respectively. A known amount of PCDD/Fs isotopically labeled surrogate standards ($^{37}Cl_4$- 2,3,7,8-TeCDD, ^{13}C- 1,2,3,4,7,8-HxCDD, ^{13}C-2,3,4,7,8-PeCDF, ^{13}C- 1,2,3,4,7,8-HxCDF, and ^{13}C-1,2,3,4,7,8,9-HpCDF) was spiked into the cartridge before field sampling in order to estimate the collection efficiency of the sampling train. The sampling flow rate was set to 0.225 m^{-3} min^{-1} ±10%. A total of four sampling campaigns, labeled as SC1, SC2, SC3, and SC4, were carried out to obtain adequate sampling volumes, amounting to more than 54 m^3 of air sampled. During each of these campaigns, various conditions were documented, including the collection of samples at temperatures of 300, 600, and 900℃, with O_2 content ranging from 2% - 10%, and residence times from 0.5 - 5 s. The sampling volumes were calibrated to the normal condition of 760 mmHg and 25℃. The samples were withdrawn Isokinetically from the gas stream and collected using the sample probe, on a glass fiber filter, and on a packed column of adsorbent material. The samples were not separated into a particle and vapor fraction. At the end of sampling campaign, all 30 samples were transported to the laboratory and stored at 4℃ until analysis.

2.3 Extraction and clean-up of extracts

Each sample (gas + particle) was spiked with a recovery standard containing 21 $^{13}C_{12}$-labelled PCDD/Fs and PCBs. Samples were individually extracted using a Soxhlet extraction unit for 18 hours with hexane 5 mL and 6 hours with 3 mL of toluene. The hexane and toluene fraction were combined and concentrated using rotary-evaporator. The extract was then re-dissolved in hexane and concentrated to approximately 5 mL with Turbo Vap II apparatus. The extracts were then purified using a multilayer 20 mm inner diameter (id) column containing a small layer of sodium sulphate, 1 g activated silica, 2 g of basic silica, 4 g of acid silica (44% ww), 1 g activated silica and a small layer of sodium sulphate (silica and sodium sulphate were baked at 450℃ overnight). The contents were eluted from the column with hexane and toluene, then evaporated to approximately 2 mL to be further purified using gel permeation column containing 6 g of Biobeads SX3. After loading the extract, the contents were eluted with acetone. The collected extracts were then concentrated to dryness under the stream of nitrogen. They were reconstituted with 250 µL of labelled ^{13}C- PCBs (30, 141 and 208) as internal standards.

2.4 Instrumental analysis

The determination of PCDD/Fs and PCBs by GC-HR/MS was performed differently using Trace 1300 gas chromatograph coupled to a Q-Exactive Orbitrap mass spectrometer (Thermo Fisher Scientific, San Jose, CA, USA), under atmospheric pressure photoionization (APPI) source supplied by MassCom Technologies GmbH (Bremen, Germany). The chromatographic separation of PCCD/Fs and PCBs was carried out using the same GC column, a DB-5ms UI (60 m × 0.25 mm I.D., 0.25-µm film thickness) fused-silica capillary column (Chemspeed Technologies, USA). In both cases, the injector was operated at 280℃ in splitless mode (1 min), using helium as carrier gas at a constant flow mode (1.0 mL min^{-1}), and the injection volume was 1.5 µL for PCDD/Fs and 1 µL for PCBs. The oven temperature program for PCDD/Fs was 140℃ (held for 1 min) to 200℃ at 20℃ min^{-1} (held for 1 min) and then to 300℃ at 2.5℃ min^{-1} (held for 20 min), and for PCBs, 140℃ (held for 2 min) to 180℃ at 20℃ min^{-1} (held for 1 min) and to 300℃ at 2.5℃ min^{-1} (held for 5 min). The transfer line and capillary temperatures were set at 280°C and 225°C, whereas the source temperature was set at 250°C and 225°C for PCDD/Fs and PCBs analyses, respectively. Native and labelled compounds were acquired by selected ion monitoring (SIM) with mass resolution maintained at 10 000 throughout the analysis.

2.5 Description of experimental procedures

The emission factor (EF) for PCDD/Fs was calculated using Eq. (1) based on the information obtained in SC 4 (highest total concentrations obtained in this study). The total mass of PCDD/Fs emitted in SC 4 was 59.74 ng TEQ/m³ and the activity data was 1 ton per day of incineration of medical waste.

$$\begin{gathered}\text{Emission Factor (EF)}_{\text{Air}} = \text{M}_{\text{PCDD/Fs}}\text{ emitted/ M}_{\text{waste}}\text{ incinerated}\\ \text{M}_{\text{PCDD/Fs}}\text{ emitted} = \text{C}_{\text{PCDD/Fs}}\text{ (ng/m}^3\text{) X total Volume (m}^3\text{)}\\ \text{Total volume of gas + particulate emitted in day was } 324\text{ m}^3\end{gathered} \tag{1}$$

EF = 5.974E-8 ng TEQ ton-waste^{-1} (significantly smaller than the Emission Factor of 1 µg TEQ/t MW incinerated recommended by UNEP 2013).

To calculate the potential release of PCDD/Fs into the environment, we used Eq. (2), the EF of 5.97 ng TEQ ton-waste^{-1} and the provided activity data of 1,000,000,000 ng/day. The EF represents the rate at which the substance is emitted into the air per unit of activity, which means that for every ng of PCDD/Fs emitted per day (ng TEQ/day), 5.97 ng TEQ are released into the air per ton-waste^{-1} incinerated.

$$\begin{gathered}\text{Potential Release} = \text{M}_{\text{waste}}\text{ incinerated (ton/day) X Emission factor (ng/ton)}\\ \text{Potential release} = 5{,}970\text{ ng TEQ/m}^3\text{ /day}\end{gathered} \tag{2}$$

2.6 Quality assurance

Several steps were taken to obtain data that would allow an assessment of the accuracy and reliability of the data. PCDD/Fs and PCB data were corrected using 21 $^{13}C_{12}$-labelled PCDD/Fs and PCBs isotope dilution standards, using the injection standard as an internal standard. The criteria for the quantification of analytes were a retention time found within 2s of the standard, isotope ratio found within 20% of standard and a signal to noise ratio of at least 3. Due to unavailability of air CRMs, spiking method using anhydrous sodium sulphate was used to check the effectiveness of the extraction and clean up procedures for the analysis of PCDD/Fs and PCBs at different concentration levels. The average spiked recoveries for surrogate standards were compared in four different tests. In SC1 the recoveries ranged between 101 - 115%, SC2 from 98 - 113%, SC3 from 99 - 113 and SC4 from 97 - 107%. This means the extraction techniques yielded comparable results, and the overall average extraction recovery rate. The average recoveries $^{13}C_{12}$-labelled standard ranged from 99 - 112%. Analytical blanks, consisting of solvent were included at a rate of one blank for every 12 samples. The method detection limit was calculated as 3 times the standard deviation of the concentrations found in the analytical blanks. If the concentrations in the blanks were below the instrumental detection limit, then the method detection limit was defined as equal to the instrumental detection limit. All results were blank corrected using the concentration of the field blanks. Field blanks were produced for each test, and they were used to calculate method detection limits (MDLs). When compounds were not detected in the field blanks, laboratory blanks produced for each quarter were used to estimate MDLs. The concentrations are reported as ng-WHO$_{2005}$ TEQ. m^{-3}.

