# Assessment of past dioxin emissions from waste incineration plants based on archive studies and process modeling: a new methodological tool

**Xiaocheng Zhang**
EPFL-ENAC: Ecole Polytechnique Federale de Lausanne Faculte Environnement Naturel Architectural et Construit
**Alexis de Aragao**
EPFL-ENAC: Ecole Polytechnique Federale de Lausanne Faculte Environnement Naturel Architectural et Construit
**Fabien Moll-François**
Unisanté DSTE: Unisante Departement sante travail et environnement
**Aurélie Berthet**
Unisanté DSTE: Unisante Departement sante travail et environnement
**Florian Breider**
`florian.breider@epfl.ch`

EPFL: Ecole Polytechnique Federale de Lausanne https://orcid.org/0000-0002-5698-0314

---

**Research Article**

**Keywords:** polychlorinated dibenzo-p-dioxin and dibenzofuran (PCDD/F), municipal solid waste incinerator (MSWI), emission history, congener profile, archival data, kinetic model

**Posted Date:** June 13th, 2024

**DOI:** https://doi.org/10.21203/rs.3.rs-4376247/v1

---

# Abstract

Pollution from past industrial activities can remain unnoticed for years or even decades because the pollutant has only recently gained attention or identified by measurements. Modeling the emission history of pollution is essential for estimating population exposure and apportioning potential liability among stakeholders. This paper proposes a novel approach for reconstructing the history of polychlorinated dibenzo-*p*-dioxin (PCDD) and polychlorinated dibenzofuran (PCDF) pollution from municipal solid waste incinerators (MSWIs) with unknown past emissions. The proposed methodology relies on the search for technical and operational data on the pollution source in archives, the extraction of representative data from the scientific literature, and the use of kinetic models of the formation and decomposition of PCDD/Fs within combustion chambers. This new methodological tool allows to estimate the MSWI's stack emission and relative profile of seventeen PCDD/F congeners over time. The approach was validated through a case study of a MSWI in Switzerland. The modeled congener profile achieved a Pearson correlation coefficient of 0.98 with measurements in fly ash washwater. Additionally, the simulated soil quantity (1,283–1,698 gTEQ$_{WHO-2022}$ or 1,115-1,419 gTEQ $_{WHO-2005}$) fell within the same order of magnitude as the estimated quantity from measurements (425 gTEQ $_{WHO-2022}$ or 371 gTEQ $_{WHO-2005}$).

# 1. Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and furans (PCDFs) are two groups of ubiquitous and persistent contaminants released from industrial and natural combustion (Kanan and Samara 2018). They exist in the environment as complex mixtures of 210 possible congeners, of which 7 PCDDs and 10 PCDFs with chlorine substitution on the 2, 3, 7, and 8 positions have been identified as toxic to human and mammals (van den Berg et al. 1998, 2006; DeVito et al. 2024). The seventeen PCDD/Fs congeners of toxicological relevance, as well as their toxic equivalency factors (TEF) are displayed in WHO Toxic Equivalency Factors of 17 PCDD/Fs in Supplementary Information (Table S1). It should be noted that this study does not cover polychlorinated biphenyls (PCBs), whose structure and mechanism of toxic action are comparable to those of PCDD/Fs.

Anthropogenic thermal processes are the most prominent source of PCDD/Fs emission. Specifically, waste incineration plays an important role as it contributes to 13% of the total PCDD/Fs emission across 86 countries (Fiedler 2016). Upon the release of combustion fumes, atmospheric transport and deposition then leads to the pollution of PCDD/Fs in the topsoil, where they demonstrate extreme persistence with half-lives ranging from years to several decades (Seike et al. 2007). The PCDD/Fs polluted soil may increase health risks to humans, not only through direct ingestion of soil, but also by the consumption of food from animal raised on the contaminated land and of cucurbitaceous vegetables cultivated in highly contaminated soil (Vernez et al. 2023). In urban environment, municipal solid waste incinerators (MSWIs) are frequently a source of concern for local populations, especially MSWIs with a long history of operation as they often lacked continuous PCDD/Fs monitoring during their early years of operation. Even when historical time series of PCDD/Fs measurements at MSWIs are available, they may not be sufficient for a detailed examination of pollution soil history and the associated human health risks, depending on the quality and frequency of the measurements.

To compensate for the missing emission data, models are required to reconstruct the PCDD/Fs emission history at MSWIs. The great complexity of PCDD/Fs synthesis pathways in incinerators and the numerous influencing factors heightened the challenge of modeling studies. Based on the available literature, no models are proposed for deriving PCDD/Fs congener profile in incinerators. A number of models exist for estimating the quantity of total PCDD/Fs emission from MSWIs. These models are largely based on the kinetics of PCDD/Fs formation and decomposition, and rely on process parameters such as temperature, residence time, fly ash properties, and the concentration of other chemicals (Shaub and Tsang 1983; Altwicker et al. 1990; Huang and Buekens 2001; Stanmore 2002). However, the impact of waste composition and air pollution control devices (APCDs) on PCDD/Fs congener profile and quantity is not addressed in these studies. These aspects were explored in a probabilistic model proposed by Koehler et al. (2011), but significant uncertainties are associated with the calculated PCDD/Fs emission factors due to the nature of the approach.

The objective of the current study was thus to develop an approach to reconstruct the history of PCDD/Fs pollution from MSWIs. To this end, two complementary modeling steps are successively performed. Firstly, the relative profiles of PCDD/Fs congeners at different periods are empirically estimated on the basis of data from similar MSWIs. Secondly, the absolute amount of PCDD/Fs emission over time is derived using a kinetic model. This takes into account the formation and decomposition of PCDD/Fs and various parameters such as waste composition and operating conditions of the MSWI, based on archives. The combination of these two modeling parts and the study of archives provides the congener-specific emissions over the entire lifetime of a MSWI under investigation.

The developed methodology was finally tested to a concrete case of PCDD/Fs pollution from a MSWI for validation purposes. It implies the PCDD/Fs extensive pollution by a former MSWI in Lausanne - Switzerland discovered in 2020 and which operated between 1958 and 2005. Simulations under different scenarios were performed to quantify the impact of important parameters, including waste composition, operating conditions, and APCDs.

## 2. Methods

The modeling framework describes the congener profile and total emission quantity of PCDD/Fs at the stack of a MSWI of interest. The model relies on historical archives, technical data, and scientific literature as sources of data.

The model’s boundaries consist of waste quantity, waste composition, operating conditions, APCD configuration, and PCDD/F formation and decomposition during incineration (Fig. 1). The key parameters include the quantity and material composition of the incinerated waste, the operating conditions, and the APCD configuration. This data is typically obtained from archival documents.

The chlorine content in the waste stream is estimated from waste composition, and the typical congener profile corresponding to this chlorine level and operating conditions is drawn from the literature. A kinetic model, available in the literature, is employed to simulate the total amount of PCDD/Fs generated in the furnace. Finally, the effect of APCDs is considered using existing literature data from MSWIs with similar APCD configurations as references.

## 2.1 Estimating PCDD/Fs Relative Profile

The proposed method for estimating the relative profiles of the 17 toxic PCDD/Fs congeners at a MSWI's stack for different time periods is fundamentally empirical. It relies on profile data obtained from other incinerators that closely resemble a target MSWI at specific time intervals. Such representative data are typically available in scientific literature, as numerous studies have investigated various types of incinerators (Oh et al. 1999; Takaoka et al. 2003; Chang et al. 2004; Lin et al. 2020; Wang et al. 2022).

