



Temporal Dynamics of PCDD/F and PCB Concentrations in Ambient Air Near a Medical Waste Incineration Facility in Johannesburg

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Abstract: An extensive assessment of ambient air quality near a medical waste incineration (MWI) facility in Johannesburg, South Africa, was conducted, focusing on the gas-particle phase partitioning and the concentrations of polychlorinated dibenzo-p-dioxins (PCDDs), dibenzofurans (PCDFs), and dioxin-like polychlorinated biphenyls (dl-PCBs). It was found that highly chlorinated congeners, specifically hexa- to octa-chlorinated, predominate in the particulate phase, while tetra- and penta-chlorinated isomers were predominantly observed in the gas phase. The concentrations of Σ PCDD/Fs in ambient air ranged from 8.3 to 108.36 fg WHO2005-TEQ/m³, Σ PCBs from 4.43 to 6.06 fg WHO2005-TEQ/m³, and Σ PCDD/Fs in soil from 59.17 to 106.05 pg WHO-TEQ/g. Seasonal variations were marked, with peak concentrations typically occurring in winter and the lowest in summer. Globally, despite a decreasing trend, the concentrations of PCDD/Fs in South Africa remain higher than those reported in other regions. The study further revealed that the daily inhalation intakes of PCDD/F emissions by the local population exceeded the recommended tolerable daily intake levels, underscoring the need for a comprehensive risk assessment that considers all exposure pathways to fully evaluate potential health risks for residents living near the incineration facility.

Keywords: Seasonal variations; PCDD/Fs; PCBs; Gas-particle partitioning; Ambient air

1. Introduction

South Africa ranks among the largest growing developing countries on the planet, facing challenges with air quality that lead to environmental health concerns. The country contends with air pollution from various sources, including dust storms, coal-fired thermal power plants, vehicle exhaust, industrial activities, unpaved roads, smokestack emissions, waste incineration, and agricultural practices (Matandirotya et al., 2022). In both developing and developed countries, waste incineration has emerged as a viable waste management method. Despite the ongoing debate, incineration plants continue to play a significant role in waste treatment in South Africa (Themba, 2020). Despite the numerous advantages associated with MWI has numerous advantages, such as reducing medical waste volume and mass, secondary pollution arises from the release of heavy metals such as PCDD and PCDF (Themba et al., 2023; Zhou et al., 2016). PCDD/Fs are primarily released to the atmosphere through the burning of high-temperature wastes including those from municipal incinerators, clinical and medical waste disposal, as well as car exhaust emissions, unintentional fires, and the combustion of biogenic fuels and biomass in processes like petroleum refining, chlorine production, and pulp and paper bleaching within the chemical manufacturing industry (Bo et al., 2022). There are 210 PCDD and PCDF congeners sharing similar structures, yet their toxicity significantly differs based on the extent and location of chlorine substitution (Dreyer & Minkos, 2023). PCDD/Fs receive heightened scrutiny among persistent organic pollutants (POPs) because of their extreme toxicity and tendency to accumulate in ecosystems, particularly the 17 2,3,7,8-substituted PCDD/F congeners (Hao et al., 2018).

PCDD/Fs have the capacity to disperse over extensive vast distances from their emission points, with ambient

air serving as the primary route for their travel (Deng et al., 2020; Li et al., 2023). The “not-in-my-back-yard” phenomenon has historically posed a challenge for MWIs, as apprehension arises regarding potential health risks linked to the release of potentially harmful compounds like PBDEs, PCDD/Fs and PCBs. A range of measures has been implemented to mitigate soil, air, and water pollution resulting from waste incineration and co-incineration, along with to minimize associated health risks for humans (Bokare et al., 2023). As MWI emission standards became stricter in 2001, constant monitoring of flue gas and air quality in the surrounding environment has become essential to assess the efficacy of associated control strategies (Paloluoğlu & Bayraktar, 2022). Numerous researches have assessed the PCDD/F concentrations in proximity to emission sources and their environmental impacts in various other regions (Paloluoğlu & Bayraktar, 2022; Zhang et al., 2023; Zhou et al., 2016) and a number of studies have confirmed that incinerators emit more PCDD/Fs pollutants (Bokare et al., 2023; Koukoulakis et al., 2020; Peng et al., 2015; Rovira et al., 2018; van Dijk et al., 2015; Yu et al., 2023).

Recent studies have indicated that incineration facilities have a significant function in elevating the overall environmental concentrations of PCDD/Fs and PCBs in ambient air in various countries (Boonyatumanond et al., 2023; Ngo et al., 2020; White et al., 2020; Yu et al., 2023; Zhou et al., 2016). The significant concern regarding the exposure of humans to PCDD/Fs arises from their persistence, toxicity, and potential to accumulate in biological systems. With the ability to be transported over long distances, these pollutants can be dispersed on a global scale and have been identified in distant regions (Ngo et al., 2020). Recent epidemiological research findings suggest that elevated levels of PCDD/F near waste treatment facilities could increase the inflammation risk and liver, heart, and blood vessel diseases in local populations (Liang et al., 2020; Yu et al., 2023). In the present study, ambient air samples were taken from areas near the incineration facilities. This article reports on a comprehensive assessment of ambient air quality in Johannesburg, South Africa. Consequently, our aim for this study was: (1) to conduct gas-particle phase partitioning; (2) to investigate the concentration levels and the PCDD/Fs and dl-PCBs profiles in ambient air around the MWI; (3) to measure PCDD/F levels in soil; and (4) to evaluate the health risks for people living near the MWI by calculating daily inhalation doses for both adults and children.

Comparing the findings of the present study in Johannesburg to those reported in other regions reveals a varied picture of PCDD/F concentrations globally. In Shanghai, China, concentrations were notably higher, ranging from 3348 to 8031 fg/m³ (Li et al., 2023), indicating a more severe level of contamination compared to Johannesburg's reported concentration of 454.88 TEQ fg/m³. Conversely, Germany demonstrated a promising trend of decreasing concentrations over time due to effective emission reduction strategies (Dreyer & Minkos, 2023), suggesting that levels in Germany may be lower than those observed in the current study. Direct comparisons with Portugal were challenging due to methodological differences in computing concentration values. However, it's worth noting that the approach used in Portugal by Coutinho et al. (2007) differed from the methodology employed in the current study. While PCDD/F concentrations for Africa as a whole are not available in most regions, reports suggest that the regions reported are comparable to or exceed those found in developed countries (Ssebugere et al., 2019), potentially aligning with the current study. Additionally, model-predicted vegetation fire-related concentrations in Africa reported by Lammel et al. (2013) were notably lower than those found in this study, indicating a different pollution source or level in the city. While the exact classification of the current study's concentrations may vary depending on the specific comparison and regional context, they generally suggest a significant level of atmospheric contamination in Johannesburg, South Africa.

2. Methodology

2.1 Studied Area and Sampling Sites

The MWI is situated in the Ekurhuleni Metropolitan Municipality, Johannesburg, South Africa, and it has been in full operation since 2001. The area is known for its significant industrial presence and is situated within the East Rand region, which is a key industrial area in Johannesburg. This area hosts a variety of industries, including those with high energy consumption and significant pollutant emissions, such as petrochemical, chemical, brick, tile, and steel manufacturing industries, and incinerators. Despite having a subtropical climate, Johannesburg experiences relatively cool weather. The highest temperatures are typically observed in January, ranging from 15°C to 29°C, with the coldest temperatures occurring around June, with averages ranging from 4°C to 16°C. The annual precipitation falls within the range of 674 to 713 mm. Figure 1 illustrates the geographic positions of the sampling sites in relation to the MWI (using satellite imagery extracted from Google Earth). During autumn (March to May) and winter (June to August), the prevailing local wind direction was southwest, with average wind speeds ranging from 2.9 to 3.8 m/s. In contrast to spring (September to November) and summer (December to February), north-easterly winds dominate, with typical wind speeds between 3.1 and 4.9 m/s (meteorological records from South African Weather Services, 2023). By analyzing historical wind data, we identified four sampling points (designated as sampling positions 1, 2, 3, and 4) situated in both the upwind and downwind directions from the incinerator. SP1 and SP2 were positioned approximately 1.1 km and 3 km northeast, respectively, (in the downwind direction) from the incinerator. Meanwhile, SP3 and SP4 were located

approximately 0.8 km and 3.2 km southeast, which is upwind from the incinerator. These sampling points were determined to be the most likely impact areas based on the prevailing local wind speed and direction.



Figure 1. PCDD/Fs sampling locations (square dots) and the MWI (round dot) in the metropolitan area in Johannesburg, South Africa

2.2 Sampling and Collection

Forty (40) ambient samples and 4 soil samples were collected from February 2022 to March 2023 using the updated US EPA Reference Method TO-9A. Each site was equipped with a high-volume air sampler (provided by Inqaba Biotechnical Industries Pty Ltd), featuring a fiberglass filter for capturing PCDD/Fs bound to particles and a glass filter cartridge for capturing PCDD/Fs in the gaseous phase. Sampling durations typically spanned 24 hours, although some longer samples were occasionally collected, with an average sample volume of approximately 300 m³. Following sampling, the samples were brought to the laboratory, refrigerated, and analyzed for a subset of congeners, including those recognized as toxic. Composite soil samples were created by gathering and blending five distinct samples from a 10 m² region at the designated sampling sites. The quantity of soil collected was adjusted to yield approximately 500 g of a homogenized sample when passed through a 60-mesh screen. A soil analysis was conducted using US EPA Method 1613B.

2.3 Extraction and Cleanup

Before starting the extraction procedure, the glass fiber filter (manufactured by Lasec South Africa, with a diameter of 10.2 cm) underwent pre-cleaning in a 450°C oven for the duration of 12 hours to eliminate some residual organic substances. Similarly, the glass tube, filled with a polyurethane foam plug (diameter: 6.3 centimeters, length: 7.6 centimeters), had been pre-cleaned via the Soxhlet extraction procedure with toluene for a duration of 24 hours. The filters had been spiked with precise quantities of mixtures containing ¹³C₁₂-PCDD/Fs (EPA-1613LCS, from Separations Simply Spectacular, South Africa), then taken to Soxhlet extraction using 400 mL of toluene (Lasec, South Africa) for 24 hours. The resulting extract was condensed to 1-2 mL using a rotary evaporator (Büchi, Switzerland). Subsequently, the extracts underwent manual clean-up utilizing multiple layers of silica, carbon adsorbents, and basic alumina.

The extract samples were initially filtered through a multilayer silica column (manufactured by Inqaba Biotechnical Industries Pty Ltd, South Africa), consisting of silica gel that has been modified with neutral silica gel, along with silica gel modified with 33% (w/w) sodium hydroxide and sulfuric acid (44% by weight), followed by a basic alumina column (Lasec, South Africa). A preliminary 90-mL fraction of hexane (Lasec, South Africa) and a subsequent 75-mL fraction of hexane-dichloromethane blend (9:1) were removed. Subsequently, the PCDD/Fs portion was extracted from the basic alumina column using 120 mL of a 1:1 hexane-dichloromethane mixture. The PCDD/F portion underwent purification utilizing a carbon column (manufactured by Separations Simply Spectacular, South Africa), and using 75 mL of toluene, PCDD/Fs were eluted. The resulting extract

samples were then concentrated using rotary evaporation and moved to vials filled with hexane. The residual solvent was evaporated to dryness using a gentle stream of nitrogen. To assess recovery rates, the final extracts were reconstituted with a specified amount of internal standard, consisting of a mix of labeled $^{13}\text{C}_{12}$ -PCDD/Fs (EPA-1613ISS, sourced from Separations Simply Spectacular, South Africa).

2.4 Analysis

The Environmental Analysis Laboratory in South Africa performed the analysis of 17 specific 2,3,7,8-substituted PCDD/F congeners. The examination of ambient air samples adhered to the US EPA Reference Method T09A and the EPA Modified Method 23. The analytical technique employed high-resolution gas chromatography combined with high-resolution mass spectrometry (HRGC/HRMS). The equipment used was an Agilent 6890 gas chromatograph coupled with a Micromass AutoSpec Ultima mass spectrometer, configured to achieve a resolving power of 10,000. The carrier gas was helium, flowing at 1.3 mL/min. The injector was maintained at 260°C. The oven's temperature program started at 100°C, holding for 1 minute, then ramped up by 10°C per minute to reach 230°C, where it stayed for another minute. Samples were injected in splitless mode. The GC-MS operated in electron impact mode with an energy of +30 eV, achieving a resolution greater than 10,000. Detection was performed in selective ion monitoring mode, with the ion source kept at 260°C. Before analyzing actual samples, a five-point calibration was conducted using standard solutions of PCDDs/PCDFs at concentrations between 0.5 and 2000 ng/mL, supplied by Separations Simply Spectacular.