3. RESULTS AND DISCUSSION

This chapter presents the impacts of temperature, O_2 levels, residence time, and the distribution of gas and solid-phase compounds on the destruction of PCDD/Fs and PCBs. Additionally, it discusses the fingerprint profile for PCDD/Fs congeners in stack emissions, the fingerprint profile of PCBs congeners in stack emissions and the emission factors and potential release of PCDD/Fs to the environment.

3.1 Effects of temperature in PCDD/Fs and PCBs destruction

The effect of temperature on the formation and destruction of PCDD/Fs and PCBs during MSWI treatment is demonstrated in Figure 1. At a temperature between 600°C and 800°C, PCDD/Fs concentrations were high to identify their isomer compositions. It was observed that the destruction of PCDD/Fs above 900°C was greater than its formation. This is consistent to the findings reported by Palmer et al. [18], Liu et al. [19], and Sørmo et al. [20]. Both PCDD/Fs were generated in solid phase at the temperature range of 300°C however, it was noted that PCDFs were more predominant in both solid and gas phase than PCDDs. The samples taken from 300°C and 600°C were similar in isomer composition except that the highly chlorinated congener such as octa-chlorinated dibenzo-p-dioxin and octa-chlorinated dibenzofuran were observed to be more dominated. These findings align with those reported by Xia et al. [21]. The typical profile for PCDFs from combustion systems were more highly chlorinated species because of the Cl content present inside the reactor. Other studies such as Chen et al. [22]; Gunes et al. [23]; Lin et al. [24]; Wei et al. [25] have confirmed that PCDDs were likely to be formed in less temperatures between 180 and 280°C through de novo synthesis. De novo synthesis is known to occur in a relatively low temperature range of 200 - 400°C. It involves the combustion of relatively innocuous chemical molecules, accompanied by simultaneous oxidation and chlorination at these lower temperatures [26]. It was also noted that the mechanism of PCDFs formation was slightly different from that of PCDDs and each formation was influenced by precursor concentration and chlorine content.

The study revealed interesting trends regarding the concentrations of PCDFs and PCDDs at varying temperatures. As the temperature increased from 300 to 500°C, there was a steady rise in both PCDD/Fs concentrations. However, a sharp increase in concentrations was observed as the temperature rose above 600°C. Both PCDDs and PCDFs exhibited similar trends concerning temperature increase but overall PCDFs were more dominant. Across the investigated temperature ranges, it was consistently observed that the total emission of PCDFs surpassed that of PCDDs, with a minor deviation noted at temperatures exceeding 900°C, this slightly contradicts of Qiu et al. [27], who measured higher concentration of PCDDs instead. At 600°C, the formation of both PCDDs and PCDFs was predominant especially for lower chlorinated congeners such as the 2,3,7,8-substituted tetra-chlorinated contributing up to 93% of the total PCDD/Fs due to favorable conditions in the combustion zones. However, as the temperature increased to 850℃, a decline in both PCDDs and PCDFs was observed with PCDFs showing slower reduction rates. At 900℃, PCDDs formation surpassed that of PCDFs but soon after, both compounds demonstrated a sharp decline indicating increased destruction rates. Shortly after this temperature point, both compounds demonstrated a sharp decline, indicating increased destruction rates. This pattern suggested a critical temperature threshold where the destruction of PCDDs and PCDFs became more efficient, possibly due to enhanced combustion conditions or increased residence time at higher temperatures. These findings align with those reported by Lin et al. [28] and Xing et al. [29]. Additionally, measurements at 670℃ revealed that the temperature at the inhibitor feeding point significantly influenced PCDD/F reductions, highlighting the importance of careful temperature control for efficient destruction. Ultimately, these findings emphasize the complex relationship between temperature and PCDD/Fs behavior underlining the need for well-designed and controlled processes to mitigate the PCDD/Fs effectively while minimizing their formation. Simultaneously, PCBs formation exhibited analogous patterns in relation to PCDD formation just in lower concentrations.

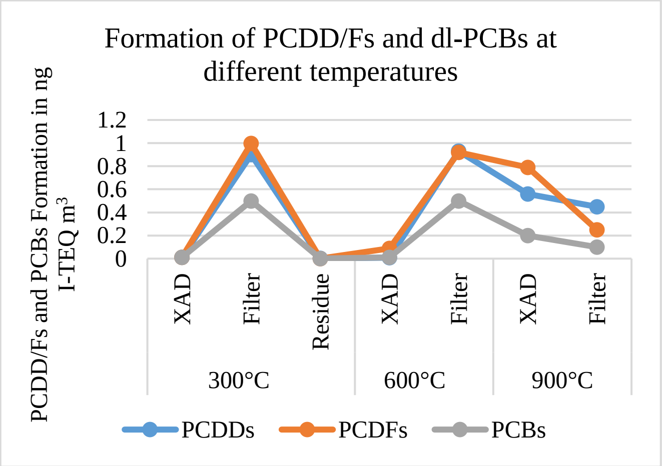

Figure 1. Formation of PCDD/Fs and PCBs at different temperatures

3.2 Effect of oxygen concentration

The O_2 concentration in combustion processes exerts a substantial influence on the intricate mechanisms of PCDD/Fs and PCBs formation and destruction. Figure 2 shows the dependence of the PCDD/Fs concentration on O_2 content in the carrier gas stream where at the temperature of 300℃, the PCDD/Fs and PCBs concentration reached its maximum formation. When O_2 concentrations in the surrounding gaseous medium was less than 1 vol.% in pyrolytic conditions, the PCDD/Fs and PCBs practically could not be formed. At the O_2 level between 2% and 4%, the formation of PCDD/Fs and PCBs started to show a slight increase however, the formation was still minimal. When the O_2 levels reached 6%, a significant reaction in the formation of PCDD/F and PCBs compounds was observed indicating a strong correlation between O_2 levels and the generation of PCDD/F. The maximum yield of PCDD/Fs and PCBs was observed when the O_2 content reached 8% which aligns with the de novo mechanism of formation. However, above 8% O_2 content PCDD/Fs and PCBs formation began showing a significant decline with almost no formation above 10% O_2 content. These findings align with those reported by Ren et al. [30], Yu et al. [31], Zhao et al. [32], and Wang et al. [33]. Nevertheless, when the O_2 levels were reduced below 2%, incomplete combustion and combustion starvation was observed leading to increased concentrations of CO. This suggests that the presence of O_2 plays a crucial role not only in the formation of PCDD/Fs and PCBs but also in the overall combustion efficiency and the formation of other combustion byproducts like CO. Adequate O_2 supply is crucial in promoting complete carbon combustion and reducing the formation of chlorinated intermediates, thus decreasing the likelihood of PCDD/F formation [34]. These observations highlight the significance of controlling O_2 levels during combustion processes to mitigate the formation of PCDD/Fs, PCBs and CO.