The degree of similarity between an incinerator and a target MSWI can be evaluated based on three crucial factors: the chlorine content of the input waste, the APCDs in place, and the operating conditions. Indeed, previous research, employing principal component analysis (PCA), has demonstrated that the chlorine content of the input waste contributes to approximately 40% of the overall variance in relative PCDD/Fs profiles, while other factors such as the APCD configuration and operating conditions account for the remaining 60% (Wang et al. 2003). Therefore, when estimating the relative PCDD/Fs profile at an MSWI stack for a specific period, the data sources should at least strive to minimize biases associated with these three explanatory factors: chlorine content of input waste, APCDs and operating conditions.

### 2.1.1 Chlorine Content of Input Waste

To estimate the average chlorine content of waste at a studied MSWI, for any undisclosed period, the following steps must be followed:

1. Ascertain the average mass composition of the waste on a per-category basis;
2. Determine the average chlorine content associated with each waste category;
3. Estimate the average chlorine content of the MSWI's input waste for the studied time by computing a weighted average across the waste categories, applying the following equation (Eq. 1):

$$\boxed{Cl_i = \sum_j Cl_j \bullet n_{i,j} \qquad \text{(Eq. 1)}}$$

where $Cl_i$ represents the average chlorine content (on a per-mass basis) of the MSWI's input waste during the period $i$, $Cl_j$ denotes the average chlorine content (on a per-mass basis) associated with the waste category $j$, and $n_{i,j}$ are the mass-share of the waste type $j$ during the period $i$.

A procedure for estimating the weight fraction of chlorine in the waste from categorical waste composition is presented in Waste Element Composition in Supplementary Information (Tables S2 and S3). This involves a search for data on the source of the pollution, which may be found in certain archives. The estimated chlorine content should be then compared against a critical threshold of 0.8–1.1%, as this range marks a distinction between two types of PCDD/Fs stack profiles (Wang et al. 2003).

### 2.1.2 Air Pollution Control Devices (APCDs)

Achieving representativeness of reference incinerators for a target MSWI demands a matching in APCDs configuration, including both sequence and equipment. This suggests having a solid understanding of the APCDs configuration of a target MSWI for the studied period. Technical documents are likely to be found in archives.

Empirical data can cover the whole APCDs chain or only part of it, when no reference incinerator fits the entire APCDs arrays' configuration, data from different sources are averaged, or the evolution of the profile throughout the treatment process is studied. More specifically, data on the efficiency of every APC chain or device in altering the amount of each PCDD/Fs congener before and after treatment, for each investigated period, is needed. Additionally, the initial PCDD/Fs profile (i.e., post-combustion profile, before any treatment) is required. Leveraging this initial profile and APCDs' efficiencies subsequently enables the systematic propagation of the PCDD/Fs relative profile from the furnace through the post-combustion zone up to the stack, applying the following equation (Eq. 2):

$$R_{i,j_{\text{out}}} = R_{i,j_{\text{in}}} \bullet \frac{\left(1-\eta_{i,j}\right)}{\sum_{k}^{17}\left[\left(1-\eta_{k,j}\right)\bullet R_{k,j_{\text{in}}}\right]} \quad \text{(Eq. 2)}$$

where $\eta_{i,j}$ represents the mass-concentration-based efficiency of the APC chain or device $j$on the congener $i$, and $R_{i,j_{\text{in/out}}}$ is the mass-fraction of the congener $i$ over the 17 relevant PCDD/Fs congeners, respectively at entrance (in) and exit (out) of the APC chain or device $j$. For cases where removal efficiencies are presented in terms of congener mass fractions, or there is an expected efficiency discrepancy between a target MSWI and a reference incinerator that necessitates adjustment, alternative methods are available in APCDs Efficiency Adjustment in Supplementary Information.

### 2.1.3 Operating Conditions

To match the operating conditions to the reference and target incinerators, temperature was identified as the primary variable influencing the formation of PCDD/Fs within incinerators, as reported in a previous study (McKay 2002). Additionally, some secondary operating factors, such as waste composition, oxygen supply, and shutdown/start-up phases, were also shown to impact the generation of PCDD/Fs congeners in incinerators (Tejima et al. 2007; Zhang et al. 2008; Li et al. 2019). However, these secondary factors have not been included in this study as explanatory variables when assessing the similarity between reference incinerators and a target MSWI. This omission is due to limited insights available in the existing literature regarding their influence on PCDD/Fs formation, the variability of these factors in incinerators, and the challenges associated with obtaining precise data for them.

For the temperature factor, the efficient elimination of PCDD/Fs found in waste materials primarily takes place within the furnace, following the “3T + E” principle. The latter implies a temperature exceeding 850°C, a residence time of more than 2 seconds, ensuring adequate turbulence, and having an excess of air (McKay 2002). However, PCDD/Fs are subsequently regenerated in the post-combustion zone as the flue gas cools down, through the following mechanisms (see PCDD/F Formation Mechanism in Supplementary Information for more details):

1. Homogeneous synthesis (500–800°C).
2. Heterogeneous de novo synthesis (200–400°C).
3. Heterogeneous precursor synthesis (200–400°C).

The temperature decrease in the post-combustion zone have thus an impact on the relative PCDD/Fs profile, given that PCDD/Fs synthesis rates are responsive to temperature levels and vary according to the specific congeners involved. Estimating the PCDD/Fs profile at the stack of a target MSWI therefore requires that the reference incinerators, which serve as data sources, show close resemblance in terms of temperature conditions at crucial points, including the furnace, the upstream post-combustion zone, and the APCDs of interest, both at their inlet and outlet. The need for similarity in temperature levels is especially critical for APCDs’ profile data where APCDs operate within the temperature range of 200–400°C. This is because these temperature conditions enable heterogeneous synthesis of PCDD/Fs congeners, which exhibit a sensitivity to temperature fluctuations, as mentioned earlier.

## 2.2 Estimating PCDD/Fs Emission Quantity

The method proposed for estimating the total emission quantity of the seventeen PCDD/Fs congeners from a MSWI stack across different time intervals relies on the use of a kinetic model introduced by Palmer et al. (2021). It enables the computation of a specific congener generation by the MSWI’s furnace. Subsequently, the total generation of PCDD/Fs by the furnace can be estimated, taking into account the proportion of the specific congener among the seventeen congeners, as inferred from the relative profile estimation (see section 2.1). Additionally, the influence of APCDs on the calculated furnace’s emission is accounted for, using data from existing literature studies. This analysis allows for deriving the total quantity of PCDD/Fs emission at the stack of a target MSWI.

The two-step model proposed by Palmer et al. (2021) to estimate the quantity of PCDD/Fs emissions in an incinerator considers the first-order kinetics of formation and decomposition of PCDD/Fs with congener-specific rate constants:

$$C + aO_2 \xrightarrow{k_{1,i}} bCO + cCO_2 + d\,[aromatics] + f_i[PCDD/Fs]_i \quad \textbf{(Eq. 3)}$$

$$[PCDD/Fs]_i + O_2 \xrightarrow{k_2} other products \quad \text{(Eq. 4)}$$

where $C$ represents the carbonaceous part of the waste (g carbon/g waste), $f_i$ represents the yield of each congener (g of congener/g of decomposed carbon), $k_{1,i}$ denotes the formation rate constant of each congener ($s^{-1}$), and $k_2$ denotes the decomposition rate constant ($s^{-1}$).

Several influencing factors on the kinetics are considered in the model, including waste chlorine and metal content, oxygen content, and temperature (see Online Resource [Emission Quantity Model]). The optimized estimates of kinetic constants are provided by Palmer et al. (2021) for three congeners: 2,3,7,8-TCDF, OCDF, and 1,2,3,6,7,8-HxCDD. The congener exhibiting the greatest relative share in the congener profile at the MSWI under investigation (as computed from section 2.1) is selected, therefore reducing vulnerability to uncertainties in parameter estimates.