When the GC-MS was calibrated by injecting standard samples ranging from 0.5 to 5 picograms, the method detection limit (MDL) typically varied from 0.058 picograms for tetrachlorodibenzofuran (TCDF) to 0.663 picograms for octachlorodibenzofuran (OCDF). Considering a total air sampling volume of 1152 cubic meters over a 24-hour period, these MDL values translate to 0.05 femtograms per cubic meter for TCDF and 0.663 femtograms per cubic meter for OCDF. The reproducibility of the analysis, measured as the relative standard error, ranged from 0.58% for OCDF to 2.29% for heptachlorodibenzofuran (HpCDF). Toxic 2,3,7,8-substituted PCDD/Fs, as well as tetra- to octa-chlorinated homologues, were quantified by maintaining isotope ratios within $\pm 15\%$ of their theoretical values, with a signal-to-noise ratio of at least 2.5. Recovery rates for internal standards of $^{13}\text{C}_{12}$ -labeled PCDD/Fs in environmental samples ranged from 60% to 120%, aligning with the criteria established by EPA Method 1613. This study's evaluation of PCDD/Fs environmental exposure among people living near the municipal waste incinerator (MWI) primarily considered inhalation exposure from ambient air. The method for calculating atmospheric inhalation exposure to PCDD/Fs was based on the most recent US EPA guidelines, published in 2009.

Overall, the instrumental analysis utilized an Agilent 6890N/5975C gas chromatograph linked to a Micromass Ultima NT high-resolution mass spectrometer (HRMS). This setup operated with a resolving power of 10,000 (with a 10% valley) and employed selected ion monitoring (SIM) for detection. The gas chromatography column was a 60-meter DB-5MS with a 0.25 mm internal diameter and a 0.25-micrometer film thickness, manufactured by Agilent J&W. Helium served as the carrier gas, flowing at a rate of 1.3 mL/min. The injector temperature was set to 260°C. The oven temperature program started at 100°C, holding for 1 minute, then increased at a rate of 10°C per minute, peaking at 230°C, where it remained for 1 minute. Samples were introduced into the injection port in splitless mode. The mass spectrometer used electron impact ionization at +30 eV, with a resolving power of at least 10,000. Detection relied on SIM, with the ion source kept at 260°C. Prior to processing real samples, a five-point calibration was carried out with PCDD/F standard solutions at concentrations between 0.5 and 2000 ng/mL. The method detection limits (MDL) for PCDD/F congeners ranged from 0.058 to 0.663 picograms. The reproducibility, expressed as a relative standard error, spanned from 0.58% to 2.29%. Quantification of toxic congeners required isotope ratios to be within $\pm 15\%$ of theoretical values and a signal-to-noise ratio of at least 2.5.

2.5 Quality Assurance

Quality assurance measures were essential to the analysis of ambient air samples in the current study, ensuring the accuracy as well as the reliability of the results. Continuous blank checks meticulously verified the cleanliness of solvents and materials in contact with the samples. Moreover, four (4) ambient air measurement blanks were routinely analyzed at consistent intervals to monitor and address potential contamination throughout the sampling process. The incorporation of ^{13}C -labeled PCBs and PCDD/Fs for sampling, extraction, and injection standards, coupled with recovery rate assessments, provided a consistent benchmark for quantification, and affirmed the accuracy of the analytical method. Sampling, extraction, and injection standards were incorporated using ^{13}C -labeled PCDD/Fs and PCBs exclusively for air sampling. The average recovery rates for the mass-labeled PCDD/F and PCB sampling standards ranged from 75% for $^{13}\text{C}_{12}$ -HpCDF2 to 88% for $^{13}\text{C}_{12}$ -PeCDF1. When analyzing ambient air samples, the average recovery rates for the extraction standards were between 70% for $^{13}\text{C}_{12}$ -TeCDD1 and 95% for $^{13}\text{C}_{12}$ -HxCDF2. For PCBs, the recovery rates ranged from 65% for $^{13}\text{C}_{12}$ -PCB 209 to 110% for $^{13}\text{C}_{12}$ -PCB 28. Surrogate recovery tests conducted on each sample fell within acceptable limits, ranging from 75% to

110%. Surrogate recovery tests carried out on each sample showed acceptable results, ranging from 75% to 110%. The surrogate recovery tests, falling within the acceptable range of 75% to 110%, provided further confirmation of the reliability of the analytical process. These stringent quality control measures collectively ensure the generation of accurate and trustworthy data essential for robust assessments of exposure to PCDD/Fs in the environment near the MWI.

2.6 Statistical Analysis

The data analysis was conducted using the Statistical Package for the Social Sciences (SPSS) for Windows, version 20, with a significance level set at 5%. Statistics, which include descriptive elements like standard error (SE), mean, and standard deviation (SD), were calculated for the various variables measured in both ambient air and soil samples. A one-way analysis of variance (ANOVA) was employed to assess significant differences between and within groups. Following the ANOVA, Tukey's test and the Games-Howell post hoc tests were used to pinpoint specific pairs of variables that demonstrated significant differences. In addition to group comparisons, a correlation analysis was conducted to identify the nature and significance of relationships among the concentrations of heavy metals in various samples. Pairwise correlation coefficients were calculated to reveal the associations between the concentrations of selected heavy metals in wastewater and soils. This comprehensive analytical approach ensured a thorough exploration of the data, allowing for both within-group and between-group comparisons, as well as a nuanced understanding of the interrelationships among heavy metal concentrations in diverse environmental samples. Additional statistical analyses, such as the Pearson correlation coefficient ($R = 0.68$) and the Mann-Whitney test ($p > 0.05$), found no significant variation in the distribution of concentrations between the two sampling sites. A variety of tests were used to identify statistically significant differences, including Kruskal-Wallis, Moore's median, Pearson correlations, the Fisher's Least Significant Difference (LSD) test, and ANOVA.

3. Results and Discussion

This chapter details the measured concentrations of specific 2,3,7,8-substituted PCDD/F congeners near the incineration facility. The data encompass measurements of partitioning of PCDD/Fs and dl-PCBs between gas and particle phases, concentrations of PCDD/Fs as well as dioxin-like PCBs collected from four distinct sampling sites during different seasons, and soil results. In this study, the meteorological data was instrumental in enhancing the accuracy and depth of our analytical investigations.

3.1 Partitioning of PCDD/Fs and dl-PCBs Between Gas and Particles

The atmosphere plays a pivotal role as the primary route of transportation for numerous environmentally concerning chemicals (Kirchner et al., 2020; Rovira et al., 2018; Santa-Marina et al., 2023). One critical factor that dictates the destiny of PCDD/F compounds within the atmosphere is their distribution between the gaseous phase and atmospheric particles (Die et al., 2015). We observed that the observed particulate fractions of PCDD/F compounds increased as the chlorine substitutions in the compounds increased. In particular, heavily chlorinated congeners like 1,2,3,6,7,8-HxCDF, OCDF, and OCDD were identified as dominant within the particle phase (Table 1). The concentration profiles for dioxin-like PCBs and PCDD/Fs remained consistent throughout the year sampled. However, distinctions were evident when comparing the gas phase and the particle phase. Overall, the less chlorinated dl-PCBs and PCDD/Fs exhibited more substantial contributions to the gas phase than the particle phase.

We observed that the mass concentrations of dl-PCBs and PCDD/Fs showed a strong direct association with each other ($r^2 = 0.56$, $p < 0.01$). These concentrations were notably elevated over the winter months (June to August) in comparison to the summer period (December to February). This aligns with the findings documented by Li et al. (2023) and Liang et al. (2020). The allocation of PCDD/F compounds among the gaseous and particulate phases is typically assessed through the utilization of the gas-particle partitioning factor. Eqs (1)-(5) as established by Falconer & Bidleman (1994), Finizio et al. (1997), Hung et al. (2002), Pankow (1994), and Yamassaki et al. (1982) have been applied for determining the allocation of semi-volatile organic compounds across gas and particle phases. These equations were useful in characterizing the partitioning of PCDD/Fs as well as the dl-PCBs across gaseous and particulate phases in the studies conducted by several other researchers (Degrendele et al., 2020; Dreyer & Minkos, 2023; Iakovides et al., 2021).

$$K_p = \frac{F / TSP}{A} \quad (1)$$

where, K_p ($m^3/\mu g$) represents a partitioning coefficient that varies with temperature; TSP ($\mu g/m^3$) denotes the total

concentration for suspended particulate matter; $F(\text{pg}/\text{m}^3)$ and $A(\text{pg}/\text{m}^3)$ refer to the respective concentrations of PCDD/Fs and PCBs in both particulate and gaseous forms.

When the $\log K_p$ is plotted against the logarithm of the subcooled liquid vapour pressure $\log P_L^0$, the partition constant was determined using the following formula proposed by Yamasaki et al. (1982):

$$\log K_p = m_r \log P_L^0 + b_r \quad (2)$$

where, m_r is the slope; b_r is the y-intercept of the trend line.

The revised correlation of subcooled liquid vapor pressure (P_L^0) for PCDD/Fs relative to gas chromatographic retention indices (GC-RI) on a non-polar GC column (DB-5), employing p,p'-DDT as a reference standard, was applied as suggested by Hung et al. (2002):

$$\log P_L^0 = \frac{-1.34(RI)}{T} + 1.67 \times 10^{-3}(RI) - \frac{1320}{T} + 8.087 \quad (3)$$

where, RI refers to the gas chromatographic retention indices; T represents the ambient temperature (in K).

Falconer & Bidleman (1994) utilised the parameters extracted from refractive index (RI) data to model the partitioning coefficient (P_L^0) of PCBs. They determined the gradient (m_L) and the intercept (b_L) values for the equation by analysing 32 different PCDD/Fs and PCBs.

$$\log P_L^0 = m_L / T + b_L \quad (4)$$

Batterman et al. (2007) published extensive data sets regarding the gas-particle partitioning of PCDD/Fs in South Africa, providing a m_r value of -1.29 and a b_r value of -7.2 , resulting in an R^2 of 0.94 . These parameters were utilized in the present study to estimate the partitioning coefficient (K_p) of PCBs.

The octanol-air partitioning coefficient (K_{oa}) was used as a key descriptor of gas-to-aerosol partition, a choice substantiated by its recognised efficacy according to Finizio et al. (1997). The connection between two pivotal parameters, $\log K_p$ and $\log K_{oa}$, was stated by the equation $\log K_p = m_r \log K_{oa} + b_r$. In scenarios of equilibrium partitioning, the anticipated value for m_r is close to $+1$.

$$\log K_p = m_r \log K_{oa} + b_r \quad (5)$$

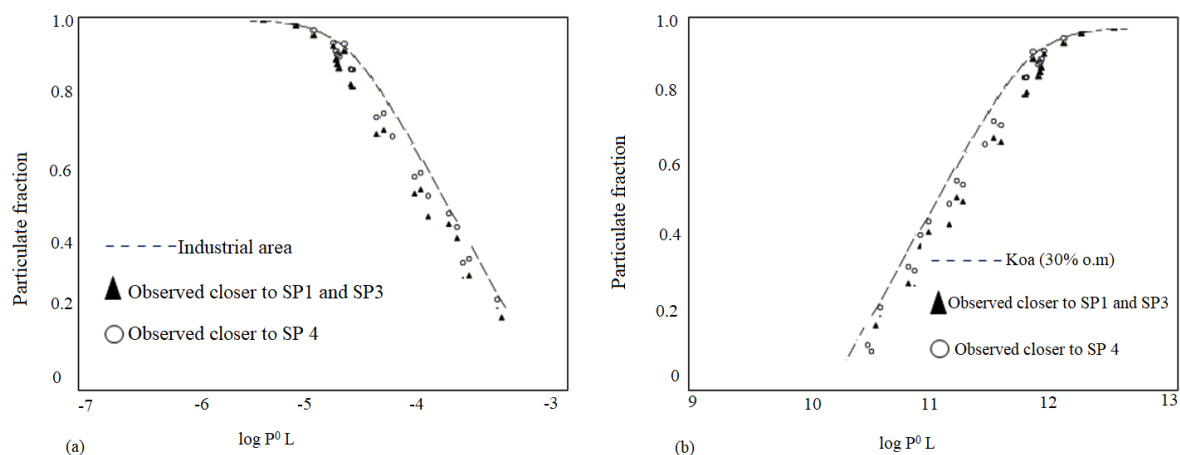


Figure 2. A graph illustrating the observed versus predicted values of PCDD/Fs in the particulate fraction, plotted against the logarithm of P_L^0 (a) and K_{oa} (b) for both the nearer (SP1 and SP3) and further away (SP4) sites

At the time of sampling, the recorded temperatures varied between 4°C and 29°C . Vapour pressures for all PCDD/F compounds as well as di-PCB congeners were subsequently determined based on temperature dependency. Our study focused on an MWI situated in an industrial area, aiming to capture data that best represents the interface between industrial and urban environments. As demonstrated in Figure 2, the average partitioning of measured PCDD/Fs aligns well with the Junge-Pankow model. It's noteworthy that congeners with higher chlorination levels (with $\log P_L^0 < -4.5$) showed a stronger alignment with the industrial partitioning curve. In contrast, congeners with lower chlorination levels (with $\log P_L^0 > -4.5$) fell between the industrial and urban

partitioning curves. This trend is comparable to the results by Koukoulakis et al. (2020). It's important to emphasize that the difference in partitioning behavior between sites near the MWI and those farther away was more distinct for lower-chlorinated congeners compared to their higher-chlorinated counterparts. As the distance from the MWI increased, the lower-chlorinated congeners showed a clear trend towards following the urban partitioning pattern.