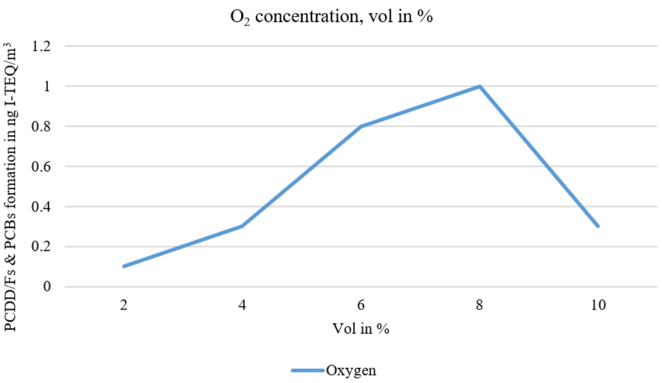

Figure 2. O_2 dependence in PCDD/Fs and PCBs formation process

Nganai and Lomnicki [35] suggested that O_2 concentration had no effect on the PCDD/Fs formation during de novo synthesis, but instead it's the presence of metal oxide/chlorides that influence the PCDD/Fs formation within the de novo synthesis model. In contrary, this study concluded that O_2 levels played a critical role in the formation of PCDD/Fs during de novo synthesis. The results of the present study are consistent with those of Zhang et al. [36], Potter et al. [37], and Xu et al. [38] indicating that both precursor formation and de novo synthesis play significant roles in the generation of PCDD/Fs within the post-combustion zone of a municipal solid waste incinerator. On the other hand, in oxygen-deficient conditions, chlorinated compounds may persist longer increasing the risk of PCDD/F generation. In terms of destruction, oxygen-rich environments as encountered in specialized incineration facilities enhance the efficient breakdown of PCDD/Fs, breaking them down into less harmful products. Nevertheless, maintaining a delicate balance is essential as excessively high O_2 concentrations may also lead to the formation of nitrogen oxides (NO_x), potentially facilitating the generation of more toxic PCDD/F congeners under specific circumstances [39]. Additionally, catalytic processes can offer an alternative means of destruction utilizing catalysts to facilitate the breakdown of PCDD/Fs at lower temperatures and with lower oxygen concentrations thereby promoting selective destruction pathways and minimizing the production of hazardous byproducts [35]. Overall, understanding the role of O_2 concentration was vital for managing and mitigating the environmental impact of PCDD/Fs in combustion processes. It is recommended that, O_2

level greater than nine percent (9%) be maintained for more efficient destruction of PCDD/Fs and PCBs, as indicated by the discussion above. At this concentration, the formation of PCDD/Fs begins to decline significantly, while still providing sufficient oxygen for efficient combustion processes and minimizing the risk of other harmful byproducts.

3.3 Effect of residence time

Residence time appeared to have a major influence on the formation of PCDD/Fs and PCBs and destruction. Based on the observations, the window of time available for the formation of PCDD/Fs and PCBs to take place was from 0.5 s during the combustion process. During this time period both PCDD/Fs and PCBs concentrations started to show a steady increase indicating the initiation of their formation. This steady increase continued until around 1.0 s suggesting that the conditions during this duration were conducive to PCDD/Fs and PCBs formation. Following this initial period, PCDFs, PCDDs, and dl-PCBs displayed different concentrations at various residence times as demonstrated in Figure 3. As the residence time increases from 0.1 s to 0.9 s, the concentrations of PCDFs, PCDDs, and dl-PCBs exhibit some fluctuations, this is consistent with the findings reported by Ma et al. [40]. For PCDFs, there is a gradual increase from 3.2 ng I-TEQm^3 at a residence time of 0.1 s to 3.8 ng I-TEQm^3 at a residence time of 0.6 s, after which it remains constant. This suggests that an extended residence time has a limited impact on PCDF concentrations beyond a certain point. In the case of PCDDs, a similar pattern was observed, with an increase from 1.5 ng I-TEQm^3 at a residence time of 0.1 s to 1.9 ng I-TEQm^3 at a residence time of 0.6 s, followed by stability. This implies that the residence time has a moderate influence on PCDD concentrations. The concentrations of dl-PCBs also follow a comparable trend, rising from 3.1 ng I-TEQm^3 at a residence time of 0.1 s to 3.7 ng I-TEQm^3 at a residence time of 0.6 s and remaining steady thereafter. Similar to PCDFs and PCDDs, dl-PCBs concentrations are notably affected by changes in residence time up to a certain threshold. The results suggest that an optimal residence time may exist for minimizing the concentrations of PCDFs, PCDDs and dl-PCBs. Beyond this point, further increases in residence time may have limited additional benefits in reducing these pollutants.

The current study also demonstrated that the samples taken with the longest residence times shifted the congener pattern towards higher PCDD/F congeners. Flue gas chlorination reaction became more efficient as the reaction of PCDD/Fs and PCBs increases. Residence time in the post-combustion region was highly dependent on the temperature intervals. It was discovered that at the shortest residence time of 0.2 - 0.3 s the most dominant congeners were TCDD, PeCDD, PeCDF, HxCDF, this aligns with the findings reported by Yang et al. [41] but in contrary to what Peng et al. [42] reported. At the medium residence time of 0.3 - 0.4 s the most dominant congeners were found to be HxCDD, HxCDF, and HxCDF in consistent with Cheruiyot et al. [43]. While at the longest residence time of 0.5 - 0.8 s the more dominant congeners were OCDF, OCDD, similar to the findings reported by Peng et al. [42], Xiao et al. [44], and Zhao et al. [32]. The samples taken during combustion in the primary chamber also shown that the concentration of PCDD/Fs and PCBs in the gas phase depended mostly on the residence time and temperature profile. Subsequently, when the residence time in the temperature ranged from 250°C - 450°C was shortened, the amount of both PCDD/Fs and PCBs decreased. Due to the pressure gradient drop caused by the exhausters installed in the incinerator, gas flow was mostly vertical from top to bottom, and the gas velocity was about 0.3 - 0.5 m/s.