Given the kinetic model and parameters, the quantity of generated PCDD/Fs in the furnace at a specific residence time can be obtained from the following analytical solution:

$$[PCDD/Fs]_i = \frac{k_{1,i} \bullet E_{\mathrm{Cl}} \bullet E_{\mathrm{metal}}}{k_2} \bullet \left(1 - \exp\left(-k_2 \bullet \lambda_{\mathrm{oxygen}} \bullet t\right)\right) \quad \text{(Eq. 5)}$$

where $[PCDD/Fs]_i$ is the generated amount of congener $i$ per unit mass of incinerated waste, $E_{\mathrm{Cl}}$ and $E_{\mathrm{metal}}$ denote the weight fraction of chlorine and metal in the waste, respectively, $\lambda_{\mathrm{oxygen}}$ is the oxygen ratio, and $t$ is the flue gas residence time in the furnace.

## 2.3 Validation Case

The approach presented in this paper has been validated by comparing the model-generated simulated emissions of PCDD/Fs congeners with the actual soil concentrations of these pollutants in the vicinity of the Vallon MSWI. This facility was situated in Lausanne, Switzerland, and was operational from 1958 to 2005. Significant PCDD/Fs pollution was discovered in Lausanne soil in 2020, and the Vallon MSWI was identified as the source. For a detailed account of the Vallon MSWI's historical background, please refer to Supplementary Information. The results of the validation study are presented and discussed in section 3.

## 2.4 Sensitivity Analysis

On the basis of the validation case, a sensitivity analysis is performed in order to identify the most relevant parameters to the emission quantity modeling results. The contribution of each input parameter to the variance in the model output is quantified by a random sampling-based method. The result of the analysis is presented as contribution factors, representing the uncertainty in model output attributed to each input parameter. The detailed methodology and results are demonstrated in the sensitivity analysis in Supplementary Information (Tables S4-S7).

## 2.5 Data Source

As part of the Vallon's validation case, archival documents related to both the pollution source (operational and technical features) and the pollution characteristics (extent and magnitude) were gathered. This comprehensive collection spans newspaper articles, Bulletins of the Communal Council of Lausanne, Annual Management Reports of the Municipality of Lausanne, technical documents, reports from regulatory inspections, and internal correspondences among relevant stakeholders, covering the period from 1948 to 2023. The sourced materials were drawn from various repositories, including the regional and municipal archives as well as of the former MSWI. For a detailed account of the Vallon MSWI's technical aspects, please refer to Supplementary information (Fig. S1-S2 and Tables S4-S8).

Regarding scientific literature data, its acquisition primarily served congener emission profile modeling and waste chlorine level estimation. The search terms included variations of “PCDD”, “PCDF”, and “dioxin”, combined with terms related to specific APCDs employed by the Vallon MSWI, such as “electrostatic precipitator” and “wet scrubber”. The retrieved papers were screened for their similarity with the target MSWI. Additionally, two studies were collected to establish the mapping between waste categorical composition and waste chlorine level. Consequently, the following studies were utilized for the present validation analysis, categorized by modeling sections:

1. Emission profile model (Takaoka et al. 2003; Chang et al. 2004)
2. Waste chlorine level (Themelis 2010; Liu et al. 2018)

# 3. Results and Discussion

## 3.1 Analysis on Data Source

### 3.1.1 Chlorine Content

The estimation of chlorine content in the input waste at Vallon is performed by segmenting the operational period of the MSWI, spanning from 1958 to 2005, into five discrete periods. The estimated values range from 0.3 to 0.7% by weight (refer to Table 1), with an upward trajectory that can be attributed to the growing proportion of plastic in household waste.

Table 1
Evolution of the waste chlorine content over time at the Vallon MSWI

| Period | Cl content (wt %) |
|---|---|
| 1958–1965 | 0.3 |
| 1965–1975 | 0.4 |
| 1975–1985 | 0.5 |
| 1985–1995 | 0.5 |
| 1995–2005 | 0.7 |

Vallon waste composition was estimated on the basis of five sources: the United States Environmental Protection Agency (EPA) national overview on materials, wastes and recycling for the year 1960, an analysis of the contents of Zurich’s garbage cans for the year 1969 reported by Desbaumes and Imhoff (1971), a waste survey carried out in Lausanne in 1982 and reported by Voelgyi (1985), a survey of the contents of Lausanne’s garbage cans in 1990 found in the Lausanne Archives, and the national analysis of waste composition carried out by the former Swiss environment office SAEFL for the years 2000/2001 (SAEFL 2003).

### 3.1.2 APCD Configuration

Based on technical documents found in archives, two main periods regarding APCDs can be distinguished at Vallon MSWI: between 1958 and 1982 when only electrostatic precipitators (ESP) were implemented and between 1982 and 2005, when electrostatic precipitators followed by wet scrubbers were operating (ESP + WS).

### 3.1.3 Operating Conditions

According to archival technical documents, the Vallon MSWI featured two “Von Roll” furnaces functioning from October 6, 1958, to December 29, 2005 (▯ in Fig. 2). The incineration chambers maintained a typical temperature range of 950 ± 50°C. Subsequently, hot flue gases exited the furnaces, entered the afterburner area, and underwent cooling to 280–300°C through boiler heat exchange (▯ in Fig. 2), allowing for significant PCDD/Fs synthesis. The flue gas then passed through ESP for particle removal (▯ in Fig. 2). While particulate PCDD/Fs were probably slightly removed in Vallon’s ESP, a significant amount was also likely produced there, due to favorable temperatures. After the ESP treatment, the flue gas temperature typically ranged between 250 and 300°C. Post-1982, flue gas was further directed to WS before exhaust (▯ in Fig. 2). The WS removed dust particles through wetting, and within Vallon’s WS, gaseous PCDD/Fs were probably partially removed through condensation. However, limited elimination of particulate PCDD/Fs is expected due to the low solubility of PCDD/F species. Noteworthy, the temperature conditions inside the WS partially overlapped PCDD/Fs synthesis windows.

Finally, flue gas was discharged into the atmosphere through the 80-meter-high stack at a low temperature, typically in the range of 60–65°C ([illegible] in Fig. 2).

## 3.2 PCDD/Fs Relative Profile

To estimate the PCDD/Fs relative profile at the Vallon MSWI's stack, profile data from similar incinerators are being sought in the literature. The evaluation of similarity is based on the three previously mentioned (section 2.1) and computed (section 3.1) explanatory factors: chlorine content of the waste input, APCD configuration, and operating conditions.

Based on the estimates of the explanatory variables, two periods (also called scenarios) have been established for reconstructing the PCDD/Fs relative profile at the Vallon MSWI's stack. Scenario n°1 (1958–1982) corresponds to the period when ESP were the sole flue gas control system in the post-combustion area. Scenario n°2 (1982–2005) pertains to the next period, during which WS were introduced to complement the ESP. Regarding the chlorine content of waste input and operating conditions, these factors can be considered uniform across both of these periods. An extensive literature search has next been carried out to find representative profile data for Vallon MSWI concerning these two scenarios.

For scenario n°1 (1958–1982), only the profile measurements carried out by Chang et al. (2004) at an MSWI in Taiwan are considered applicable to the Vallon case. Indeed, the similarities between the Vallon MSWI and this Taiwanese incinerator are multiple. Both processes primarily solid household waste and seem to have chlorine levels below the 0.8–1.1% threshold. The temperature of the furnace in Taiwan is between 850 and 1050°C, close to the 900 to 1000°C announced at Vallon. In addition, the pollution control system after the boiler consists of an ESP followed by a WS in Taiwan, exactly as at Vallon. However, the ESP inlet temperature of the flue gas is lower in Taiwan (i.e., 234°C instead of 280 to 300°C at Vallon). Higher ESP inlet temperature implies higher vapor pressure of PCDD/Fs, leading to a greater percentage in the gas phase and decreased global removal efficiency because ESP is only effective to particle-bound PCDD/Fs. The removal efficiencies of the ESP on congener fractions as measured by Chang et al. (2004) for the particulate fraction are therefore corrected to take into account the higher temperature at Vallon. The applied adjustment method is presented in Vallon Congener Profile Estimation in Supplementary Information (Tables S9-S15). Table 2 shows the final estimates for Vallon ESP. In column a), the ratios of the 17 congeners to the total PCDD/Fs concentration before the ESP are indicated, as well as the gas/particle phase distribution. Column b) refers to the situation after the ESP. Column c) lists the absolute removal efficiencies of the ESP on the PCDD/Fs congeners, also with phase distinction.