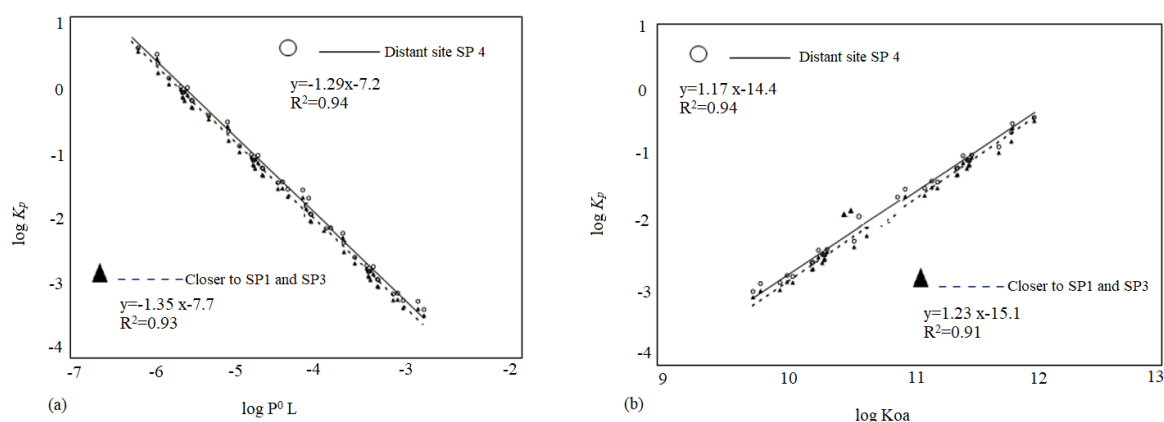


Figure 3. (a) Log K_p to log P^0_L and (b) log K_p to log K_{oa} graphs for PCDD/Fs at both the nearer (SP1 and SP3) and further away (SP4) sites

Figure 3 visually conveys the robustness of connections among the logarithm of K_p and the logarithm of K_{oa} , with high significance levels ($R^2 \leq 0.91$; $P < 0.001$). Notably, the average gradient at sites in closer proximity to the source ($m_r = +1.23$) substantially deviated from +1 (with a P -value < 0.05). In contrast, partitioning of PCDD/Fs at the site farther away ($m_r = +1.6717$) suggested an alignment with equilibrium partitioning (where $P > 0.1$). This observation underscores the trend of PCDD/Fs progressively nearing equilibrium partitioning ($m_r = +1$) as the distance away from the MWI increases, consistent with findings from log K_p versus log P^0_L plots. Combining insights from both models, the regression slopes for the remote site (P^0_L : -1.29 ; K_p : 1.17) exhibited a less steep inclination compared to those for the nearer sites (P^0_L : -1.35 ; K_p : 1.23). This nuanced analysis emphasizes the spatial variations in partitioning behaviour, highlighting the intricacies of PCDD/Fs dynamics in connection to both the distance away from the MWI and key physicochemical parameters.

Distinct patterns of PCDD/F congeners were evident in the gaseous and particulate phases. The particulate gaseous phase was predominantly characterised by highly chlorinated congeners, ranging from hexa- to octa-chlorinated forms, whereas the gas phase was dominated by low chlorinated PCDD/Fs, specifically tetra- and penta-chlorinated congeners. This aligns with the findings published by Li et al. (2023) and Yu et al. (2023). Nonetheless, an intriguing trend emerged: as the degree of chlorination in PCDD/F congeners increased, the fraction of PCDD/Fs present in the gaseous phase decreased. This observed variation can be explained by the effect of the vapour pressure of PCDD/F congeners. The differences in concentration between gas and particle phases may be owing to the chemical and physical characteristics of the congeners and their affinity for particulate matter, as affirmed by Tian et al. (2021). The high concentrations of PCDDs and PCDFs in the particulate phase indicated that these compounds may be more likely to deposit onto surfaces or be inhaled by organisms in the vicinity of the MWI.

When considering PCDD/Fs together with dl-PCBs, the ratios also indicated a dominant presence of highly chlorinated homologues within the particle phase, while the less chlorinated homologues displayed a preference for the gas phase. This could be attributed to the lower saturated vapour pressure exhibited by highly chlorinated homologues, making them more likely to reside in the particle phase. Their dominant factor influencing their distribution was represented by Log K_{oa} (the octanol-air partition coefficient) rather than the “exogenous” factor related to the prevailing climatic environment. These findings align with the findings presented by Batterman et al. (2007) and Boonyatumanond et al. (2023). The general consensus from most studies suggests that congeners with elevated levels of chlorination and lower vapour pressures (P_v) tend to be more likely to be distributed in the particulate phase. Additionally, there is an observed trend where the proportion of PCDD/Fs present in the particulate phase increases as the molecular weight of the isomers rises (Li et al., 2023).

The partitioning of PCDDs as well as PCDFs between gas and particulate phases was consistent across all sampling locations, with greater concentrations typically observed in the particulate phase. The particle phase of PCDD/F isomers was influenced by the abundance of fine aerosols and increased deposition on surfaces due to rain events. Precipitation can wash out PCDD/Fs from the atmosphere, depositing them on water and soil surfaces. Furthermore, the noticeable disparities in sampling rates between the gaseous and particulate phases underscored their heightened vulnerability to seasonal fluctuations. As a result, Li et al. (2023) recommended calculating the

rate of sampling for the chemical's hybrid phase while considering uncertainties. The Σ PCDF concentrations in SP3 (closer to the incineration facility and closer to the mine dumps) indicated a negative relationship correlating with ambient temperature ($r = 0.730$, p -value less than 0.01), a negative relationship with wind speed (with a correlation of $r = -0.618$; p -value less than 0.05), but a positive relationship with relative humidity (with a correlation of $r = 0.686$, p -value less than 0.01). These three meteorological elements—greater relative humidity, cooler temperatures, and decreased wind speeds—converged during the winter season, setting it apart from the typical conditions observed throughout the rest of the year. These unique meteorological conditions during the winter were linked to the highest concentrations of PCDD/Fs. The similar conclusion was reached by Degrendele et al. (2020), Hu et al. (2019), Santa-Marina et al. (2023), Zhang et al. (2023).

PCDD/Fs predominantly resided in the particle phase of ambient air, whereas dl-PCBs were primarily present in the gaseous phase. This aligns with the findings presented by Boonyatumanond et al. (2023). The distribution of PCDD/Fs between gaseous and particulate phases across all sampling locations exhibited a consistent distribution trend. The results consistently indicated that the particle phase contained a substantial portion of the total PCDD/Fs at each location. Specifically, the mean PCDD/Fs concentration in the particulate phase represented approximately 85.09% in SP1, 81.49% in SP2, 84.15% in SP3, and 76.52% in SP4. As a result, a notably higher presence of PCDD/Fs in the particulate phase during the winter months was noted, aligning with findings reported in numerous other studies (Kirchner et al., 2020; Paloluoglu & Bayraktar, 2022; Torre et al., 2023). Coffey & Atkinson (1996) conducted a comprehensive review of the atmospheric chemistry of PCDD/Fs and PCBs. Considering factors like gas/particle partitioning, chemical transformations (including direct photolysis), catalytic changes in the particulate phase, reactions with ozone, hydroxyl radicals (OH), and NO₃ radicals in the gas phase, and both wet and dry deposition, it is concluded that the principal removal mechanism in the gas phase is primarily attributed to reactions with OH radicals.

Table 1. Mean concentrations (fg/m³) of gaseous (G) and particulate (P) phase PCDD/Fs were recorded simultaneously at the four sampling locations

Location Congeners	SP 1		SP 2		SP 3		SP 4	
	G	P	G	P	G	P	G	P
2,3,7,8-TCDD	15.00	11.10	15.44	3.81	12.43	8.97	12.75	5.87
1,2,3,7,8-PeCDD	18.45	14.20	26.37	11.80	17.33	16.93	15.67	15.61
1,2,3,4,7,8-HxCDD	8.68	26.16	12.40	35.18	15.46	48.74	7.37	47.84
1,2,3,6,7,8-HxCDD	12.88	40.13	18.41	56.81	18.38	49.85	17.94	49.87
1,2,3,7,8,9-HxCDD	12.18	136.10	17.40	72.10	11.40	49.10	10.35	64.10
1,2,3,4,6,7,8-HpCDD	14.96	319.16	21.38	432.10	15.34	534.12	12.71	522.10
OCDD	20.60	515.10	29.44	539.11	12.49	746.78	67.51	21.10
2,3,7,8-TCDF	16.36	12.21	53.38	32.81	58.43	18.98	63.91	48.90
1,2,3,7,8-PeCDF	39.18	21.10	87.40	32.82	93.31	75.10	76.30	84.19
2,3,4,7,8-PeCDF	25.63	15.23	72.33	31.10	55.34	137.83	53.30	142.89
1,2,3,4,7,8-HxCDF	10.06	69.20	69.38	144.10	21.40	148.97	58.55	151.98
1,2,3,6,7,8-HxCDF	42.20	87.10	57.44	149.84	71.45	138.11	10.37	55.10
2,3,4,6,7,8-HxCDF	8.74	28.10	12.49	42.73	19.44	67.77	47.434	80.86
1,2,3,7,8,9-HxCDF	14.93	130.13	21.33	145.11	68.31	136.86	52.68	251.97
1,2,3,4,6,7,8-HpCDF	32.89	237.22	58.42	541.10	66.36	542.85	60.95	545.98
1,2,3,4,7,8,9-HpCDF	5.67	20.20	22.39	40.79	12.39	99.81	13.31	99.88
OCDF	6.35	231.11	23.37	342.89	16.33	465.94	13.89	452.10
Σ PCDDs	102.75	1062.95	140.84	1150.91	102.83	1455.49	144.30	726.49
Σ PCDFs	202.41	841.50	419.83	1063.29	482.66	1822.32	451.67	1913.85
Σ PCDD/Fs	299.40	1709.60	562.27	2463.59	571.84	3027.78	703.60	2287.46
WHO 2005 TEQ	31.715	92.32	77.5	162.53	78.66	174.35	63.51	159.09

PPCDD/Fs were determined by summing the concentrations of tetra- to octa-chlorinated 2,3,7,8-substituted dibenzo-p-dioxins and dibenzofurans.

3.2 PCDD/Fs Congener Distribution and Concentrations During Different Seasons

Table 2 displays the concentrations of PCDD/F congeners in the ambient air near the MWI in Johannesburg, sampled from February 2022 to March 2023. In Johannesburg, South Africa, strong winds typically occur during the late winter and spring months from July to October. During this period, the city experiences more pronounced wind patterns, often due to weather systems and atmospheric conditions associated with the transition from winter to spring. These strong winds can be a result of cold fronts, pressure systems, and other meteorological factors. This observation aligns with the findings from this study, indicating that wind speed played a significant role in the correlation between PCDD/Fs levels and temperature. TEQ concentrations in ambient air near the MWI (measured through passive sampling) in Johannesburg exhibited similarities to those observed in Seoul, Korea, as reported by Kirchner et al. (2020). However, they were marginally below the ones recorded within the industrial

area of Bou Ismaïl, Algeria, according to White et al. (2020), a bit greater than the ones observed within Shanghai's urban background area in the study by Tian et al. (2021), and notably greater than the ones documented in the vicinity of a Spanish waste facility in the study conducted by Bokare et al. (2023).