In addition to the observed trends in PCDD/Fs and PCBs concentrations, further analysis revealed interesting insights into the relationship between residence time and the formation of these pollutants. Specifically, longer residence times in the post-combustion region were found to enhance the efficiency of the flue gas chlorination reaction, resulting in a shift towards higher PCDD/F congeners. This phenomenon suggests that prolonged exposure to specific temperature intervals facilitated more extensive chlorination reactions, leading to the formation of higher chlorinated congeners. Moreover, the study also highlighted the impact of residence time variations on the composition of the gas phase during combustion in the primary chamber. It was observed that alterations in residence time within the temperature range of 250°C - 450°C had discernible effects on the concentrations of PCDD/Fs and PCBs. Notably, shorter residence times within this temperature range correlated with decreased pollutant concentrations. This trend may be attributed to changes in the combustion dynamics and the availability of precursor compounds under different residence time conditions [42]. The findings also indicated that variations in residence time led to shifts in the dominant congeners present, reflecting changes in the combustion kinetics and precursor availability. These findings highlighted the intricate interplay between residence time, temperature profiles, and pollutant formation mechanisms within incineration processes.

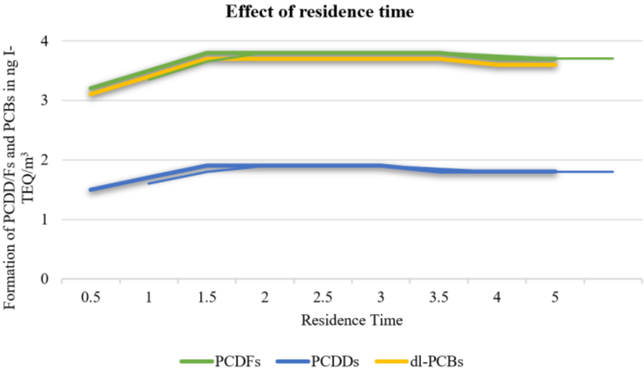

Figure 3. PCDD/F and PCBs levels at different residence time

3.4 Gas and solid phase compound distribution

During the study, we observed significant variations in the emission behavior of PCDD/Fs and PCBs as the temperature increased. Initially, at 300°C, most PCDD/Fs were emitted in the solid phase suggesting that they are not fully vaporized and remain bound to particulate matter, but at 600°C, they tended to be trapped in filters and XAD resin, this shift suggests an increased volatilization and subsequent capture by these collection media (Figure 4). Conversely, higher temperatures led to a slight increase in PCDFs in the XAD-II resin, with more PCDFs being destructed at 900°C. PCBs, on the other hand, were found at higher concentrations in the gas phase between 600 and 900°C compared to 300°C, consistent with previous findings by Guo et al. [45] and Hsu et al. [46]. Remarkably, PCBs in the gas phase were slightly more abundant than PCDD/Fs. As gas phase temperatures rose above 600°C, both PCDFs and PCBs exhibited a sharp increase, followed by a slower rise in PCDDs, as reported by Xiong et al. [47]. The transition temperature for PCDD/Fs to enter the gas phase occurred below 400°C, while for PCBs, it occurred above 800°C. Despite variations in waste types, combustion conditions, and furnace types, multiple studies have demonstrated strong correlations between PCBs and PCDD/Fs, consistent with the results presented by Ying et al. [48].

Some researchers have suggested that PCBs may act as precursor molecules for the formation of PCDD/Fs during the combustion process [9, 46, 49, 50]. Our study found that under normal operation conditions, the total PCDDs emission ranged from 0.1 to 3.45 ng I-TEQ/m^3. However, during manual poking, which is regarded as unfavorable combustion conditions, a significant amount of dust deposition in the primary chamber resulted in a drastic increase in PCDFs concentration up to 5.24 ng I-TEQ/m^3. As illustrated in Figure 4, the concentration of PCDD/Fs in the flue gas increased from the low-temperature zone of the incinerator to the outlet, and it further decreased significantly in the filter baghouse. However, concentrations of both PCDD/Fs and PCBs decreased at temperatures above 900°C in the secondary chamber inlet. This contrasts slightly with the findings presented by Zhong et al. [51], who reported no changes at temperatures above 900°C. For comprehensive emission control, the destruction of PCDD/Fs occurred in the baghouse outlet (quenching tower) and in the cooling system as temperatures dropped to between 280°C and 230°C. Overall, our results indicate that higher combustion temperatures generally lead to reduced concentrations of PCDDs, PCDFs, and PCBs, regardless of the collection method. The XAD method consistently recorded lower concentrations than the filter method for all pollutants and temperatures.

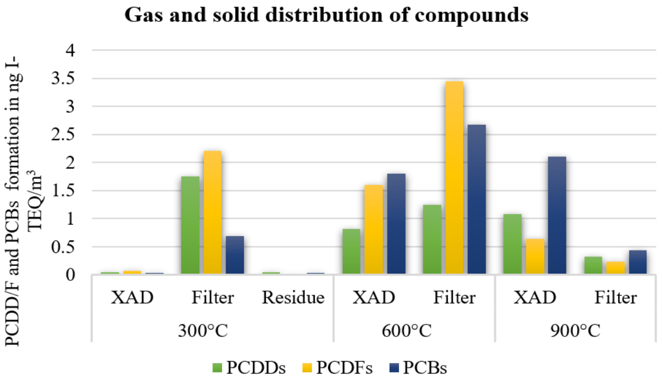

Figure 4. The distribution of PCDD/Fs, and PCBs at 300, 600, and 900°C combustion

When comparing the concentrations of PCDFs across different combustion temperatures, it was observed that, the value was higher when burned at 600°C. This could be attributed to several factors: At 600°C, PCDFs exhibit increased volatility, leading to greater liberation from solid surfaces and enhanced transfer to the gas phase. However, simultaneous adsorption onto filter media and XAD resin occurred, resulting in higher concentrations being captured in these collection media. The increase in temperature from 300°C to 600°C accelerated the thermal decomposition of precursor compounds, leading to enhanced PCDF formation. As a result, more PCDFs were available for capture by the filters and XAD resin. This is consistent with the findings reported by Hsu et al. [46]. It was also observed that, the combustion process at 600°C was more efficient in breaking down precursor molecules into PCDFs, leading to higher concentrations of PCDF compounds being released into the gas phase and subsequently captured by filters and XAD resin. Xiong et al. [34] suggested that, the kinetics of PCDF formation favors higher concentrations at 600°C due to optimal reaction rates under these conditions, resulting in increased PCDF capture by filters and XAD resin. Overall, the combination of increased volatility, enhanced thermal decomposition, improved combustion efficiency, and favorable formation kinetics at 600°C contributed to the largest PCDF filter value observed at this temperature during combustion.