As one can see, the passage through the ESP notably affects the congener gas/particle phase distribution, with a sharp decrease in the particulate fraction (55% before the ESP, 20% after). The total (gaseous + particulate) congener pattern is also affected, with significant reductions of highly chlorinated fractions such as OCDF, 1,2,3,4,6,7,8-HpCDF and to a lesser extent OCDD. According to Chang et al. (2004), the gas/particle phase distribution depends essentially on the vapor pressure of each congener, and thus on the temperature. As temperature decreases in the after combustion area, so do the vapor pressures, and more congeners are adsorbed onto the particles. The latter are susceptible to removal by the ESP, while gaseous PCDD/Fs mostly pass through. Highly chlorinated congeners as well as PCDFs have a lower vapor pressure. This is the reason why 1,2,3,4,6,7,8-HpCDF and OCDF are more likely to condense on the particles and undergo higher removal. Interestingly, the conditions inside the ESP correspond to the temperature window of the de novo synthesis (200–400°C), and many gaseous PCDD/Fs are likely to form in this after combustion area. This is confirmed by the total PCDD/Fs removal efficiency of the ESP, which is estimated to be strongly negative (– 161% on a PCDD/Fs concentration basis).

Table 2
PCDD/Fs profile before and after ESP, along with ESP (concentration-based) removal efficiencies, categorized by gaseous (G.), particulate (P.), and total (G. + P.) phases, as estimated for the Vallon MSWI

| **Congener** | **a) Before ESP (% PCDD/Fs conc.)** | | | **b) After ESP (% PCDD/Fs conc.)** | | | **c) ESP removal efficiency (% conc.)** | | |
|---|---|---|---|---|---|---|---|---|---|
| | G. | P. | G. + P. | G. | P. | G. + P. | G. | P. | G. + P. |
| 2,3,7,8-TeCDD | 0.1 | 0.1 | 0.2 | 0.1 | 0.0 | 0.1 | −173 | 54 | −79 |
| 1,2,3,7,8-PeCDD | 0.4 | 0.3 | 0.7 | 0.9 | 0.1 | 1.0 | −479 | 1 | −279 |
| 1,2,3,4,7,8-HxCDD | 0.4 | 0.4 | 0.8 | 1.1 | 0.2 | 1.3 | −631 | −29 | −334 |
| 1,2,3,6,7,8-HxCDD | 0.8 | 0.7 | 1.5 | 2.9 | 0.5 | 3.3 | −857 | −71 | −479 |
| 1,2,3,7,8,9-HxCDD | 0.5 | 0.5 | 1.0 | 1.4 | 0.3 | 1.7 | −610 | −37 | −318 |
| 1,2,3,4,6,7,8-HpCDD | 3.8 | 4.6 | 8.4 | 12.0 | 2.6 | 14.6 | −719 | −46 | −352 |
| OCDD | 11.1 | 14.9 | 26.0 | 20.4 | 5.1 | 25.5 | −380 | 11 | −156 |
| 2,3,7,8-TeCDF | 0.6 | 0.4 | 1.0 | 0.8 | 0.1 | 1.0 | −265 | 27 | −141 |
| 1,2,3,7,8-PeCDF | 0.9 | 0.8 | 1.8 | 1.7 | 0.3 | 1.9 | −363 | 15 | −186 |
| 2,3,4,7,8-PeCDF | 1.8 | 1.7 | 3.6 | 3.7 | 0.7 | 4.5 | −429 | −11 | −226 |
| 1,2,3,4,7,8-HxCDF | 1.3 | 1.4 | 2.7 | 2.9 | 0.5 | 3.4 | −484 | 0 | −236 |
| 1,2,3,6,7,8-HxCDF | 1.5 | 2.0 | 3.6 | 3.4 | 0.8 | 4.2 | −470 | −3 | −205 |
| 1,2,3,7,8,9-HxCDF | 0.1 | 0.2 | 0.3 | 0.3 | 0.1 | 0.4 | −403 | −17 | −205 |
| 2,3,4,6,7,8-HxCDF | 3.7 | 3.8 | 7.5 | 5.9 | 1.6 | 7.5 | −320 | −8 | −161 |
| 1,2,3,4,6,7,8-HpCDF | 8.3 | 9.4 | 17.7 | 12.1 | 3.0 | 15.1 | −283 | 18 | −123 |
| 1,2,3,4,7,8,9-HpCDF | 1.2 | 1.6 | 2.7 | 1.8 | 0.6 | 2.4 | −312 | 1 | −131 |
| OCDF | 8.3 | 12.4 | 20.7 | 8.9 | 3.4 | 12.3 | −180 | 29 | −55 |
| Σ PCDDs | 17 | 21 | 39 | 39 | 9 | 47 | −491 | −6 | −221 |
| Σ PCDFs | 28 | 34 | 61 | 42 | 11 | 53 | −291 | 15 | −123 |
| Σ PCDDs + PCDFs | 45 | 55 | 100 | 80 | 20 | 100 | −367 | 7 | −161 |

Regarding scenario n°2 (1982–2005), integrating the effect of WS, only data from Takaoka et al. (2003) and once more, Chang et al. (2004), are considered applicable. The incinerators studied in these two papers closely match the Vallon MSWI concerning the three criteria of interest, including chlorine content, the presence of APCDs, and operating conditions. The incinerators investigated by Takaoka et al. (2003) consist of two MSWIs (named MSWI-A and MSWI-B) commissioned respectively in 1980 and

1985, which covers the period of operation of the Vallon. In addition, MSWI-A and MSWI-B are only equipped with an ESP before the WS, exactly as at Vallon. It should be noted that MSWI-A differs from MSWI-B in several respects regarding WS. The scrubbing water circulation rate in MSWI-A is higher, and the salt concentrations in the scrubbing water are maintained at 3% and 8% in MSWI-A and in MSWI-B respectively.

When considering WS treatment, two notable effects on PCDD/F profiles become apparent. Firstly, there is a substantial decrease (65%) in congener distribution within the gas phase during wet scrubbing, primarily attributed to congener condensation resulting from the temperature decrease across the WS. Secondly, the efficiency of WS improves with lower congener chlorination and for PCDDs. This is likely because these compounds, characterized by higher vapor pressure, are more prevalent in the gas phase before treatment, making them more susceptible to removal by the WS process. Additionally, less chlorinated compounds may potentially exhibit higher solubility and reactivity with the scrubbing solution.

Figure 3 and Table S12 from Supplementary information summarize the PCDD/Fs congener profiles for the total phase (gas + particulate) before ESP, after ESP (scenario n°1), and after WS (scenario n°2) as estimated for the Vallon MSWI. The scenario n°1, after ESP, is estimated to be the situation at stack between 1958 and 1982, and scenario n°2, after WS, is estimated to be the situation at stack between 1982 and 2005.

## 3.3 PCDD/Fs Emission Quantity

The total quantity of the 17 PCDD/Fs congeners generated in the furnace is shown in Fig. 4. A description of the input parameters used in the simulation is provided in Emission Quantity Model in Supplementary Information. The simulation with the kinetic model was performed for the congener OCDF. To obtain the total emission quantity, the amount of OCDF generated in the furnace was then divided by a factor of 20.7%, which represents its estimated weight fraction in the total PCDD/Fs (see section 3.2). The congener was selected because of its relatively large share in the congener profile, and it is thus less prone to uncertainty in the profile estimation.