Table 2. PCDD/Fs congener concentration in ambient air (fg/m³) collected during different seasons

Congeners Sampling Points	Summer				Autumn				Winter				Spring			
	SP 1	SP 2	SP 3	SP 4	SP 1	SP 2	SP 3	SP 4	SP 1	SP 2	SP 3	SP 4	SP 1	SP 2	SP 3	SP 4
2,3,7,8-TCDD	25.1	23.24	13.16	12.61	14.75	13.39	23.13	23.82	11.1	20.81	38.97	50.87	24.72	21.85	14.20	18.04
1,2,3,7,8-PeCDD	25.25	23.34	19.19	15.65	17.53	16.43	20.16	20.78	14.2	21.8	36.93	54.91	15.71	24.23	15.70	25.79
1,2,3,4,7,8-HxCDD	28.7	24.94	12.16	7.49	9.1	7.74	17.59	18.12	16.16	25.18	48.74	47.84	8.51	25.22	16.40	15.79
1,2,3,6,7,8-HxCDD	26.1	27.27	13.16	11.01	12.24	11.74	21.27	21.90	20.13	26.81	49.85	49.87	9.67	22.07	14.35	9.24
1,2,3,7,8,9-HxCDD	28.3	23.15	12.16	11.08	10.23	11.06	18.67	19.23	16.1	22.1	39.1	44.1	25.96	22.07	14.35	16.17
1,2,3,4,6,7,8-HpCDD	28.28	23.65	14.66	12.8	15.71	13.55	28.08	23.74	19.16	22.1	34.12	52.1	15.96	6.84	17.49	16.16
OCDD	20.53	26.38	17.5	17.4	19.57	18.65	28.05	18.60	15.1	29.11	46.78	51.1	31.58	22.57	14.70	15.24
2,3,7,8-TCDF	26.4	24.55	14.9	13.87	14.40	14.71	24.34	25.05	12.21	22.81	38.98	48.9	26.55	22.60	14.69	21.56
1,2,3,7,8-PeCDF	31.36	20.20	15.83	16.2	20.14	17.22	16.80	17.30	21.21	22.82	35.1	44.19	16.59	21.32	13.85	24.43
2,3,4,7,8-PeCDF	25.9	28.27	15.16	13.2	14.84	13.99	13.69	14.13	15.23	21.1	37.83	42.89	25.08	30.15	19.60	11.02
1,2,3,4,7,8-HxCDF	21.76	23.77	12.16	8.61	9.1	9.01	20.82	21.47	19.2	24.1	48.97	51.98	35.47	14.26	22.21	12.30
1,2,3,6,7,8-HxCDF	22.4	25.94	13.07	10.49	12.81	11.34	10.68	19.23	17.1	29.84	38.11	55.1	40.30	19.40	19.11	20.11
2,3,4,6,7,8-HxCDF	29.56	26.07	13.17	7.57	8.74	7.9	17.66	18.17	18.1	22.73	37.77	50.86	34.59	31.23	20.27	20.28
1,2,3,7,8,9-HxCDF	30.53	27.88	15.74	12.72	15.99	13.95	19.10	19.68	20.13	25.11	36.86	51.97	6.39	8.09	18.28	21.10
1,2,3,4,6,7,8-HpCDF	26.26	25.8	15.14	10.88	14.0	11.54	27.83	19.83	17.22	21.1	42.85	45.98	13.05	8.37	18.44	27.98
1,2,3,4,7,8,9-HpCDF	32.36	22.51	15.83	13.27	15.00	14.18	20.69	21.36	20.2	20.79	39.81	39.88	33.38	9.52	19.18	8.04
OCDF	30.30	27.04	18.16	13.79	14.35	14.84	14.31	14.74	21.11	22.89	42.94	52.1	34.73	16.83	25.43	5.79
∑PCDD/Fs	458.26	423.52	250.96	208.64	242.41	235.82	343.02	345.64	293.45	40.12	693.71	834.64	365.77	346.27	289.35	309.06
WHO 2005 TEQ	61.7	48.15	33.85	28.05	8.29	8.03	62.03	63.44	32.07	48.20	85.14	108.36	86.10	71.04	60.92	82.41

PCDD/Fs were calculated as sum of tetra- to octa-chlorinated 2,3,7,8- substituted PCDD/Fs.

Summer Season

In summer, SP1 reported a ∑PCDD/F concentration of 458.26 fg/m³ with 1,2,3,4,7,8,9-HpCDF as a major congener with a concentration of 32.36 fg/m³. The mass concentrations were primarily influenced by CDF, contributing 66.29%, while CDD contributed 40.83%. The congener distribution was observed as 1,2,3,4,7,8-HxCDD: 6.25%, 1,2,3,7,8,9-HxCDD: 6.18%, 1,2,3,4,6,7,8-HpCDD: 6.11%, 1,2,3,7,8-PeCDF: 6.84%, 2,3,4,6,7,8-HxCDF: 6.45%, 1,2,3,7,8,9-HxCDF: 6.66%, 1,2,3,4,7,8,9-HpCDF: 7.05%, and OCDF: 6.55, while the remaining congeners contributed less than 5% each (Figure 4). A similar trend was published by Kirchner et al. (2020) and Tian et al. (2021). The observed distributions and elevated levels of PCDFs are associated with thermal processes, suggesting the potential impact of MWI and/or activities associated with ferrous foundries, including iron ore sintering, situated in the northern vicinity of SP1. SP2 reported a ∑PCDD/F concentration of 423.52 fg/m³ (48.15 fg WHO-TEQ/m³), featuring 2,3,4,7,8-PeCDF marked as a dominant congener with a concentration of 28.27 fg/m³. The other congeners showed a similar trend with the distribution as 1,2,3,6,7,8-HxCDD: 6.36%; OCDD: 6.23%; 2,3,4,7,8-PeCDF: 6.68%; 1,2,3,6,7,8-HxCDF: 6.12%; 2,3,4,6,7,8-HxCDF: 6.16%; 1,2,3,7,8,9-HxCDF: 6.58%; 1,2,3,4,6,7,8-HpCDF: 6.09% and OCDF: 6.38%, while the rest of the congeners contributed less than 5%. Despite SP2 being situated at a greater distance from the incineration facility, the elevated concentrations in the ambient air can be attributed to wind directions and the impact of distinct stationary sources in the vicinity of the industrial park.

Conversely, SP3 reported a ∑PCDD/F concentration of 250.96 fg WHO-TEQ/m³ (33.85 fg WHO-TEQ/m³),

with 1,2,3,7,8-PeCDD counting as the major congener with a concentration of 19.00 fg/m³. SP3 was also dominated by PCDF 52.30% with the congener distribution of 1,2,3,7,8-PeCDD: 7.57%; OCDD: 6.98%; 2,3,7,8-TCDF: 5.94%; 1,2,3,7,8-PeCDF: 6.31%; 2,3,4,7,8-PeCDF: 6.04%; 1,2,3,7,8,9-HxCDF: 6.27%; 1,2,3,4,6,7,8-HpCDF: 6.03%; 1,2,3,4,7,8,9-HpCDF: 6.31% and OCDF: 7.24%, while the remaining congeners contributed less than 5%. Although SP3 is situated close to the MWI, the prevailing winds, and minimal industrial and human activities because of open land and a lake led to lower PCDD/Fs detected at this location during the summer. SP4 reported a Σ PCDD/F concentration of 208.64 fg/m³ (28.05 fg WHO-TEQ/m³) with OCDD reported as a major congener with a concentration of 17.4 fg/m³, while 1,2,3,4,7,8-HxCDD had the lowest concentration of 7.49 fg/m³. SP4 was also dominated by furans with the congener distribution of 2,3,7,8-TCDD: 6.05%; 1,2,3,7,8-PeCDD: 7.50%; 1,2,3,4,6,7,8-HpCDD: 6.13%; OCDD: 8.32%, 2,3,7,8-TCDF: 6.64%; 1,2,3,7,8-PeCDF: 7.76%; 2,3,4,7,8-PeCDF: 6.32%; 1,2,3,7,8,9-HxCDF: 6.10%; 1,2,3,4,7,8,9-HpCDF: 6.37% and OCDF: 6.61%.

The concentration pattern suggests a decrease in concentration when moving from northeast to southwest, following the wind direction. According to the South African Meteorological Administration, summer precipitation in eastern Johannesburg primarily occurs during the austral summer months of November to March in South Africa and is characterised by regular showers, thunderstorms, and occasional cyclones in specific regions. Consequently, the summertime experiences notably higher rainfall compared to the winter season. Given that wet deposition is a primary method for removing the majority of suspended organic compounds, increased rainfall results in elevated wet deposition, consequently leading to lower PCDD/F concentrations in ambient air throughout the rainy season.

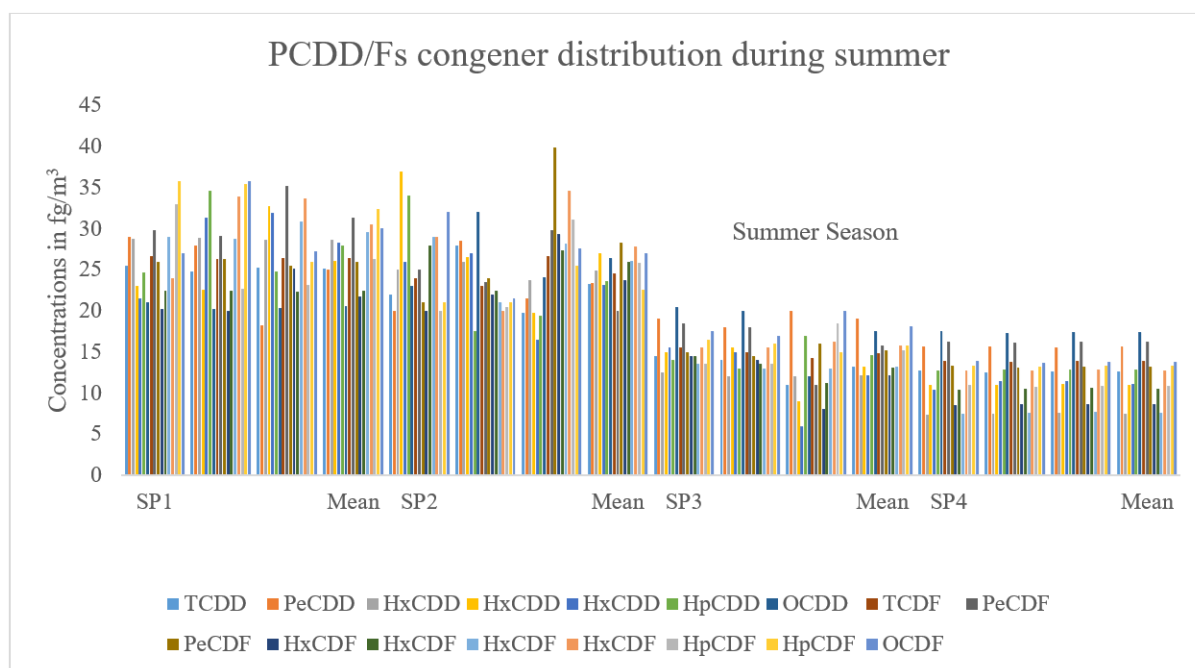


Figure 4. Distribution of PCDD/Fs homologues (fg/m³) in ambient air during summer

Autumn Season

During autumn, the Σ PCDD/F concentration in SP1 was 242.41 fg/m³ (TEQ of 8.29 fg WHO-TEQ/m³), similar to the levels observed in SP1 during the summer season. The major congener was 1,2,3,7,8-PeCDF with a concentration of 20.14 fg/m³, while 2,3,4,6,7,8-HxCDF was the least dominant congener, exhibiting a concentration of 8.74 fg/m³. The mass concentration was predominantly composed of PCDF, with the congener distribution observed as: 2,3,7,8-TCDF: 6.12%; 1,2,3,7,8-PeCDF: 8.56%; 2,3,4,7,8-PeCDF: 6.31%; 1,2,3,4,7,8-HxCDF: 3.86%; 1,2,3,6,7,8-HxCDF: 5.46%; 2,3,4,6,7,8-HxCDF: 3.72%; 1,2,3,7,8,9-HxCDF: 6.79%; 1,2,3,4,6,7,8-HpCDF: 5.94%; 1,2,3,4,7,8,9-HpCDF: 6.36% and OCDF: 6.11%.

This trend was slightly different from what Ngo et al. (2020) reported, namely that the most elevated PCDD/F levels are present in heavily industrialized areas. As ambient temperatures decreased in autumn, the PCDD/F concentrations rose, indicating that the increase may be attributed to domestic heating sources involving combustion. SP2 measured the Σ PCDD/Fs concentration of 235.82 fg/m³ (TEQ of 8.03 fg WHO-TEQ/m³). OCDD was identified as the dominant congener with a concentration of 18.65 fg/m³, while 2,3,4,6,7,8-HxCDF was found to be the least congener with a concentration of 7.99 fg/m³. It is noteworthy that in this sample, PCDD made the most substantial contribution, representing 59.03% of the total mass concentration, whereas PCDF accounted for 41.22%. The findings indicated that the mass distribution of congeners was observed as: 2,3,7,8-TCDD (5.68%),

1,2,3,7,8-PeCDD (6.95%), 1,2,3,4,7,8-HxCDD (3.28%), 1,2,3,6,7,8-HxCDD (4.92%), 1,2,3,7,8,9-HxCDD (4.69%), 1,2,3,4,6,7,8-HpCDD (6.37%), and OCDD (7.91%). This may be ascribed to the supplementary emission source of PCDD/Fs from the nearby industrial park, which stands in contrast to the findings of Ngo et al. (2020).