3.5 Optimal fingerprint profile for PCDD/Fs congeners in stack emissions

Seventeen (17) 2,3,7,8 -PCDD/Fs homolog patterns were used to generate distinct fingerprints representative of incineration plant emissions, as detailed in Table 1. Throughout the study, four sampling campaigns were conducted, denoted as SC1, SC2, SC3, and SC4. To ensure accuracy and reliability of the results, consistent sampling conditions were maintained across all campaigns. This included keeping the temperature, oxygen concentration, residence time, and waste type consistent throughout each sampling campaign. This rigorous approach minimized potential variables that could influence the emission behavior of PCDD/Fs and PCBs, ensuring reliable data for analysis and comparison. The analysis of the PCDD/Fs congener profiles in the stack demonstrated the understanding of PCDD/Fs destruction mechanisms using good combustion practices. The most dominant congener in SC1 was 2,3,4,7,8-PeCDF with a measured concentration of 6.035 ng I-TEQ/m^3 measured at 900ºC. Following closely was the congener 1,2,3,7,8-PeCDD which exhibited a concentration of 3.72 ng I-TEQ/m^3 at the same temperature interval. These results indicate that during SC1, when samples were exposed to the high temperature of 900ºC, 2,3,4,7,8-PeCDF was the most abundant congener of PCDF present, significantly surpassing the concentration of the other congeners, with 1,2,3,7,8-PeCDD being the second most prevalent. The findings are consistent with the results presented by Cai et al. [52] and Xia et al. [21]. In contrast to the dominant PCDF and PCDD congeners measured during SC1, octachlorodibenzo-p-dioxin (OCDD) and octachlorodibenzofuran (OCDF) were found to be much less prevalent in all samples at different temperature intervals. Both OCDD and OCDF reported concentrations of less than 0.003 ng I-TEQ/m^3 indicating their less dominance under the conditions of the test. The low concentrations of OCDD and OCDF are significant because they are also members of the PCDD and PCDF family and can exhibit toxic properties similar to other congeners with higher concentrations. However, in this particular test, their concentrations were notably negligible compared to the more dominant congeners like 2,3,4,7,8-PeCDF.

The low concentrations of OCDD and OCDF during SC1 were attributed to several factors, such as temperature, residence time (0.8 s), O_2 concentration (10%) and the presence of certain metal catalysts. This aligns with the observation reported by Lin et al. [53]. The conditions during the incineration process did not favor the formation of OCDD and OCDF congeners leading to their low presence in the samples. This incineration facility is equipped with advanced emission control technologies such as scrubbers and filters to capture and remove hazardous pollutants from the exhaust gases. These technologies effectively captured and reduced the release of OCDD and OCDF into the stack. This contrasts with the findings of Qiu et al. [54], who indicated that bag filters alone are ineffective in reducing PCDD/F, emphasizing the need for a combination of technologies. OCDD and OCDF are known to be less volatile compared to some other PCDD/Fs [45]. The findings obtained during this campaign highlights the potential risks posed by PCDD/Fs when exposed to high temperatures emphasizing the importance of monitoring and mitigating their presence in various environmental settings to safeguard public and ecological health. The congener distributions observed in the current study are notably similar to those reported by Hsu et al. [46], Xia et al. [21], and Jiang et al. [55], who also measured concentrations in the ranges of 0.049 ng I-TEQ/m^3 - 11.28 ng I-TEQ/m^3 from incineration stacks.

During SC2, the most dominant congeners in the stack were 2,3,4,7,8-PeCDF measuring 4.26 ng I-TEQ/m^3, followed closely by 1,2,3,7,8-PeCDD measuring 1.98 ng I-TEQ/m^3 both at 900ºC respectively. This differs slightly from the findings reported by Ying et al. [56] who reported a dominance of OCDD. As with other PCDD and PCDFs, these congeners are toxic environmental pollutants and can pose health and environmental risks. Understanding the distribution and levels of specific congeners like 2,3,4,7,8-PeCDF and 1,2,3,7,8-PeCDD is crucial for assessing the potential impact of emissions from industrial processes and guiding appropriate measures to control and reduce their release. In SC2, OCDD and OCDF were the least dominant congeners measuring less than 0.001 ng I-TEQ/m^3 indicating their minimal presence in the stack emissions which was parallel with the findings reported by Fujimori et al. [57] and Ying et al. [48]. The composition of the materials being incinerated significantly impacted the formation of OCDD and OCDF during SC2. According to studies by Wang et al. [17], Zhu et al. [58], Zhang et al. [59], and Qiu et al. [54] more-chlorinated PCDD homologs contribute more to total PCDD concentrations in stack gas samples. On the contrary, the current study did not detect any variations in PCDF concentrations between the more chlorinated and less chlorinated homologs.

Out of all the campaigns conducted, it was precisely SC3 that exhibited superior performance in efficiently destructing a greater number of PCDD/Fs congeners. This remarkable outcome was achieved through the meticulous implementation of optimal combustion practices. It is important to note that the effectiveness of SC3 in reducing the PCDD/Fs congeners was unparalleled when compared to the other campaigns in the study. Among the measured congeners in SC3, 2,3,4,7,8-PeCDF was the most dominant with a concentration of 1.16 ng I-TEQ/m^3, followed far behind by 1,2,3,7,8-PeCDD measuring 0.60 ng I-TEQ/m^3. On the other hand, the least dominant congeners were OCDD, OCDF, and 1,2,3,4,7,8,9-HpCDF, all measuring less than 0.0001 ng I-TEQ/m^3 respectively. Stringent regulations and emission standards for dioxins and furans in many countries including South Africa have prompted incineration facilities to adopt measures that minimize the formation and release of these compounds. It is important to note that the reasons for the lower concentrations of OCDD and OCDF during the incineration process depended on the operating conditions, technologies employed and the composition of the waste being incinerated. According to the findings, although most PCDF WHO$_{2005}$-TEQ/PCDD WHO$_{2005}$-TEQ ratios were less than 0.1 ng I-TEQ/m^3, PCDFs slightly dominated PCDD/s congeners. Several congeners, including OCDD, OCDF and 1,2,3,4,7,8,9-HpCDF measured much lower concentrations during post-combustion zone indicating that de novo synthesis played a significant role in the low-temperature zone.

The results from SC4 indicate that among the congeners measured, 2,3,4,7,8-PeCDF was the most dominant exhibiting a concentration of 5.64 ng I-TEQ/m^3 at 900ºC. Following closely was 1,2,3,7,8-PeCDD with a concentration of 3.06 ng I-TEQ/m^3 also at 900ºC. In contrast, OCDD was the least dominant congener in this campaign as in other tests. Similar results have been reported in North China, Zhu et al. [58] who measured the concentration between 0.11 - 2.53 ng I-TEQ/m^3 and 0.007 - 0.059 ng I-TEQ/m^3, respectively. While the most dominant PCDD/F congeners in SC1 - 4 were 2,3,4,7,8-PeCDF and 1,2,3,7,8-PeCDD. However, TCDD, PeCDD, PeCDF, and HxCDF were dominant during the combustion phase which is in agreement with Liu et al. [8] and Ying et al. [48]. We compared the congeners profile in the incineration process with other industrial sources and found that they were all dominated by PCDFs as in the findings by Zou et al. [60] and Li et al. [9]. Xia et al. [21] reported a different pattern that the PCDD/Fs in stack gas were usually characterized by higher fractions of OCDF, 1,2,3,4,6,7,8-HpCDF, OCDD and 1,2,3,4,6,7,8-HpCDD. However, the dominant congener profiles in this study remained constant. Previous studies such as Zhu et al. [58], Qiu et al. [54], and He et al. [61] have shown that most PCDD/Fs were formed through de novo synthesis when the PCDF WHO2005-TEQ/PCDD WHO2005-TEQ ratio was >1. That coincided with our conclusion that PCDD/Fs were mostly formed through de novo synthesis during the incineration processes.