The effect of APCDs on the flue gas concentration of PCDD/Fs was considered in the aforementioned two scenarios: n°1 with ESP alone (1958–1982) and n°2 with ESP and WS (1982–2005). The temperature window in the ESP is favorable for PCDD/Fs formation, leading to an estimated removal efficiency of − 161% (Table 2). For a discussion of the mass balance scheme in the wet scrubber, please refer to Vallon Wet Scrubber Mass Balance in Supplementary Information.

Current knowledge of Vallon WS does not allow a precise estimate of its removal efficiency on PCCD/Fs. However, two sources provide valuable information. First, an article by Ruegg and Sigg from their time at Von Roll suggests a very low efficiency for elementary wet scrubbers using a mechanism similar to Vallon's, citing the low solubility of PCDD/Fs in water (Ruegg and Sigg 1992). In addition, Ruegg and Sigg's article proposes improvement methods to achieve 50% efficiency with the WS system, suggesting that the efficiency of elementary WS is significantly lower. Secondly, a report by Moll-François et al. (2024) mentions two measurements carried out in 2001 at the Vidy WWTP, Lausanne, using a LAB wet scrubber without denitrification. The measurements showed positive (75%) and then negative (– 44%) efficiencies for PCDD/Fs. The average, although not meaningful with only two measurements, is 15%. It is important to note here that extrapolating the results of the Vidy WWTP to the context of the Vallon MSWI is not straightforward, given the significant differences in technical and operational parameters. For example, the Vidy plant only burns sewage sludge, unlike the Vallon one.

Nevertheless, in view of this limited knowledge, PCDD/F emissions from the stack are estimated for two scenarios, representing the lower and upper limits of a reasonable efficiency range: (1) assuming a 0% WS removal efficiency; and (2) assuming a 40% WS removal efficiency. It should be emphasized, however, that this 0 – 40% range is only a modeling scenario derived from a limited set of observations and assertions, and does not fully reflect the reality of the Vallon MSWI context. Vallon could well have experienced higher WS efficiencies, or even negative efficiencies.

Figure 4 shows the estimated annual PCDD/Fs production in the furnace and emission at the stack of the Vallon MSWI over the entire operating period. The generated amount in the furnace demonstrated a rapid increase during the first 10 years of operation, mostly due to the rise in annual incinerated waste amount. It then gradually decreased during 1970–1990, corresponding to the decline in incinerated waste amount and metal content, and followed by a gradual increase from 1990 to 2005 that can be attributed to the increase in chlorine and metal content. On the other hand, the installation of WS in 1982 could have resulted in a sharp drop in stack emission. Still, there exists large uncertainty with the mass balance of PCDD/Fs in the WS that requires further research.

## 3.4 Validation Analysis

The model-derived estimates for the Vallon case are here compared to actual measurements in order to validate the proposed methodology. Three validations methods are used:

1. The first validation method involves comparing the congener distribution in the particulate phase at the electrostatic precipitators (ESP) predicted by the model for the Vallon MSWI with that measured at the Vallon MSWI in 1996. It is important to note that the measurements were taken in the wash water of the ESP’s ash, not in exhaust gas samples.
2. The second, more advanced validation method begins by calculating the Vallon annual emission amounts of each congener based on the emission profile and quantity model. Subsequently, the results are integrated over time up to 2022, considering the degradation of congeners in soil according to their half-lives. A prior correction for soil sorption phenomena is applied. The resulting residual soil profile is then compared to a reference soil profile, calculated from the weighted average of soil measurements conducted in the Lausanne region in 2021–2022.
3. The third validation method consists of comparing the residual amount of PCDD/Fs present in Lausanne soil in 2022, as derived from the profile and quantity model and from the spatial interpolation of the 2021–2022 soil measurements.

The detailed descriptions of the three methods, along with their corresponding results, can be found in Validation Analysis in Supplementary Information (Fig. S3-S5). Collectively, these three validation approaches tend to support the legitimacy of the proposed methodology. Notably, the observed congener profiles in Lausanne align with the modeled profiles (see Fig. 5).

Additionally, the quantity of PCDD/Fs derived from measurements in Lausanne (425 $\text{gTEQ}_{\text{WHO-2022}}$ or 371 $\text{gTEQ}_{\text{WHO-2005}}$) falls within a similar range as the modeled levels (1,283–1,698 $\text{gTEQ}_{\text{WHO-2022}}$ or 1,115-1,419 $\text{gTEQ}_{\text{WHO-2005}}$). It should be noted that a significant overestimation of the quantity derived by the model was expected, primarily due to the assumption in the validation analysis that all emitted PCDD/Fs have settled on the ground and remained within the boundaries of Lausanne (see Validation Analysis in Supplementary Information).

# 4. Limitations of the Approach

Overall, the proposed emission profile and quantity model provides a tool for estimating the magnitude and time evolution of PCDD/F emission at the stack of a MSWI of interest. In the Vallon MSWI case, the model is, however, not without limitations due to data unavailability and simplifications. Literature data used for examining the effects of ESP and WS on PCDD/F emissions and congener distribution is selected based on the similarity to the configuration of the studied incinerator, but the difference in operating conditions necessitates adjustments. The corrections made to the available literature data are limited to accounting for temperature effects on phase partitioning of PCDD/Fs, while the temperature dependence of other parameters such as de novo synthesis rate and the effect of other factors including residence times, dust concentration and ESP electric field strength are not considered. Additionally, the validation analysis of the model is simplified to considering only the atmospheric deposition and half-lives in soil of the PCDD/F congeners. Half-life data is extracted from studies on paddy soil and sludge-amended soil, as these are the only available literature data; however, their applicability to the studied site is constrained by the potentially different soil properties, including pH, redox condition, and texture. Due to the overall uncertainty level inherent in various parameters arising from both the modeling and validation processes, the proposed methodology should undergo more robust validations in the future.

# 5. Conclusion

A two-step model based on congener profile and emission quantity of PCDD/Fs at a MSWI is proposed in this study. The validation case study yielded a good agreement between measurements and modeling results for the Vallon MSWI in Switzerland. As a future work, the model can be advanced by including additional processes and factors. For example, methods can be developed to model the influence of different APCD systems on PCDD/F emission, taking into account the operational parameters of these systems. This would facilitate a case-specific understanding of how APCD characteristics influence PCDD/F emissions and allow for their integration into the model framework. As the model complexity increases, the importance of establishing an inventory of PCDD/F monitoring data becomes evident. The database should comprise incineration systems with diverse configurations, waste compositions, and operating conditions. This comprehensive database would enable various applications, such as identifying congener distribution patterns for typical waste compositions and estimating the magnitude of emission quantities associated with different APCD systems. Overall, the developed model provides a useful analysis tool on the PCDD/F emission history at MSWIs and can assist in the evaluation of human exposure and health effects.

# Declarations

**Ethical approval** No human or animal trials were involved in this study.

**Consent to participate** Not applicable.

**Consent to publish** All authors have read, understood, and have complied as applicable with the statement on “Ethical responsibilities of Authors” as found in the Instructions for Authors

**Author Contributions** X. Zhang: methodology, formal analysis, software, writing the original draft. A. de Aragao: methodology, formal analysis, software, writing the original draft. F. Moll-François: supervision, acquisition of archival data. A. Berthet: supervision, review and editing the manuscript. F. Breider: supervision, review and editing the manuscript. All authors contributed to the study conception and design, commented on previous versions of the manuscript, and approved the final manuscript. X. Zhang and A. de Aragao are equal contributors to this work and designated as co-first authors

**Funding** This work was supported by the CROSS program 2023 funded by EPFL and the University of Lausanne (UNIL)

**Competing Interests** The authors have no competing interests to declare that are relevant to any material discussed in this article.