SP3 reported the Σ PCDD/F concentration of 343.02 fg/m³ (TEQ of 62.03 fg WHO-TEQ/m³) and demonstrated a dominant presence of OCDD, 1,2,3,4,6,7,8-HpCDD as well as 1,2,3,4,6,7,8-HpCDF, with the reported concentrations of 28.05 fg/m³, 28.08 fg/m³, and 27.27 fg/m³, respectively. These findings were attributed to emissions from nearby foundries, steel facilities, and incinerators located close to the sampling site. The measurements revealed that the mass distribution of congeners was reported as: 2,3,7,8-TCDD: 6.74%; 1,2,3,7,8-PeCDD: 5.87%, 1,2,3,4,7,8-HxCDD: 5.14%, 1,2,3,6,7,8-HxCDD: 6.20%, 1,2,3,7,8,9-HxCDD: 5.45%, 1,2,3,4,6,7,8-HpCDD: 8.18%; OCDD: 8.17%, 2,3,7,8-TCDF: 7.10%; 1,2,3,4,7,8-HxCDF: 6.05%; 2,3,4,6,7,8-HxCDF: 5.15%; 1,2,3,7,8,9-HxCDF: 5.56%; 1,2,3,4,6,7,8-HpCDF: 7.95% and 1,2,3,4,7,8,9-HpCDF: 6.05% with the remaining congeners accounting for less than 5%. These concentration levels resembled those observed during the summer, but there was a gradual increase in concentrations from May to June, indicating the approach of the winter season. The PCDD/Fs levels in the ambient air exhibited a strong correlation with both meteorological conditions and the intensity of emissions, as confirmed by Deng et al. (2020) and Yu et al. (2023).

SP4 reported a Σ PCDD/Fs 345.64 fg/m³ (TEQ of 63.44 fg WHO-TEQ/m³), similar to the findings documented by Kuo et al. (2015). In this sample, dioxins and furans contributed nearly equally to the distribution. The congener distribution was as follows: 2,3,7,8-TCDD: 6.90%; 1,2,3,7,8-PeCDD: 6.00%; 1,2,3,4,7,8-HxCDD: 5.24%; 1,2,3,6,7,8-HxCDD: 6.32%; 1,2,3,7,8,9-HxCDD: 5.57%; 1,2,3,4,6,7,8-HpCDD: 6.86%; OCDD: 5.37%, 2,3,7,8-TCDF: 7.24%; 1,2,3,4,7,8-HxCDF: 6.21%; 1,2,3,6,7,8-HxCDF: 5.57%; 2,3,4,6,7,8-HxCDF: 5.25%; 1,2,3,7,8,9-HxCDF: 5.69%; 1,2,3,4,6,7,8-HpCDF: 5.76% and 1,2,3,4,7,8,9-HpCDF: 6.19%. A trend of PCDD/Fs congeners in autumn and spring was somewhat intermediate. As temperatures and solar radiation vary during these seasons, the partitioning and transformation of gas-phase PCDD/Fs were influenced by climatic conditions during that period.

Winter Season

During the winter season, SP1 reported a Σ PCDD/F concentration of 293.45 fg/m³ (TEQ of 32.07 fg WHO-TEQ/m³), with OCDF reported as a major congener at 21.11 fg/m³ and 2,3,7,8-TCDD as the least congener with measurements of 11.1 fg/m³ (Figure 5). The mass PCDD/Fs concentration was dominated by furans comparable to the findings presented by Kirchner et al. (2020), with the congener distribution observed as 1,2,3,6,7,8-HxCDD: 6.86%; 1,2,3,4,6,7,8-HpCDD: 6.54%; 1,2,3,7,8-PeCDF: 7.15%; 1,2,3,4,7,8-HxCDF: 6.55%; 2,3,4,6,7,8-HxCDF: 6.17%; 1,2,3,7,8,9-HxCDF: 6.86%; 1,2,3,4,7,8,9-HpCDF: 6.88% and OCDF: 7.21%.

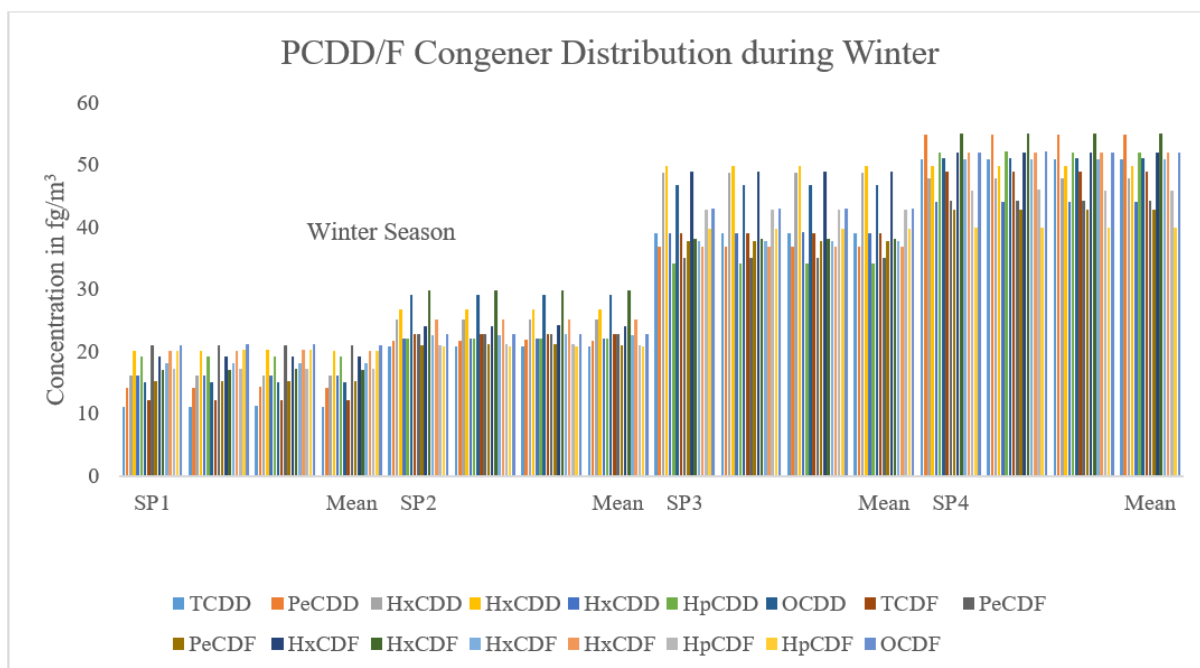


Figure 5. Distribution of PCDD/Fs homologues (fg/m³) in ambient air during winter

The amount of Σ PCDD/F found in SP2 was 401.2 fg/m³ (48.20 fg WHO-TEQ/m³), and the amount of 1,2,3,6,7,8-HxCDF was 29.84 fg/m³. Unlike the summer results, a different trend was observed in SP2, where all congeners reported high concentrations, suggesting multiple emission sources. A number of mechanisms could

account for the seasonal variations observed in air pollutant distribution at these two sampling sites. Key contributing factors include a reduced boundary layer height during winter, which limits vertical mixing, as well as a slower rate of oxidation reactions at colder temperatures. Additionally, summer often brings higher levels of atmospheric oxidants, which can increase the rate of pollutant degradation, as well as other seasonal changes in weather conditions (Hao et al., 2018).

SP2 mass concentrations were also dominated by PCDF, with a major congener distribution of 1,2,3,4,7,8-HxCDD: 6.28%; 1,2,3,6,7,8-HxCDD: 6.68%; OCDD: 7.25%; 1,2,3,4,7,8-HxCDF: 6.01%; 1,2,3,6,7,8-HxCDF: 7.45% and 1,2,3,7,8,9-HxCDF: 6.25%. SP3 reported a \sum PCDD/F of 693.71 fg/m^3 (TEQ of 85.14 fg WHO-TEQ/ m^3), along with 1,2,3,6,7,8-HxCDD as the most dominant congener at 49.85 fg/m^3 . Similar to SP2, most congeners displayed consistently high concentrations with a mass concentration dominated by 58.29% PCDF (similar to the findings presented by Cao et al. (2018)), with a congener distribution of 1,2,3,4,7,8-HxCDD: 7.03%, 1,2,3,6,7,8-HxCDD: 7.19%; 1,2,3,7,8,9-HxCDD: 5.64%; OCDD: 6.74%; 1,2,3,4,7,8-HxCDF: 7.07%; 1,2,3,4,6,7,8-HpCDF: 6.18% and OCDF: 6.20%, while the rest of the congeners accounted for less than 5%.

SP4 reported a \sum PCDD/F concentration of 834.64 fg/m^3 (TEQ of 108.36 fg WHO-TEQ/ m^3), along with 1,2,3,6,7,8-HxCDF as the major congener at 55.1 fg/m^3 . The mass PCDD/Fs concentration was dominated by 56.82%, while PCDD constituted 41.15% of the total. The congener distribution was 2,3,7,8-TCDD: 6.10%; 1,2,3,7,8-PeCDD: 6.58%; 1,2,3,4,6,7,8-HpCDD: 6.24%; OCDD: 6.12%; 1,2,3,4,7,8-HxCDF: 6.22%; 1,2,3,6,7,8-HxCDF: 6.60%; 2,3,4,6,7,8-HxCDF: 6.09%; 1,2,3,7,8,9-HxCDF: 6.23% and OCDF: 6.24%. Owing to the low atmospheric temperature in winter, the share of PCDD/Fs was higher than in summer. This aligns with the findings reported by Dreyer & Minkos (2023), Ngo et al. (2020), Tian et al. (2021). This characteristic, combined with the increase in PCDD/Fs concentration during the winter, contributed to the differences in seasonal characteristics observed in passive atmospheric data. The PCDD/Fs levels across all four sampling sites were comparable, except for a few months (summer vs. winter) as the trend of high concentrations was also observed in SP1, SP3, and SP4 during the winter season.

The shift in dominant congeners between SP1 and SP2 during the winter season cannot exclude industrial activities as a major source of OCDD and HxCDF. During this timeframe, there is an increase in combustion activities linked with the emission of dioxin and furan emissions, primarily stemming from heating activities. Furthermore, a significant observation arose from the prevailing wind patterns during the winter and autumn seasons in Johannesburg, which predominantly blow from the south-westerly direction. The direction of the prevailing wind suggests that we can exclude the MWI facility as a significant contributor to the elevated PCDD/Fs levels in SP1 during the winter. Instead, the origins of PCDD/Fs may be associated with other industrial activities, specifically engineering, coal-fired boilers, and forging companies positioned south of the incineration plant. The congeners exhibited distinct seasonal patterns, typically peaking in winter and decreasing in summer, as published by Li et al. (2023), López et al. (2021), Santa-Marina et al. (2023). These variations are likely linked to factors such as combustion sources, temperature inversions, and various mechanisms that lead to PCDD/Fs removal, such as photolysis, chemical reactions, absorption by vegetation, and wet and dry deposition.

The TEQ concentration was the lowest in summer, similar in autumn, though the concentration started picking up at the end of May and in spring (October and November), and the concentrations started to decline at the beginning of September. This seasonal trend is consistent with that reported by various studies (Ngo et al., 2020; Tian et al., 2021; van Drooge et al., 2021). The elevated levels of PCDD/Fs during the winter can be attributed to consistent seasonal patterns. These trends likely stem from the dry and cold winter conditions, which tend to favor a broader dispersion of PCDD/Fs compared to the summer months. PCDD/Fs can be removed from the atmosphere through several mechanisms, such as wet and dry deposition or by reacting with hydroxyl (OH) radicals.