In SC1, the total TEQ measurement was 19.40 ng I-TEQ/m^3, while SC2 recorded a total of 13.37 ng I-TEQ/m^3. The lowest TEQ reading of 3.85 ng I-TEQ/m^3 was obtained during SC3, whereas SC4 yielded the highest measurement at 20.04 ng I-TEQ/m^3. Higher proportions of PCDFs over PCDDs was observed in this study which was contradictory to Pan et al. [62] who reported higher proportions of PCDDs over PCDFs in the flue gases from CFB and MWI. Formation of low-chlorinated PCDDs (1,2,3,7,8-PeCDD, 1,2,3,4,7,8-HxCDD, 1,2,3,6,7,8-HxCDD and 1,2,3,7,8,9-HxCDD) possessed strong correlation and the chlorophenols were the important precursors of low-chlorinated PCDDs which were generated within the low chlorinated content [62]. The stack emissions presented certain similarities with an increasing chlorinated level, the content of the 2,3,7,8-PCDD congener increased but the content of 2,3,7,8-PCDF congener showed irregularities. This is consistent with the results presented by Dong [63] and Gul et al. [64]. Based on the results obtained from these campaigns, it appears that relying solely on good combustion practices is not sufficient to completely destruct PCDD/Fs emissions. Even with the implementation of optimal combustion techniques, certain congeners were still measured in abundance. To achieve a more comprehensive destruction of PCDD/Fs, a combination of combustion practices and additional measures such as dry sorbent injections is necessary. By implementing this complementary technique along with improved combustion practices, it becomes more feasible to achieve complete destruction and minimize the environmental and health risks associated with PCDD/F compounds.

Table 1. PCDDs, PCDFs stack emission measurement survey (concentrations reported in ng I-TEQ/m^{-3})

SC	**1**			**2**			**3**			**4**		
O$_2$	%	09.00		%	09.44		%	09.01		%	10.45	
Sampled volume (dry)	ng I-TEQ/m^{-3}	0.80		ng I-TEQ/m^{-3}	0.77		ng I-TEQ/m^{-3}	0.81		ng I-TEQ/m^{-3}	0.84	
Temperature intervals	300°C	600°C	900°C	300°C	600°C	900°C	300°C	600°C	900°C	300°C	600°C	900°C
PCDDs												
2,3,7,8-TCDD	0.08	0.10	0.31	0.04	0.057	0.13	0.01	0.01	0.03	0.06	0.09	0.19
1,2,3,7,8-PeCDD	2.23	1.34	3.72	0.8	1.17	1.98	0.23	0.29	0.60	1.09	1.65	3.06
1,2,3,4,7,8-HxCDD	0.10	0.05	0.15	0.10	0.05	0.15	0.02	0.03	0.06	0.04	0.10	0.30
1,2,3,6,7,8-HxCDD	0.05	0.01	0.04	0.02	0.02	0.04	0.01	0.002	0.011	0.02	0.04	0.08
1,2,3,7,8,9-HxCDD	0.03	0.01	0.04	0.02	0.02	0.05	0.01	0.001	0.02	0.04	0.05	0.06
1,2,3,4,6,7,8-HpCDD	0.004	0.01	0.01	0.01	0.01	0.02	0.004	0.01	0.01	0.01	0.02	0.04
OCDD	0.003	0.01	0.001	0.002	0.001	0.001	0.001	0.001	0.001	0.001	0.002	0.004
Total I-TEQ ∑PCDD	8.27			4.68			1.34			6.93		
PCDFs												
2,3,7,8-TCDF	0.04	0.05	0.12	0.02	0.03	0.05	0.004	0.01	0.01	0.02	0.04	0.08
1,2,3,7,8-PeCDF	0.01	0.02	0.04	0.01	0.02	0.03	0.003	0.004	0.01	0.02	0.02	0.04
2,3,4,7,8-PeCDF	1.63	2.03	6.04	1.54	1.65	4.26	0.42	0.54	1.16	2.15	3.10	5.64
1,2,3,4,7,8-HxCDF	0.06	0.08	0.23	0.08	0.12	0.224	0.02	0.03	0.06	0.23	0.13	0.22
1,2,3,6,7,8-HxCDF	0.06	0.09	0.20	0.001	0.06	0.17	0.02	0.03	0.02	0.15	0.14	0.27
2,3,4,6,7,8-HxCDF	0.06	0.08	0.20	0.002	0.12	0.23	0.03	0.04	0.09	0.14	0.16	0.31
1,2,3,7,8,9-HxCDF	0.01	0.02	0.05	0.02	0.003	0.06	0.01	0.01	0.001	0.01	0.04	0.09
1,2,3,4,6,7,8-HpCDF	0.001	0.002	0.004	0.001	0.002	0.01	0.001	0.001	0.01	0.004	0.005	0.01
1,2,3,4,7,8,9-HpCDF	0.001	0.001	0.004	0.0004	0.0002	0.0001	0.0001	0.001	0.002	0.01	0.02	0.03
OCDF	0.002	0.01	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.002	0.02	0.001
Total I-TEQ ∑PCDFs	11.13			8.69			2.51			13.07		