# References

1. Altwicker ER, Schonberg JS, Konduri RKNV, Milligan MS (1990) Polychlorinated dioxin/furan formation in incinerators. Hazard Waste Hazard Mater 7:73–87. https://doi.org/10.1089/hwm.1990.7.73
2. Chang MB, Chi KH, Chang-Chien GP (2004) Evaluation of PCDD/F congener distributions in MWI flue gas treated with SCR catalysts. Chemosphere 55:1457–1467. https://doi.org/10.1016/j.chemosphere.2004.01.005
3. Desbaumes P, Imhoff C (1971) Determination of the dust content of flue gases in incineration plants. Bull de l’Association Romande pour la Prot des Eaux et de l’Air (ARPEA) 44:46–55 (in French)
4. DeVito M, Bokkers B, van Duursen MBM et al (2024) The 2022 world health organization reevaluation of human and mammalian toxic equivalency factors for polychlorinated dioxins, dibenzofurans and biphenyls. Regul Toxicol Pharmacol 146:105525. https://doi.org/10.1016/j.yrtph.2023.105525

5. Fiedler H (2016) Release inventories of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans. In: Alaee M (ed) Dioxin and Related Compounds: Special Volume in Honor of Otto Hutzinger. Springer International Publishing
6. Huang H, Buekens A (2001) Chemical kinetic modeling of de novo synthesis of PCDD/F in municipal waste incinerators. Chemosphere 44:1505–1510. https://doi.org/10.1016/S0045-6535(00)00365-9
7. Kanan S, Samara F (2018) Dioxins and furans: A review from chemical and environmental perspectives. Trends Environ Anal Chem 17:1–13. https://doi.org/10.1016/j.teac.2017.12.001
8. Koehler A, Peyer F, Salzmann C, Saner D (2011) Probabilistic and technology-specific modeling of emissions from municipal solid-waste incineration. Environ Sci Technol 45:3487–3495. https://doi.org/10.1021/es1021763
9. Li X, Ma Y, Zhang M et al (2019) Study on the relationship between waste classification, combustion condition and dioxin emission from waste incineration. Waste Dispos Sustain Energy 1:91–98. https://doi.org/10.1007/s42768-019-00009-9
10. Lin X, Ma Y, Chen Z et al (2020) Effect of different air pollution control devices on the gas/solid-phase distribution of PCDD/F in a full-scale municipal solid waste incinerator. Environ Pollut 265:114888. https://doi.org/10.1016/j.envpol.2020.114888
11. Liu F, Liu H-Q, Wei G-X et al (2018) Characteristics and treatment methods of medical waste incinerator fly ash: A review. Processes 6:173. https://doi.org/10.3390/pr6100173
12. McKay G (2002) Dioxin characterisation, formation and minimisation during municipal solid waste (MSW) incineration: review. Chem Eng J 86:343–368. https://doi.org/10.1016/S1385-8947(01)00228-5
13. Moll-François F, Mavrot C, Elsig A et al (2024) The oldest factory in the world. Socio-history of the Vallon incinerator (1958–2005), CROSS research report (in French). https://serval.unil.ch/resource/serval:BIB_665BEA79DE6A.P001/REF. Accessed 14 April 2024
14. Oh J-E, Lee K-T, Lee J-W, Chang Y-S (1999) The evaluation of PCDD/Fs from various Korean incinerators. Chemosphere 38:2097–2108. https://doi.org/10.1016/S0045-6535(98)00419-6
15. Palmer D, Pou JO, Díaz-Ferrero J et al (2021) Kinetics of the formation and destruction of PCDD/Fs in a laboratory tubular furnace. Chemosphere 276:130175. https://doi.org/10.1016/j.chemosphere.2021.130175
16. Ruegg H, Sigg A (1992) Dioxin removal in a wet scrubber and dry particulate remover. Chemosphere 25:143–148. https://doi.org/10.1016/0045-6535(92)90499-H
17. Seike N, Kashiwagi N, Otani T (2007) PCDD/F contamination over time in Japanese paddy soils. Environ Sci Technol 41:2210–2215. https://doi.org/10.1021/es062318i
18. Shaub WM, Tsang W (1983) Dioxin formation in incinerators. Environ Sci Technol 17:721–730. https://doi.org/10.1021/es00118a007
19. Stanmore BR (2002) Modeling the formation of PCDD/F in solid waste incinerators. Chemosphere 47:565–573. https://doi.org/10.1016/S0045-6535(02)00005-X

20. Swiss Federal Office for the Environment (SAEFL) (2003) Analysis of the composition of waste 2001/02. 356:67Environmental Series
21. Takaoka M, Liao P, Takeda N et al (2003) The behavior of PCDD/Fs, PCBs, chlorobenzenes and chlorophenols in wet scrubbing system of municipal solid waste incinerator. Chemosphere 53:153–161. https://doi.org/10.1016/S0045-6535(03)00437-5
22. Tejima H, Nishigaki M, Fujita Y et al (2007) Characteristics of dioxin emissions at startup and shutdown of MSW incinerators. Chemosphere 66:1123–1130. https://doi.org/10.1016/j.chemosphere.2006.06.015
23. Themelis NJ (2010) Chlorine sources, sinks, and impacts in WTE power plants. In: North American Waste-to-Energy Conference. American Society of Mechanical Engineers Digital Collection, pp 77–84. https://doi.org/10.1115/NAWTEC18-3577
24. van den Berg M, Birnbaum L, Bosveld ATC et al (1998) Toxic equivalency factors (TEFs) for PCBs, PCDDs, PCDFs for humans and wildlife. Environ Health Perspect 106:775–792. https://doi.org/10.1289/ehp.98106775
25. van den Berg M, Birnbaum LS, Denison M et al (2006) The 2005 World Health Organization re-evaluation of human and mammalian toxic equivalency factors for dioxins and dioxin-like compounds. Toxicol Sci 93:223–241. https://doi.org/10.1093/toxsci/kfl055
26. Vernez D, Oltramare C, Sauvaget B et al (2023) Polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) soil contamination in Lausanne, Switzerland: Combining pollution mapping and human exposure assessment for targeted risk management. Environ Pollut 316:120441. https://doi.org/10.1016/j.envpol.2022.120441
27. Voelgyi G (1985) Thermal recovery of municipal waste and flue gas treatment at the Lausanne household waste incineration plant. VDI Berichte, 204–222 (in French)
28. Wang L, Lee W, Lee W et al (2003) Effect of chlorine content in feeding wastes of incineration on the emission of polychlorinated dibenzo-*p*-dioxins/dibenzofurans. Sci Total Environ 302:185–198. https://doi.org/10.1016/S0048-9697(02)00306-6
29. Wang P, Yan F, Cai J et al (2022) Emission levels and phase distributions of PCDD/Fs in a full-scale municipal solid waste incinerator: The impact of wet scrubber system. J Clean Prod 337:130468. https://doi.org/10.1016/j.jclepro.2022.130468
30. Zhang H-J, Ni Y-W, Chen J-P, Zhang Q (2008) Influence of variation in the operating conditions on PCDD/F distribution in a full-scale MSW incinerator. Chemosphere 70:721–730. https://doi.org/10.1016/j.chemosphere.2007.06.054