Spring Season

In spring, the congener distribution was similar to what was observed in autumn, similar to the findings published by Klima et al. (2020) and Liu et al. (2022). SP1 reported the \sum PCDD/Fs of 365.77 fg/m^3 (TEQ of 86.10 fg WHO-TEQ/ m^3) the highest among all four sampling points, while SP2 measured a slightly lower \sum PCDD/Fs at 346.27 fg/m^3 (TEQ of 71.04 fg WHO-TEQ/ m^3). It was observed that 1,2,3,4,7,8-HxCDF as well as 2,3,4,6,7,8-HxCDF reported relatively high levels compared to the other congeners. SP2 shared some similarities with SP1 in terms of congener distribution, but at slightly lower levels. SP3 reported a lower \sum PCDD/Fs concentration of 289.35 fg/m^3 (TEQ of 60.92 fg WHO-TEQ/ m^3), along with 1,2,3,4,7,8-HxCDD as well as 1,2,3,7,8-PeCDF reported as major congeners. SP3 exhibited a different congener distribution pattern compared to SP1 and SP2. SP4 reported a \sum PCDD/Fs concentration of 309.06 fg/m^3 . It seemed that each site has its own unique distribution of congeners, possibly influenced by various local factors. These variations can be influenced by local sources, meteorological conditions, and environmental characteristics at each sampling point. As the operation of the incineration facility typically remains constant throughout the year, the observed seasonal variation in atmospheric congener levels is more likely to be attributed to factors such as domestic burning and other environmental influences. Due to the presence of buildings and major traffic routes in industrial areas, the predominant PCDD/F concentrations at the sampling sites were minimally affected by wind direction.

Comparing the results of our study with previously reported data, we found that only in the case of SP1, the average concentrations were akin to those usually observed in urban and industrial areas. Samples collected during the summer months consistently exhibited lower concentrations compared to those collected during the winter months. Throughout the sampling period, the dominant wind direction was from a south-westerly direction, which placed SP4 upwind of the MWI, while SP1 and SP2 were downwind. Consequently, concentrations at locations SP1 and SP2 tended to decrease in the north-westerly downwind direction. In the present study, the *D/F* ratios at urban sites (0.448) were found to be below those at incineration sites (0.496). While these values indicate the influence of thermal processes at all sites, they suggest a variation in the degree of impact between industrial and incineration settings. It is therefore improbable that the elevated concentrations at SP4 can be solely attributed to the MWI; instead, they may be linked to alternative local sources of emissions, as confirmed by a sampling ratio. This seasonal pattern was evident in the statistical data for stations influenced by the incineration facility (i.e., SP1 and SP3) and stations SP2 and SP4, both in summer and winter.

A t-test was conducted at a very high level of significance, with $p < 0.001$, to compare the summer values of SP1-SP4 with their respective winter values. The results of the t-test confirmed that the discrepancies between the summer and winter means are statistically significant. Interestingly, when comparing the average PCDD/F values at stations #1 and #3 with those of stations #2 and #4, both summer and winter showed no statistically significant geographic differences ($p > 0.1$). These fluctuations have been attributed to factors such as increased combustion emissions in cold weather or various meteorological conditions, which include higher rainfall, changes in air mass patterns, shifts in predominant winds, or alterations in the altitude of the boundary layer.

3.3 PCBs Congener Concentrations and Distribution

Passive air samples were collected from four distinct sites to determine the concentration of \sum PCB near the MWI. In the current study, we examined the ways in which certain fundamental meteorological factors, such as the levels of particulate, gaseous, and total concentrations of PCDD/Fs and dlPCBs, may be influenced by ambient temperature, boundary layer height, wind speed, and precipitation rate. In line with the earlier discussions regarding seasonal fluctuations, there was a positive correlation between the ambient temperature and the overall concentrations for most individual PCDD/Fs and dl-PCBs. The same findings were reported by Hao et al. (2018) and Kirchner et al. (2020). Seasonally, the dl-PCBs concentrations were high during the summer compared to the winter, while the concentrations remained constant in other seasons. On average, during summer, dl-PCB concentrations were ten times higher compared to winter, representing a 1.2-fold increase. This study reported the highest \sum PCB concentration of 846 fg/m³ from PS4, comparable with the 536.4 pg/m³ concentration reported by Sari et al. (2023), but much higher than the 270 ± 44 pg/m³ concentration reported by Bokare et al. (2023) during the summer season in Washington, DC, and 145 ± 80 pg/m³ in East China (Zhejiang Province) at the background sites by Mao et al. (2020).

In summer, SP1 reported a \sum PCB concentration of 693 fg/m³ (13.04 fg WHO-TEQ/m³), with a notable congener distribution where #77, #189, #105, and #114 played significant roles, each contributing between 10.67% and 13.99%, respectively. Conversely, #101 and #52 had the lowest individual contributions at 1.30% and 1.44%, respectively (Figure 6). SP2 reported a \sum PCB concentration of 684 fg/m³ (11.67 fg WHO-TEQ/m³) and, remarkably, all congeners displayed high concentrations, with most contributing more than 10% except for #169 and #52, which contributed 1.46% each. SP3 reported a \sum PCB concentration of 605 fg/m³ (8.83 fg WHO-TEQ/m³), with prominent congeners including #169, #52, and #81 contributing between 10.25%, 11%, and 11.57%, while #101 and #114 had lower concentrations at 6.78% and 6.61%, respectively. SP4 had the highest \sum PCB concentration in the study at 846 fg/m³ (15.93 fg WHO-TEQ/m³) and, like SP3, all congeners reported high concentrations with the exception of #105 which had the lowest contribution at 1.18%. These findings indicated diverse environmental influences and pollutant sources affecting the PCB concentrations across the sampling sites. The findings are in line with previous findings by Degrendele et al. (2020), Rovira et al. (2018), Song et al. (2022) conducted in Europe, demonstrating a level of comparability.

In autumn, SP1 had a \sum PCB of 359 fg/m³ (4.06 fg WHO-TEQ/m³) with notable contributions of #77: 10.86%, #81: 12.53%, #28: 10.31%, #105: 9.19%, and #114: 11.14%. SP2 reported a higher \sum PCB concentration of 431 fg/m³ (7.08 fg WHO-TEQ/m³) with #126, #77, #169, #101, and #105 reported as major congeners. A sharp increase was observed in SP3, with a mass exhibiting the highest \sum PCB concentration of 594 fg/m³ (9.34 fg WHO-TEQ/m³). The congener distribution was reported as #77: 10.90%, #126: 11.60%, #169: 10.21%, #189: 9.05%, #52: 9.98%, #101: 9.51%, and #105: 10.90%, while #169 and #189 were the least congeners, contributing 1.68% each. The concentration values observed in SP3 were marginally higher than those documented in the same season. This could be indicative of a sustained impact from primary atmospheric PCB emissions. In addition, this indicated the presence of multiple local emission sources at some background sites. Fluctuations over time affected the distribution of PCB levels in the environment, likely impacting the observed PCB concentrations. Moreover, studies by Cetin et al. (2017) and Othman et al. (2022) have proposed an inverse correlation between PCB concentrations and OH radical levels in the atmosphere. Variations in concentration data may stem from regional

characteristics, measurement dates and periods, and the number of congeners studied. In contrast, SP4 displayed a more even distribution among all congeners, resulting in a $\sum\text{PCB}$ of 444 fg/m^3 ($7.24 \text{ fg WHO-TEQ/m}^3$). The congener distribution was #77: 10.81%, #81: 10.81%, #126: 10.36%, #169: 10.81%, #189: 9.46%, #28: 10.36%, #52: 10.59%, #101: 8.56%, #105: 9.46%, and #114: 8.78%. This data suggests diverse environmental influences and pollutant sources at the different sampling points during the autumn season. In addition, it was confirmed that PCBs were introduced into the ambient air through combustion processes linked to residential heating and vehicular emissions (Bokare et al., 2023).

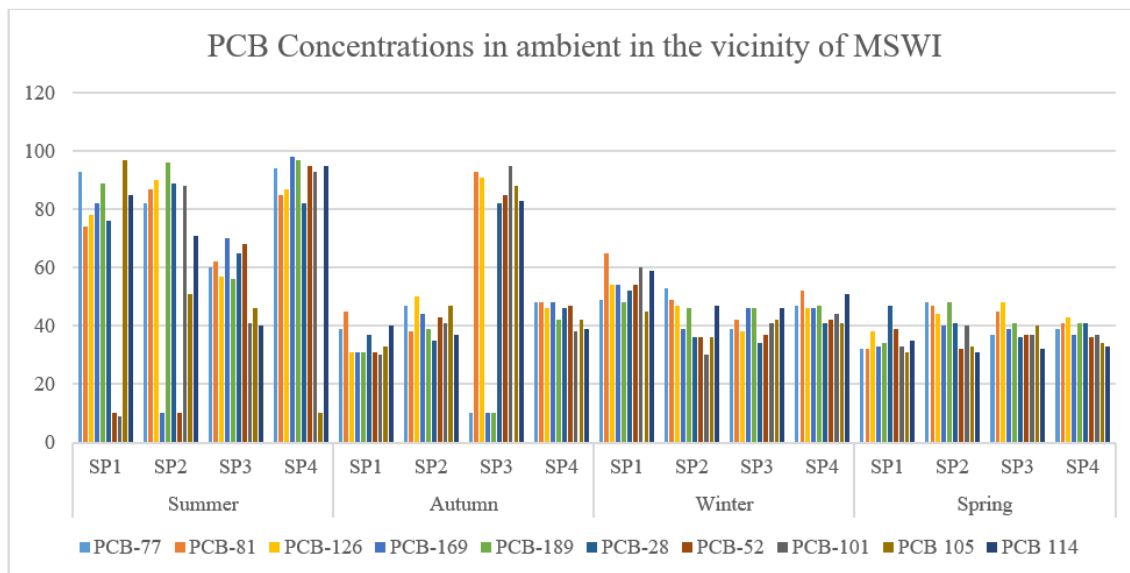


Figure 6. PCBs concentration in ambient air (fg/m^3) near the incineration facility in Johannesburg

During the winter season, SP1 reported significant congeners with the following distribution: #81 at 12.04%, #126 at 10.00%, #169 at 10.00%, #52 at 10.00%, #101 at 11.11%, and #114 at 10.93% (Figure 6). The $\sum\text{PCB}$ concentration in the ambient was measured at 540 fg/m^3 ($9.63 \text{ fg WHO-TEQ/m}^3$). Conversely, SP2 reported major congeners with the following composition: #77 at 12.98%, #81 at 11.99%, #126 at 11.49%, #189 at 11.26%, and #114 at 11.49%. The total $\sum\text{PCB}$ concentration was 409 fg/m^3 ($7.43 \text{ fg WHO-TEQ/m}^3$). SP3 reported major congeners with a composition similar to SP2, including PCB-77 at 12.98%, PCB-81 at 11.99%, PCB-126 at 11.49%, PCB-189 at 11.26%, and PCB-114 at 11.49%. The $\sum\text{PCB}$ concentration in SP3 was 407 fg/m^3 ($7.95 \text{ fg WHO-TEQ/m}^3$). SP4 reported major congeners as #77 at 12.98%, #81 at 11.99%, #126 at 11.49%, #169 at 9.54%, and #114 at 11.49% with a $\sum\text{PCB}$ concentration of 457 fg/m^3 ($7.55 \text{ fg WHO-TEQ/m}^3$). Throughout the winter and spring, the concentrations of PCBs remained at relatively low levels, which is contrary to the findings reported by Boonyatumanond et al. (2023), who reported high concentrations in the spring. The decline observed can be attributed in part to meteorological conditions influencing transport, dispersion, removal, and evaporation mechanisms. Across all sampling sites, the peak concentrations of PCBs were observed during the summer, while the lowest levels typically occurred in the winter. This trend is likely due to higher atmospheric concentrations of PCBs during the summer, driven by their evaporation from surface waters and soil. Additionally, the improper storage and disposal of PCB-containing waste, along with evaporation from contaminated surfaces, also contribute to this seasonal pattern, contribute to this trend, and the presence of household and industrial waste contributes to the increased PCB concentrations (Othman et al., 2022).

During spring, the PCB concentrations in SP1 displayed a consistent pattern across all sampling locations, with #126 appearing as the dominant congener at 10.44%. Other significant congener distributions included #169 at 9.07%, #189 at 9.34%, #28 at 12.91%, #52 at 10.71%, #101 at 9.07%, and #114 at 9.62%. The $\sum\text{PCB}$ was reported to be 364 fg/m^3 and $5.81 \text{ fg WHO-TEQ/m}^3$. SP2 exhibited a congener distribution with notable distributions for various PCB congeners, including #77 at 11.88%, #81 at 11.63%, #126 at 10.89%, #189 at 11.88%, and #28 at 10.15%. The $\sum\text{PCB}$ concentration at SP2 was reported as 404 fg/m^3 and $6.06 \text{ fg WHO-TEQ/m}^3$. At SP3, the congener distribution displayed a slightly different profile, with #77 at 9.44%, #81 at 11.48%, #126 at 12.24%, #169 at 9.95%, #189 at 10.46%, #28 at 9.18%, #52 at 9.44%, #101 at 9.44%, and #105 at 10.20%. The $\sum\text{PCB}$ at SP3 was reported as 392 fg/m^3 and $5.83 \text{ fg WHO-TEQ/m}^3$. For SP4, the congener distribution featured #77 at 10.24%, #81 at 10.76%, #126 at 11.28%, #169 at 9.71%, #189 at 10.76%, #28 at 10.76%, #52 at 9.45%, and #101 at 9.71%. The $\sum\text{PCB}$ was reported as 381 fg/m^3 and $4.43 \text{ fg WHO-TEQ/m}^3$, however, the TEQ contribution from dl-PCBs was low. The different sampling points exhibited unique congener distributions and total PCB

concentrations, while other congeners had varying levels of significance across the locations. These variations could be attributed to different environmental conditions and sources at each sampling point. Conversely, the concentrations were found to exhibit a positive correlation with wind speed and ambient temperature (with a correlation coefficient of 0.632 and a p-value of less than 0.05).