3.6 Optimal fingerprint profile of PCBs congeners in stack emissions

In the current study, fingerprints of incineration plant emissions were established using twelve (12) homolog patterns of PCBs, as illustrated in Table 2. During SC1, the most dominant congener was #52 measuring 0.445 ng I-TEQ/m^3 at 900°C followed shortly by congener #44 reporting a measurement of 0.352 ng I-TEQ/m^3 at 300°C. The least congeners were observed to be #110 measuring 0.011 ng I-TEQ/m^3 at 300°C and congener #153 reporting a concentration of 0.015 at 600°C. This differs slightly from the findings reported by Hsu et al. [46] who reported a dominance of #118 and #156. For most PCB congeners their concentrations decreased as the temperature increased. This is a common trend in PCB degradation studies as the temperature rises, the compounds undergone thermal degradation leading to a decrease in their concentration [41, 65]. Congeners such as #44 and #118, showed a relatively high concentration at 300°C which decreased significantly at 900°C. While #153 and #110 had relatively low concentrations across all three temperatures indicating that these congeners were less prevalent in the sample and less stable under the conditions tested. Congeners #18 and #28 exhibited fluctuations in concentration as the temperature increased i.e. #18: 0.171 ng I-TEQ/m^3 at 300°C, 0.205 ng I-TEQ/m^3 at 600°C and 0.117 ng I-TEQ/m^3 at 900°C; #28: 0.236 ng I-TEQ/m^3 at 300°C, 0.173 ng I-TEQ/m^3 at 600°C and 0.103 ng I-TEQ/m^3 at 900°C. The decrease in ∑PCBs with increasing temperature suggested that higher temperatures were more effective at degrading these compounds and reducing their overall toxicity. These fluctuations can be attributed to the complex chemical reactions occurring at different temperature ranges, which may lead to variations in the formation and destruction rates of these congeners. Furthermore, these fluctuations emphasize the importance of understanding the temperature-dependent behavior of individual congeners to accurately assess their emissions and potential environmental impact. Such detailed analysis provides valuable insights into the mechanisms driving the formation and destruction of these POPs in combustion processes, aiding in the development of more effective mitigation strategies [30]. Additionally, the fluctuations observed in the concentrations of congeners #18 and #28 highlight the dynamic nature of the combustion process and the intricate interplay between various factors influencing the formation and destruction of these compounds. These fluctuations may be attributed to factors such as changes in reaction kinetics, thermodynamic equilibria, and the availability of precursor molecules at different temperature intervals [50]. Moreover, the presence of catalytic species or inhibitors in the combustion environment further modulated the behavior of individual congeners, contributing to the observed variations in their concentrations.

In SC2 the most dominant congener was #170 measuring 0.493 ng I-TEQ/m^3 at 300°C followed closely by congener #101 with a measurement of 0.475 ng I-TEQ/m^3 at 600°C. The least reported congeners were #170 measuring 0.003 ng I-TEQ/m^3 and #138 measuring 0.022 ng I-TEQ/m^3 both at 600°C respectively. These findings align with the outcomes reported by Shen et al. [66] in the steel making electric arc furnace. Overall, most congeners exhibited a decrease in concentration as the temperature increased. This suggested that, in this SC higher temperatures also lead to a reduction in the concentration of these compounds due to thermal degradation. In contrary to Mila et al. [50], several congeners such as #101, #110, and #170 show relatively high concentrations compared to the other temperatures. This indicated that these congeners were less stable at this intermediate temperature and were more susceptible to degradation or transformation. Congeners such as #180, #44 and #138 had very low concentrations at 900°C. The ∑PCBs for SC2 was 7.8 ng I-TEQ/m^3 which was higher than the corresponding value of 6.44 ng I-TEQ/m^3 in SC1. This indicated that the PCB congeners in SC2 had a higher overall toxic equivalency compared to SC1 due to differences in the composition and concentration of congeners in the two samples.

In SC3 the most dominant congener observed was #110 demonstrating a concentration of 0.484 ng I-TEQ/m^3 at 900°C followed by congener #180 with a concentration of 0.462 ng I-TEQ/m^3 at 600°C. Conversely, the less dominant congeners were #153 measuring 0.023 ng I-TEQ/m^3 at 300°C and congener #170 reporting 0.021 ng I-TEQ/m^3 at 900°C. This is in line with the findings reported by Dat et al. [67] from the secondary copper plant, but differs slightly from the findings reported by Hombrecher et al. [68] during the silicone rubber production. Most congeners show a decrease in concentration as the temperature increases. This is consistent with the general trend that higher temperatures lead to the degradation of PCBs [30, 69, 70]. Congeners such as #18, #28, #52, #118, #180 and #110, exhibited their highest concentrations at 900°C. The ∑PCBs for SC3 was 9.27 ng I-TEQ/m^3 higher than the corresponding values in SC1 and SC2. The data in SC3 provided further evidence of the complex behavior of PCB congeners under different temperature conditions. While the general trend of decreasing concentrations with increasing temperature was observed, the specific responses of individual congeners can vary significantly.

In SC4 the most dominant congener observed was #101 demonstrating a concentration of 0.49 ng I-TEQ/m^3 at 300°C followed by #180 with a measurement of 0.486 ng I-TEQ/m^3 at 900°C. Conversely, the less dominant congeners were #52 measuring 0.022 ng I-TEQ/m^3 at 300°C and #118 reporting a concentration of 0.093 ng I-TEQ/m^3 at 600°C. Most PCB congeners in SC4 exhibited a decrease in concentration as the temperature increases. This consistent trend suggested that higher temperatures promote the thermal degradation of PCBs [41, 43, 71]. Congeners #18, #28, #52, and #194, showed their highest concentrations at 900°C as observed in SC3. Unlike SC3, congeners, such as #52 and #118 had lower concentrations at 600°C. This suggested that the conditions at 600°C are not ideal for the stability of these congeners. The ∑PCBs for SC4 was 8.59 ng I-TEQ/m^3 which was higher than in SC1 and SC2 but lower than SC3. The four SC showed differences in the specific behavior of individual congeners. Some congeners displayed higher concentrations at certain temperatures in one SC but not in others indicating that the composition and reactivity of congeners can vary between samples. The ∑PCBs varies among the SC, with SC3 having the highest value (9.27 ng I-TEQ/m^3), followed by SC4 (8.59 ng I-TEQ/m^3), SC2 (7.8 ng I-TEQ/m^3), and SC1 (6.44 ng I-TEQ/m^3).

Table 2. PCBs stack emission measurement survey (concentrations reported in ng I-TEQ/m^3)

	SC1			**SC2**			**SC3**			**SC4**		
O_2		09.00			09.44			09.01			10.45	
Sampled volume (dry)	ng I-TEQ/m^3	0.80		ng I-TEQ/m^3	0.77		ng I-TEQ/m^3	0.81		ng I-TEQ/m^3	0.84	
Temperature intervals	300°C	600°C	900°C	300°C	600°C	900°C	300°C	600°C	900°C	300°C	600°C	900°C
						PCBs						
PCB18	0.17	0.21	0.12	0.56	0.31	0.21	0.19	0.38	0.44	0.15	0.18	0.34
PCB28	0.24	0.17	0.10	0.33	0.18	0.14	0.38	0.44	0.13	0.36	0.27	0.27
PCB52	0.10	0.11	0.45	0.30	0.19	0.10	0.40	0.28	0.12	0.02	0.19	0.23
PCB101	0.16	0.23	0.22	0.20	0.48	0.05	0.34	0.11	0.11	0.49	0.10	0.14
PCB118	0.21	0.32	0.34	0.29	0.38	0.14	0.14	0.39	0.45	0.39	0.09	0.14
PCB194	0.27	0.04	0.13	0.14	0.12	0.24	0.33	0.03	0.04	0.26	0.33	0.36
PCB153	0.04	0.02	0.35	0.17	0.28	0.13	0.02	0.13	0.34	0.10	0.13	0.10
PCB138	0.06	0.21	0.22	0.37	0.02	0.05	0.16	0.12	0.46	0.38	0.13	0.19
PCB180	0.09	0.36	0.09	0.30	0.21	0.03	0.13	0.46	0.34	0.13	0.23	0.49
PCB44	0.35	0.09	0.33	0.02	0.21	0.10	0.55	0.02	0.23	0.10	0.35	0.23
PCB110	0.01	0.12	0.24	0.10	0.12	0.40	0.36	0.39	0.48	0.29	0.38	0.37
PCB170	0.12	0.03	0.15	0.49	0.003	0.45	0.17	0.18	0.02	0.20	0.39	0.10
Total I-TEQ ∑PCBs		6.44			7.80			9.27			8.59	