# Figures

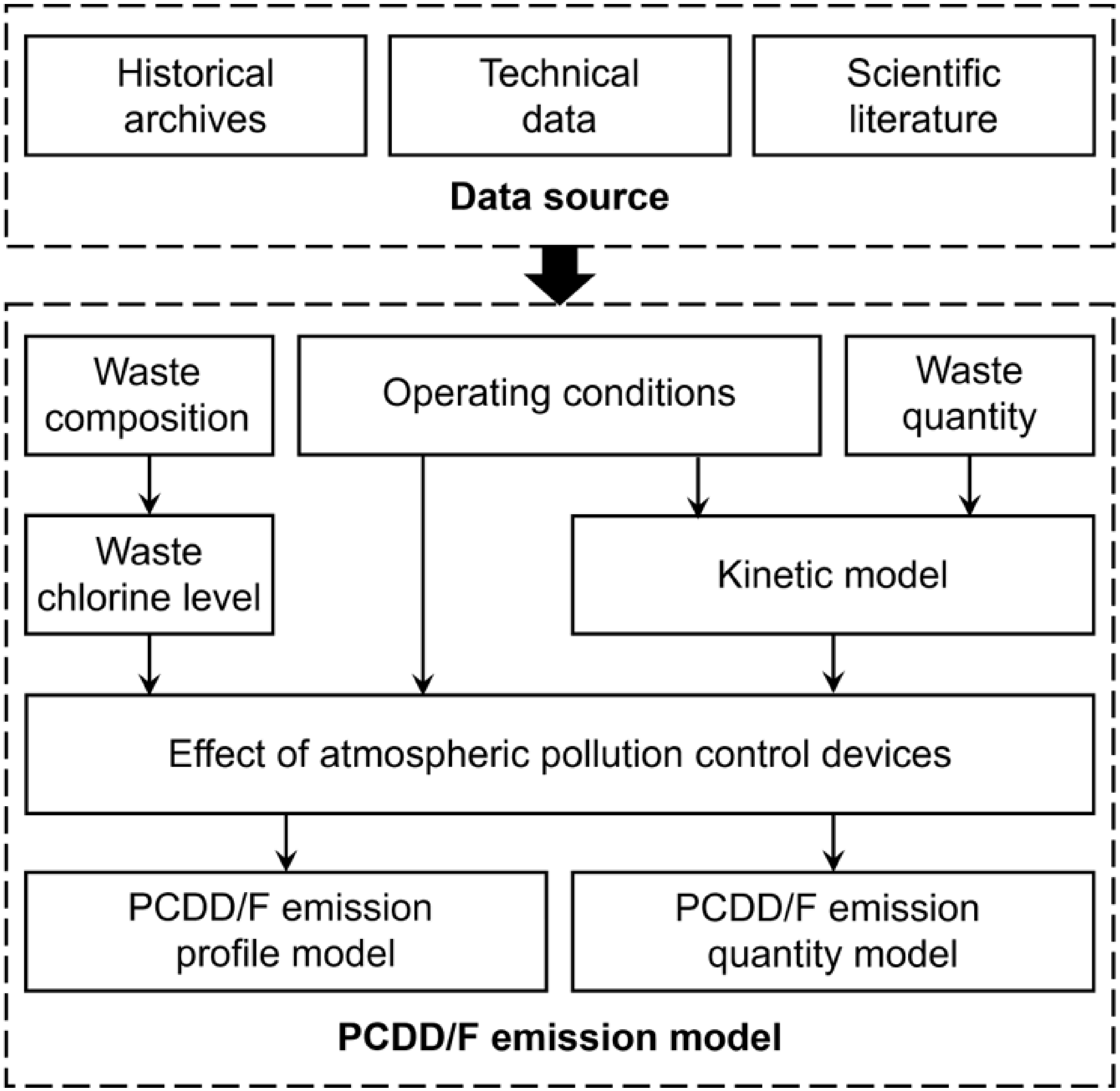

**Figure 1**

Model framework for PCDD/Fs congener profile and emission quantity at a MSWI stack