SP1 and SP3 consistently recorded the highest atmospheric concentration levels across the entire sampling period. This was largely because these sites are located closer to industrial activities and MSWI operations compared to other sampling locations. Furthermore, the statistical analysis, including the Mann-Whitney test (with $p > 0.05$) and the Pearson correlation coefficient ($R = 0.68$), indicates no significant variation in concentration distributions among these two sampling points. The majority of PCB levels were clearly associated with and can be attributed to local surface exchange processes. This means that these PCBs are primarily influenced by interactions occurring at or near the surface of the environment in the study area. However, when it comes to #81 and #126, there is an indication that factors related to long-range transport may also be at play. In the present study, the major contributing congeners varied depending on the season and location. However, some congeners, such as #77, #81, #126, and #114, consistently appeared as significant contributors. Conversely, #77, #81, and #126 are commonly associated with sources such as road traffic emissions, while #114 was likely influenced by different factors in the studied area. The variations in PCBs' environmental occurrence and homologous patterns can be impacted by a combination of factors, including ambient temperature, chemical volatility, atmospheric transport, and soil organic matter content. These factors are crucial in predicting the potential health risks linked with human exposure (Degrendele et al., 2020; Othman et al., 2022).

3.4 Comparison of PCDD/Fs Levels from other Atmospheric PCDD/F Studies

The data from this study was subjected to various comparisons with similar studies conducted worldwide. For a detailed comparison, we considered several factors, such as location, sample size, ambient results, and the type of incineration facility in each case. Figure 7 shows a comparative analysis of the findings from this study on atmospheric PCDD/Fs in Johannesburg with those from other studies conducted in various locations, including New Zealand, US National Parks (US National Dioxin Air Monitoring Network, US NDAMN), Slovakia, Spain, Japan, Durban, Algeria, Egypt, Kenya, Mauritius, Mali (Batterman et al., 2007), China (Bo et al., 2022; Hu et al., 2019; Li et al., 2023; Xu et al., 2019), South Korea (Kirchner et al., 2020), and Taiwan (Ngo et al., 2020). The PCDD/Fs TEQ levels in Johannesburg reported an average of 454.88 TEQ fg/m^3 (ranging from 226.72 to 852.15 TEQ fg/m^3) and exceeded levels reported in other regions except for an older study in Krakow, Poland, in 1995, where PCDD/F levels varied from 950 to 12,000 TEQ fg/m^3 . The PCDD/F levels observed in Africa and Latin America were similar to the ones reported in Europe.

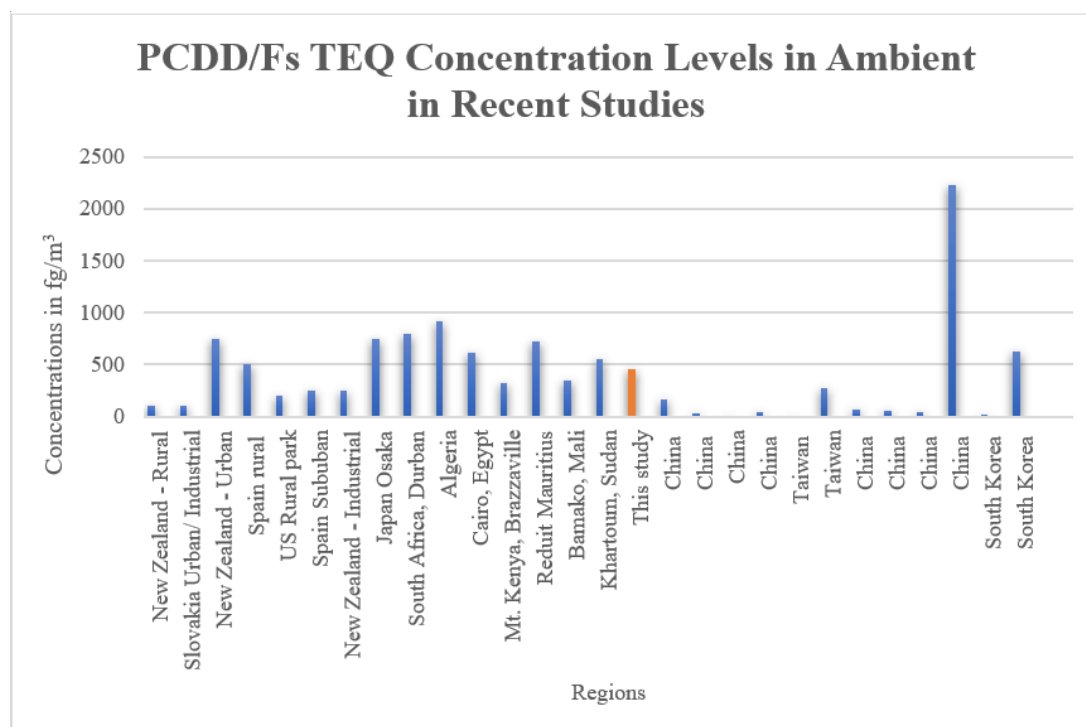


Figure 7. PCDD/Fs concentrations as in industrial sites in the vicinity of incineration facilities as collected from other countries

A comparative analysis revealed an interesting trend. The findings of this study were consistent with those observed in rural Spain (500 TEQ fg/m³) and Khartoum, Sudan (555 TEQ fg/m³), but much higher than the concentrations of 322 TEQ fg/m³ reported from Mount Kenya and Brazzaville and 345 TEQ fg/m³ from Bamako, Mali. Our findings were significantly higher than the concentration of 100 TEQ fg/m³ observed in rural New Zealand and industrial or urban Slovakia. Meanwhile, rural areas in the US, suburban Spain, and industrial areas in New Zealand reported concentrations ranging from 200 to 250 TEQ fg/m³. Cairo, Egypt, reported a comparative 616 TEQ fg/m³, which aligns with the figures of 750 TEQ fg/m³ reported in New Zealand and urban Osaka, Japan, and 724 TEQ fg/m³ reported in Reduit, Mauritius. Durban in South Africa reported a concentration of 800 TEQ fg/m³ (Batterman et al., 2007), while Algeria reported a higher concentration of 923 TEQ fg/m³ (White et al., 2020). The highest concentration recorded reached 2225 TEQ fg/m³ in China (Hu et al., 2019). In the broader context of Africa, the PCDD/Fs data from this study (average 454.88 TEQ fg/m³) are consistent with figures varying from 322 to 780 TEQ fg/m³ observed in the past across the continent (White et al., 2020). These findings indicate a pattern of declining PCDD/Fs levels in South Africa in the last ten years, which corresponds to previous research by Kirchner et al. (2020), who reported an average of 3300 fg/m³ in Seoul, South Korea, between 2002 and 2009.

The decline in PCDD/Fs levels in South Africa can be attributed to the rigorous enforcement of air quality regulations that have been implemented since the early 2000s. While the observed reductions in concentration levels are promising, a broader perspective shows that South Africa still has room for improvement when compared to levels in other regions around the globe. In a global context, the PCDD/Fs concentrations in South Africa, although on a decreasing trend, remain relatively higher when compared to levels observed elsewhere around the globe. The comparatively elevated concentrations may indicate that, despite regulatory efforts, South Africa still faces challenges in mitigating PCDD/Fs emissions and achieving air quality standards on par with some countries. Therefore, while the progress is commendable, it highlights the ongoing importance of continued efforts to further reduce PCDD/Fs levels in South Africa to align more closely with the lower levels achieved in other regions, such as other parts of China, ensuring better air quality and environmental health.

3.5 PCDD/Fs Concentration in Soil in the Vicinity of the Incineration Facility

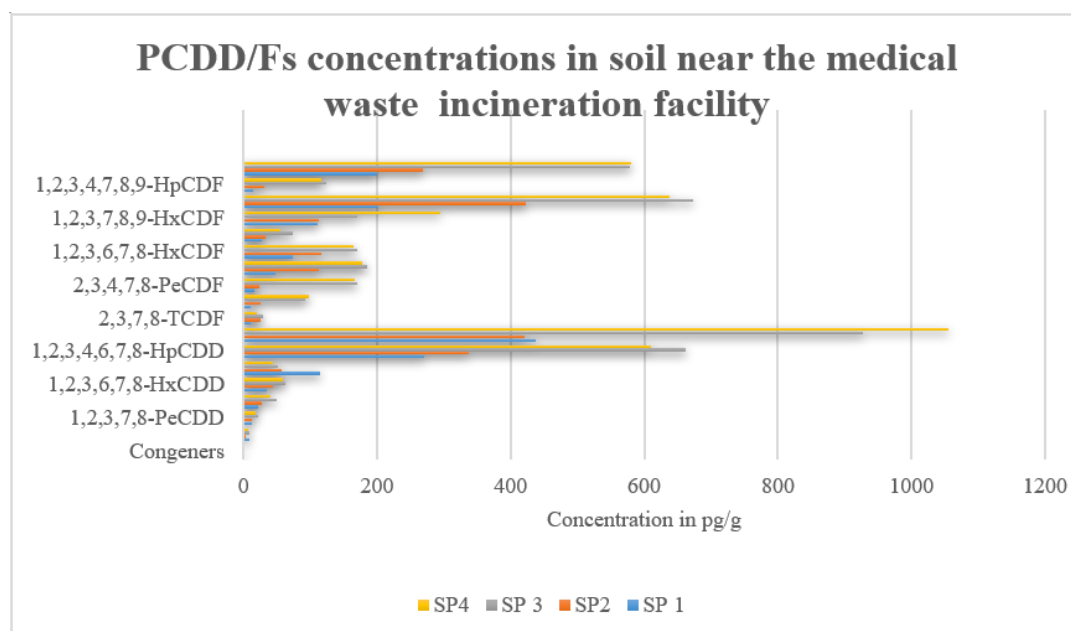


Figure 8. The PCDD/Fs profile in soil in Johannesburg, South Africa, near the MWI facility

Figure 8 provides findings on the PCDD/Fs concentration levels and I-TEQ values found from soil samples collected near the incineration facility under study. There was significant variation in the distribution of congener profiles among the samples. The recorded PCDD/F levels varied from 2.97 to 1054.67 pg/g, while the corresponding I-TEQ figures varied between 59.17 and 106.05 pg WHO-TEQ/g. Significantly, the I-TEQ values for PCDD/Fs were under the 40 ng I-TEQ/kg threshold for risk screening and well below the 400 ng I-TEQ/kg intervention limit. These limits are specified in the risk control standards for soil contamination on development land (GB 36600, 2018). SP1 reported the \sum PCDDs in the soil samples of 902.56 pg/g (58.70%) and the \sum PCDFs of 715.87 pg/g (46.56%), resulting in a \sum PCDD/Fs of 1537.04 pg/g and (59.17 pg I-TEQ/g), indicating a significant presence of PCDDs in soil. The SP1 sample had notably high concentrations of PCDD/F congeners,

including OCDD with 437.83 pg/g (28.436%), 1,2,3,4,6,7,8-HpCDD with a concentration of 271.28 pg/g (17.633%); 1,2,3,4,6,7,8-HpCDF with 201.63 pg/g (13.108%), and OCDF with 200.44 pg/g (13.037%). On the other hand, 2,3,7,8-TCDD had the lowest concentration among isomers, with just 9.43 pg/g (0.673%). This is comparable to the findings reported by Song et al. (2022). Surprisingly, these findings were approximately 11.21% lower than what had been previously reported in the particle phase at the same sampling point. This decrease in PCDD/F levels may potentially be attributed to the influence of precipitation and wet weather conditions during the sampling period.