3.7 PCDD/Fs emission factors and potential released to the environment

The EF for PCDD/Fs in the current study was 5.974E-8 ng TEQ ton-waste^{-1} (significantly lower than the Emission Factor of 1 µg TEQ/t MW incinerated recommended by UNEP 2013). Different studies reported PCDD/F EFs from different waste types showing significant variations as demonstrated in Table 3. Zhang et al. [72] reported the EF of 3.0 - 650 ng TEQ ton-waste^{-1} from MSW, while in a comparable study, household waste exhibited a considerably higher range of 510 ng TEQ ton-waste^{-1} [73]. In contrast, rice straw emissions reported notably lower EF of 12.6 - 14.5 ng TEQ ton-waste^{-1} [74] while electronic wastes reported the EF of 92 ng TEQ ton-waste^{-1} [75]. Cheruiyot et al. [76] reported that the EF from MWIs and hazardous waste incinerators (HWIs) were approximately 2-fold greater than those for MSWIs. The selection and arrangement of APCDs also play a crucial role in influencing the EF of PCDD/F from waste incineration facilities. Cheruiyot et al. [76] observed that MSWIs utilizing activated carbon injection exhibited lower EF of 0.711 µg I-TEQ ton-waste^{-1}. Pham et al. [77] reported the EF ranging from 0.011 - 374 ng TEQ kg-waste^{-1} while recently, Ruiz et al. [78] reported the lower EF of 1.85 ng TEQ kg-waste^{-1}. The comparison of our EF findings with Pham et al. [77] and Ruiz et al. [78] supports the hypothesis highlighted by Cheruiyot et al. [76] that the combination of dry scrubber and baghouse is effective for simultaneous reduction of EF in flue gas emissions.

The potential release of PCDD/Fs to the environment was calculated using EF which represent the amount of PCDD/Fs released per unit of activity or substance burned. Using Eq. (2) the potential release of PCDD/Fs into the environment was estimated to 5,970 ng TEQ/m^3 /day, much lower than the maximum permitted limit for MWI (525,000 µg TEQ/m^3) indicating that the potential release to the environment is within the acceptable limits set for incineration facilities. Because this facility (study area) is equipped with a dry scrubber, the release of PCDD/Fs to water was prevented.

Release of PCDD/Fs to water could only occur when wet scrubbers are employed for the removal of particulate matter and quench water is used to cool ashes.

Table 3. Emission factors from different waste types

No.	Region	Type of Waste	Emission Factors	References
1.	South Africa	South Africa	5.974E-8 ng TEQ kg-waste^{-1}	This study
2.	China	MSW	3.0 - 650 ng TEQ ton-waste^{-1}	[72]
3.	Mexico	Household waste	510 ng TEQ ton-waste^{-1}	[73]
4.	Taiwan	Rice straw	12.6 - 14.5 ng TEQ kg-waste^{-1}	[74]
5.	USA	Electronic wastes	92 ng TEQ kg-waste^{-1}	[75]
6.	Taiwan	MSW using activated carbon	0.711 ng TEQ kg-waste^{-1}	[76]
7.	Spain	Cement	1.85 ng TEQ kg-waste^{-1}	[78]
8.	Vietnam	MSW	0.011 - 374 ng TEQ kg-waste^{-1}	[77]

4. CONCLUSION

The study investigated the destruction of PCDD/Fs and PCBs emissions using different temperature intervals and exploring effective combustion practices. The samples taken at 300°C and 600°C were similar in isomer composition except that the higher chlorinated congener such as octa-chlorinated dibenzo-p-dioxin and octa-chlorinated dibenzofuran were observed to be more dominated. At 600°C, the formation of both PCDDs and PCDFs was predominant especially for lower chlorinated congeners such as the 2,3,7,8-substituted tetra-chlorinated. However, as the temperature increased to 850°C, a decline in both PCDDs and PCDFs was observed with PCDFs showing slower reduction rates. At 900°C, PCDDs formation surpassed that of PCDFs but soon after both compounds demonstrated a sharp decline indicating increased destruction rates. The O_2 content had a significant influence on PCDD/F formation, with the optimal O_2 level between 4% to 9% for maximum PCDD/F and PCBs production. Additionally, the residence time of 0.8 s had a major impact on PCDD/F formation and inhibition with both PCDDs and PCDFs demonstrating similar effects at different residence times. However, these compounds share similar precursors and formation pathways, which make their behaviors interdependent under the same resident time during combustion processes. Based on the results obtained in the current study, it appears that relying solely on good combustion practices is not sufficient to completely destruct PCDD/Fs and PCBs emissions. Even with the implementation of optimal combustion techniques, certain congeners such as 2,3,4,7,8-PeCDF and 1,2,3,7,8-PeCDD were still measured in high concentrations. Subsequently, additional techniques such as sorbent injections are necessary for a comprehensive adsorption and destruction of PCDD/Fs and PCBs to meet more stringent environmental requirements. This highlights the complexity and importance of implementing effective emission control strategies to minimize the release of PCDD/Fs and PCBs into the environment.

Furthermore, the analysis of gas-solid compound distribution provided valuable insights into the behavior of PCDD/Fs and PCBs at different temperature intervals, elucidating their partitioning between gas and solid phases. The findings from the current study contribute to the existing body of knowledge by providing detailed insights into the formation and destruction mechanisms of PCDD/Fs and PCBs in medical waste incineration settings. By elucidating the complex interplay between combustion parameters and pollutant behavior, this research offers valuable guidance for optimizing incineration processes to minimize environmental and health risks associated with these hazardous compounds. Moreover, this study extends previous research by examining the specific congeners of PCDD/Fs and PCBs present in stack emissions and elucidating their distribution patterns under different combustion conditions. The identification of dominant congeners and their variations across temperature intervals enhances our understanding of PCDD/Fs behavior and facilitates the development of targeted mitigation strategies. The findings offer valuable guidance for improving combustion practices and implementing effective emission control measures to mitigate the environmental and health impacts of these pollutants.

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