The findings in SP2 revealed that the Σ PCDDs matched the Σ PCDDs reported in SP1, both measuring 901.61 and 902.56 pg/g, respectively. However, a significant increase was observed in the Σ PCDFs with SP2 reporting 1041.92. The Σ PCDD/Fs was reported at 2399.25 pg/g (55.96%) more than what was reported in SP1. The TEQ was reported at 59.11 pg WHO-TEQ/g similar to what was observed in SP1. Among the congeners, 1,2,3,4,6,7,8-HpCDF and OCDD were reported as major contributors with a concentration of 422.17 (17.59%) and 420.98 pg/g (17.55%), respectively. Interestingly, it was observed that as the distance from the incineration facility increased, the concentrations of all congeners also increased. Notably, 1,2,3,4,6,7,8-HpCDF reported a more than twofold increase in concentration compared to the levels reported nearer the incineration facility. This suggested that the incinerator alone may not be the primary source of these compounds, and other nearby industrial operations such as smelting, coal-fired boilers, and foundry operations could not be eliminated as contributors to the elevated concentrations of PCDD/F. The ratio of PCDD/F levels (F/D ratio) is a helpful indicator for identifying the sources of PCDD/F levels in the environment. If the F/D ratio exceeds 1, it suggests that the PCDD/F levels originate primarily from combustion sources. On the contrary, a F/D ratio less than 1 suggests a variety of sources for PCDD/F levels in the atmosphere, with waste incineration possibly being a significant contributor among them (Li et al., 2023). In the present study, the F/D ratio varied between 0.33 and 3.44, with a mean of 1.885. Out of the four soil samples, three had F/D ratios below 1. This implies that the incineration facility was not the primary contributor to PCDD/Fs in the soil samples. Moreover, it suggested that the impact of the investigated MSW incineration plants on PCDD/F levels in the soil might have been relatively low in the study area.

The findings in SP3 revealed that the congeners varied significantly in concentrations, with OCDD measuring the highest at 927.43 pg/g (18.21%), followed by 1,2,3,4,6,7,8-HpCDF with 673.14 pg/g (13.22%), and 1,2,3,4,6,7,8-HpCDD with 662.85 pg/g (13.03%). The Σ PCDD/Fs was reported at 5090.81 pg/g and the TEQ at 104.041 pg WHO-TEQ/g. Furthermore, the increased Σ PCDD/Fs value in the soil samples compared to the particle phase highlights the complex interplay of various factors such as emission sources and atmospheric deposition. The highly chlorinated PCDD/Fs (particularly PCDDs) made up a large part of the homolog profiles in SP3 samples near MWI sources. This observation aligns with the findings of Bo et al. (2022).

The findings in SP4 reported OCDD as the major congener with a concentration of 1054.67 pg/g (19.47%), followed by 1,2,3,4,6,7,8-HpCDD at 610.57 pg/g (11.24%). The Σ PCDDs and Σ PCDFs demonstrated concentrations reaching 1833.46 and 2316.80 pg/g, respectively. The Σ PCDD/Fs concentrations of 5430.70 pg/g (106.05 pg WHO-TEQ/g) highlighted the significance of contamination in the sampled site. By contrast, low-chlorinated PCDD/Fs represented lower concentrations, which was consistent with the particle phase results as there were no significant differences between them (t-test, $p=0.661$, exceeding <0.05). The PCDD/F concentrations in soil in this study exceeded those recorded in South Africa, which ranged from 0.34 to 20 pg WHO-TEQ/g, as documented by Nieuwoudt et al. (2009). However, they were comparable to the concentrations reported in Taiwan, which ranged from 1.52 to 134 pg WHO-TEQ/g (Ngo et al., 2020). In addition, the current findings were consistent with numerous other studies, including those by Lei et al. (2020), Rovira et al. (2018), Yu et al. (2023), where PCDD/F levels varied from 2.41-3880 pg/g (0.07-127 pg TEQ/g). The concentrations of PCDD/Fs showed minimal variation, even with changes in season and across different sites. This suggests that the soil concentration remained relatively stable.

3.6 Inhalation Risk Assessment

According to VoPham et al. (2020) as well as Trinh & Chang (2018), the primary exposure pathways for humans to toxic pollutants, including PCDD/Fs, are oral ingestion, inhalation, and dermal contact. The inhalation risk exposure was conducted based on the toxic equivalent values obtained during different seasons from all sampling points. The calculation of the average daily TEQ intake per unit of body weight was predicated on the assumption that individuals experienced continuous exposure to polluted air around the clock. It was also assumed that the indoor air pollution level was equivalent to the outdoor air pollution level. The daily exposure doses to PCDD/Fs were determined using the following equation (Zhou et al., 2016):

$$Inh = \frac{T_f V_r F_r C_{air}}{Bw} \quad (6)$$

where, *Inh* represents inhalation exposure in pg I-TEQ/(kg/day); t_f stands for the exposed time fraction,

conservatively assumed as 1; V_r denotes the ventilation rate, set at 20 m³/day for adults and 7.60 m³/day for children; f_r represents the alveolar fraction that remains in the lungs, which is 0.750 for both adults and children; C_{air} signifies the average air concentration of dioxin in pg I-TEQ/m³; BW indicates body weight, assumed as 70 kg for adults and 15 kg for children.

Table 3 provides information on the estimated daily intake of PCDD/Fs through inhalation for human exposure (pg I-TEQ per kg per day) for both adults and children at four different sampling points (SP1, SP2, SP3, and SP4) during various seasons (summer, autumn, winter, and spring). The data clearly indicate that individuals residing near the incineration facility were subject to PCDD/Fs exposure. The daily inhalation doses varied, with values spanning from 0.230–14.646 pg I-TEQ/kg/day for adults and 13.558–60.301 pg I-TEQ/kg/day for children. There was a significant variation observed in exposure levels between the sampling points and seasons. For instance, the highest exposure doses were generally measured in the winter, with the lowest doses found in the autumn for both adults and children. It was evident that children consistently experience higher inhalation exposure doses compared to adults at each sampling point and in all seasons. This underscores the vulnerability of children to environmental pollutants. SP3 and SP1, which are exposed to an MWI, consistently showed higher exposure doses compared to SP2 and SP4, indicating that proximity to the pollution source has an impact on exposure levels. In general, the inhalation exposure doses were noticeably higher during the winter compared to the summer for both adults and children across all sampling points. This suggests that the population in the area is exposed to higher levels of PCDD/Fs during the colder months. Children consistently experience higher exposure doses compared to adults at all sampling points and in both seasons. The exposure values were similar to the findings by Li et al. (2023) in Guangzhou and Deng et al. (2020) in Shanghai, China.

Table 3. Assessment of inhalation risk from PCDD/F exposure near the MWI

Sampling Point	Spring		Autumn		Summer		Winter	
	Inhalation exposure dose (pg I-TEQ/(kg/day))		Inhalation exposure dose (pg I-TEQ/(kg/day))		Inhalation exposure dose (pg I-TEQ/(kg/day))		Inhalation exposure dose (pg I-TEQ/(kg/day))	
Population	Adults	Children	Adults	Children	Adults	Children	Adults	Children
SP1	8.535	30.205	0.234	0.714	4.347	13.953	8.251	29.559
SP2	6.642	24.535	0.230	0.665	6.548	27.003	7.442	25.614
SP3	4.677	16.369	8.115	28.194	11.339	46.753	6.218	21.441
SP4	3.889	13.558	8.352	28.837	14.646	60.301	7.482	25.741

In 1998, the European Centre for Environment and Health, a division of the World Health Organization, established guidelines for a tolerable daily intake (TDI) of dioxins and dioxin-like compounds, suggesting a range of 1 to 4 pg WHO-TEQ per kilogram of body weight each day. This recommendation emerged from growing concerns about the health risks associated with exposure to these toxic substances, leading to a push for stricter environmental standards and health regulations. Research indicates that over 90% of the average person's PCDD/F exposure comes from their diet, with inhalation accounting for only about 2.61% of the total daily intake (Yu et al., 2023). When comparing the daily inhalation intakes of PCDD/Fs for the residents residing near the MWI in this study with the TDI range, it is evident that the inhalation exposure in this study falls above the recommended TDI levels. However, based on the findings by Yu et al. (2023) and Zhou et al. (2016), the population in Table 3 appears to be at relatively lower risk from inhalation exposure to PCDD/Fs. The estimation that inhalation intake contributes to only approximately 2.61% of the total daily intake of PCDD/Fs suggests that the majority of the exposure (over 90.0%) comes from dietary sources. This indicates that the primary route of exposure is through the consumption of contaminated food rather than the inhalation of PCDD/Fs. Although it is imperative to monitor and manage all potential sources of exposure, the relatively lower contribution from inhalation suggests that the population's overall risk from inhalation exposure to PCDD/Fs is not as significant as the risk associated with dietary intake. Nevertheless, a comprehensive risk assessment should consider all exposure routes to ensure a holistic understanding of the potential health hazards for the community residing near the incineration plant in South Africa.

3.7 Implications for Waste Management Policies in South Africa

The present study sheds light on the concerning PCBs and PCDD/F concentrations measured near an incineration plant in South Africa, raising significant consequences for both environmental health and waste management policies. The findings reveal elevated concentrations of PCBs and PCDD/Fs compounds, particularly during the summer months, indicating potential health risks for nearby residents. These variations in concentrations across seasons and sampling points indicate the complex interplay of environmental factors and pollutant sources. As a result, there is an urgent need for stringent regulatory measures to address emissions from incineration

facilities and other industrial activities contributing to PCBs and PCDD/Fs contamination. Priority should be given to preventive measures such as enhancing waste management practices, bolstering air quality monitoring, and implementing technologies to curb emissions. It's imperative that waste management policies prioritize the reduction, reuse, and recycling of waste materials to minimize reliance on incineration. Furthermore, enforcing strict regulations to ensure incinerators are equipped with advanced emission control technologies is essential. Promoting cleaner production practices and incentivizing industries to adopt less polluting waste disposal methods are also crucial steps forward. Collaborative efforts involving government agencies, industries, and communities are vital for developing and implementing comprehensive waste management policies that prioritize environmental health protection. By embracing these measures, South Africa can effectively mitigate the environmental and health risks associated with PCBs and PCDD/Fs contamination while advancing sustainable development goals and environmental stewardship.

4. Conclusions

In this article, we report on an extensive ambient air assessment programme in Johannesburg, South Africa. The objectives of this study were to: (1) conduct gas-particle phase partitioning; (2) examine the concentrations and profiles of PCDD/Fs and dl-PCBs in the ambient air around the MWI; (3) determine the PCDD/F concentrations in soil; and (4) evaluate the health impact on people living near the MWI by calculating daily inhalation doses for both children and adults. The particulate phase was dominantly characterised by highly chlorinated congeners ranging from hexa- to octa-chlorinated forms, whereas the gas phase was dominated by low-chlorinated PCDD/Fs, specifically tetra- and penta-chlorinated congeners. Concentrations of ambient air Σ PCDD/Fs, Σ PCBs, Σ PCDD/Fs in soil ranged from 8.3 to 108.36 fg WHO2005-TEQ/m³, 4.43 to 6.06 fg WHO2005-TEQ/m³ and 59.17 to 106.05 pg WHO-TEQ/g, respectively. The congeners exhibited distinct seasonal patterns, typically peaking in winter and decreasing in summer. These variations are likely linked to factors such as combustion sources, temperature inversions, and various mechanisms that lead to PCDD/Fs removal, including processes such as dry and wet deposition, chemical reactions, photolysis, and absorption by vegetation.

In a global context, the PCDD/Fs concentrations in South Africa, despite a decreasing trend, remain relatively higher when compared to levels observed in many other parts of the world. The comparatively elevated concentrations may indicate that, despite regulatory efforts, South Africa still faces challenges in mitigating PCDD/Fs emissions and achieving air quality standards on a par with some countries. While the progress is commendable, it highlights the ongoing importance of continued efforts to further reduce PCDD/Fs levels in South Africa to align more closely with the lower levels achieved in other regions, ensuring better air quality and environmental health. When comparing the daily inhalation intakes of PCDD/Fs for the residents living near the MWI in the present study with the TDI range, it is evident that the inhalation exposure fell above the recommended TDI levels. However, the estimation that inhalation intake contributes to only approximately 2.61% of the total daily intake of PCDD/Fs suggests that the majority of the exposure (over 90.0%) comes from dietary sources. Although it is important to monitor and manage all potential sources of exposure, the relatively lower contribution from inhalation suggests that the population's overall risk from inhalation exposure to PCDD/Fs is not as significant as the risk associated with dietary intake. Nevertheless, a comprehensive risk assessment should consider all exposure routes to ensure a holistic understanding of the potential health hazards for residents residing near the incineration plant in Johannesburg, South Africa.

Author Contributions

Nomathemba Themba: conceptualisation, methodology, initial draft writing, review and editing. Tlou B. Chokwe: conceptualisation, methodology, supervision, writing (editing and review). Linda L. Sibali: project administration, supervision. All authors have read and agreed to the published version of the manuscript. The relevant terms are explained in the CRediT taxonomy.

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Informed Consent Statement

The manuscript does not include any personal data of individuals in any form (such as individual details, images, or videos).

Data Availability

The data supporting the findings of this study are available upon request.

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Conflicts of Interest

The authors have no conflicts of interest to declare.

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