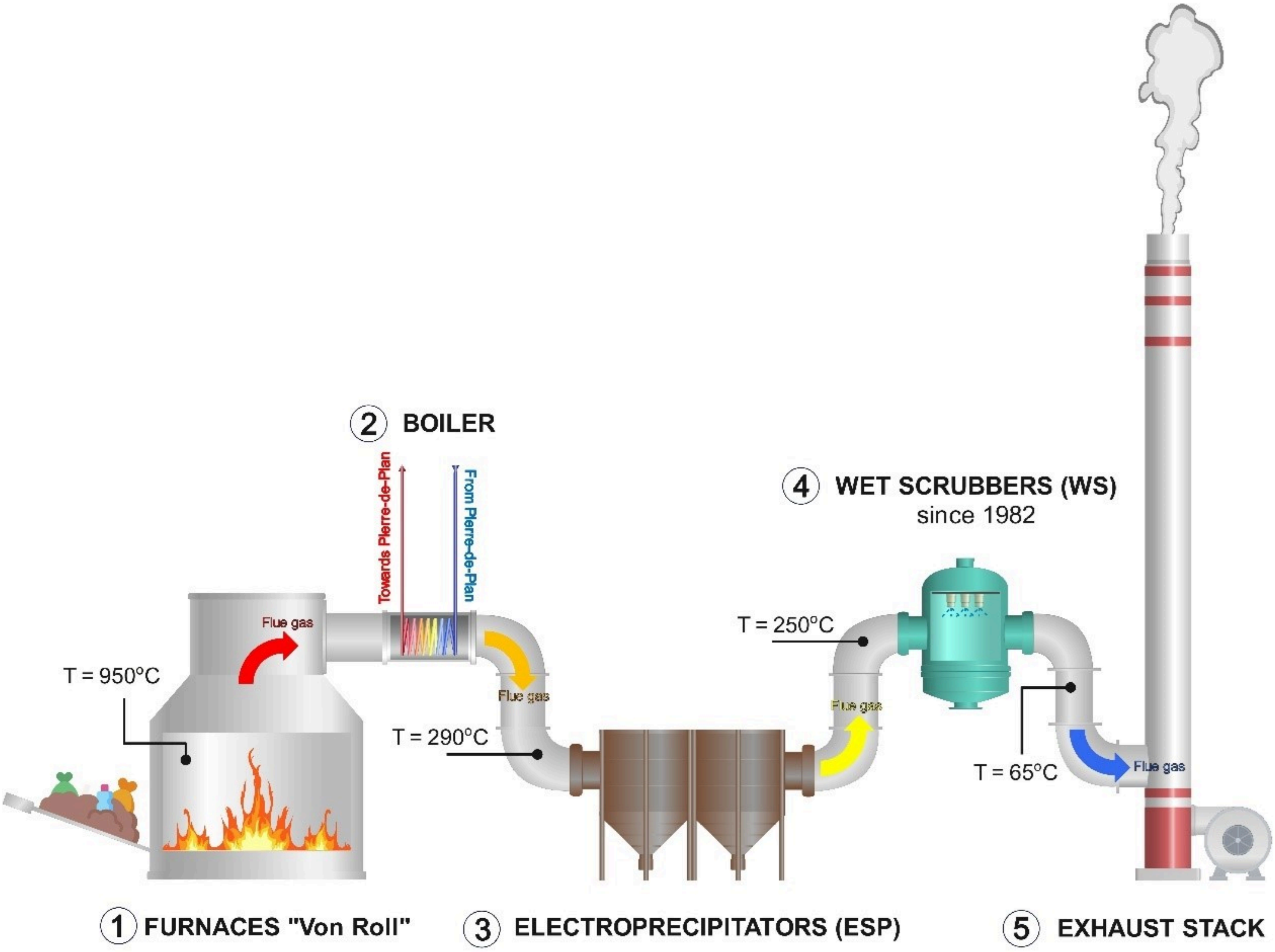

Figure 2

Main technical and operational aspects of the Vallon MSWI

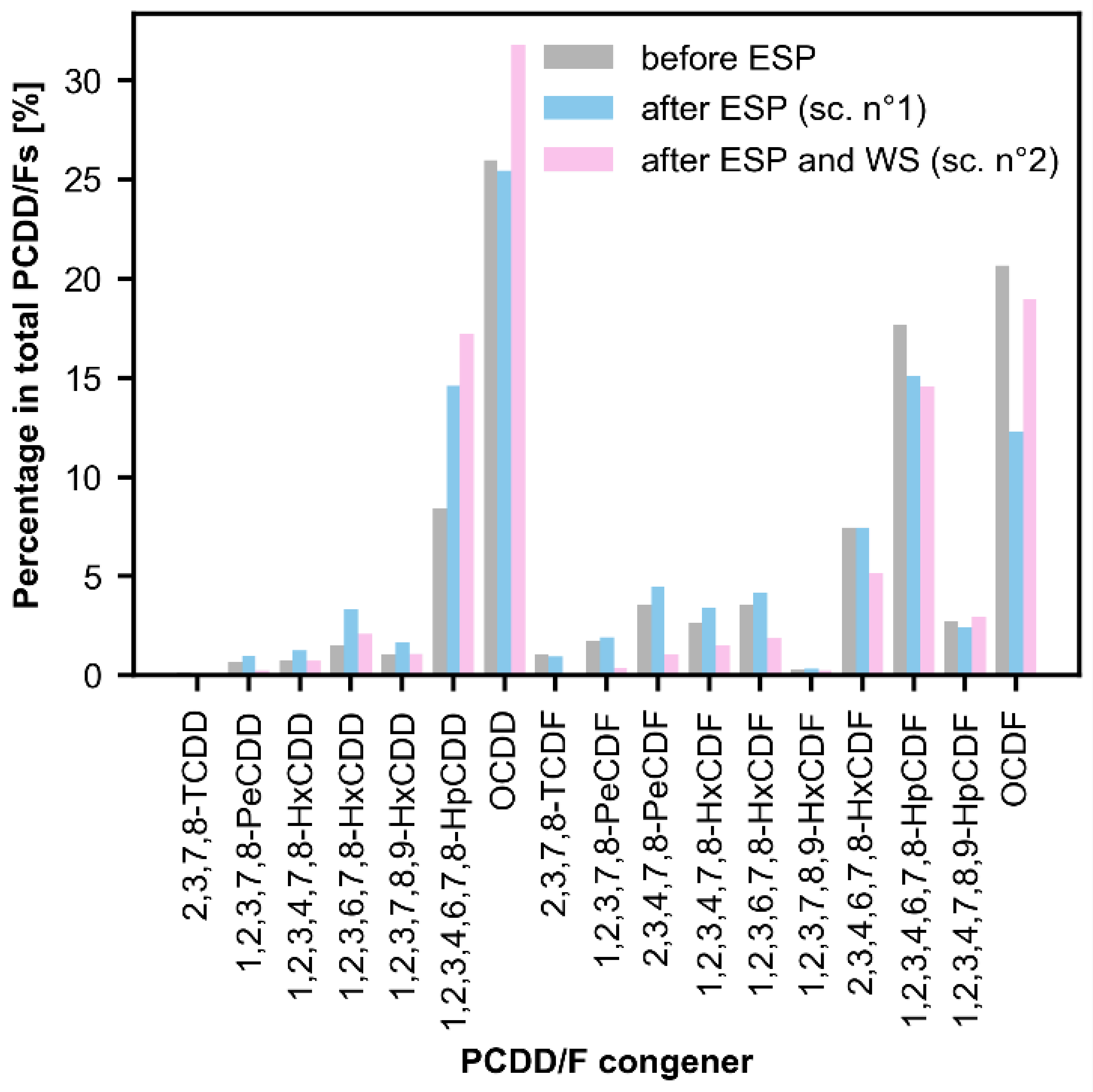

**Figure 3**

PCDD/Fs total (gaseous + particulate) congener profile before ESP (gray bars), after ESP (scenario n°1, blue bars), and after ESP and WS (scenario n°2, pink bars), as estimated for the Vallon MSWI

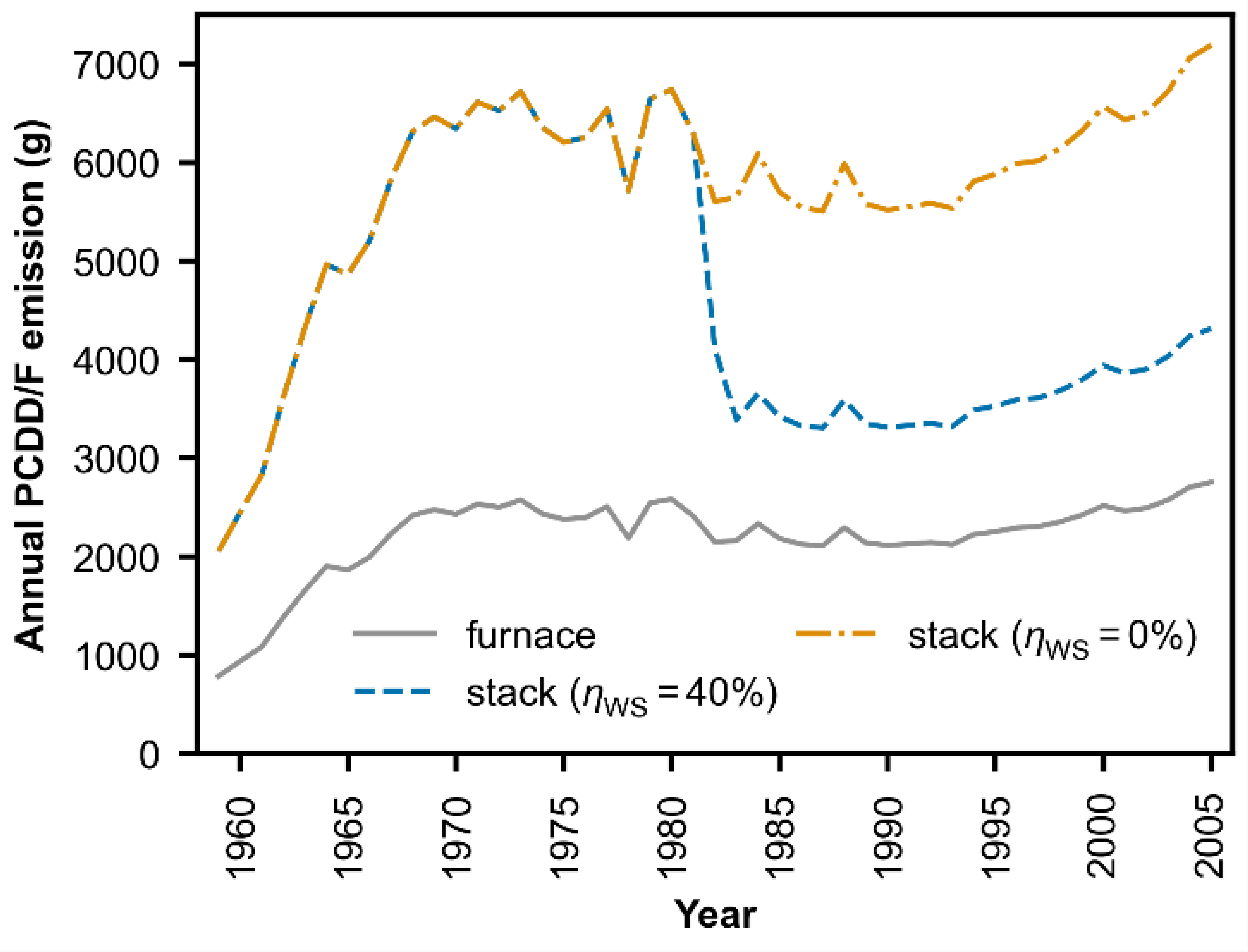

**Figure 4**

Estimated annual production of PCDD/Fs in the furnace and emission at the stack of Vallon MSWI over the period 1958–2005, with two cases of WS removal efficiency ($\eta_{WS}$)

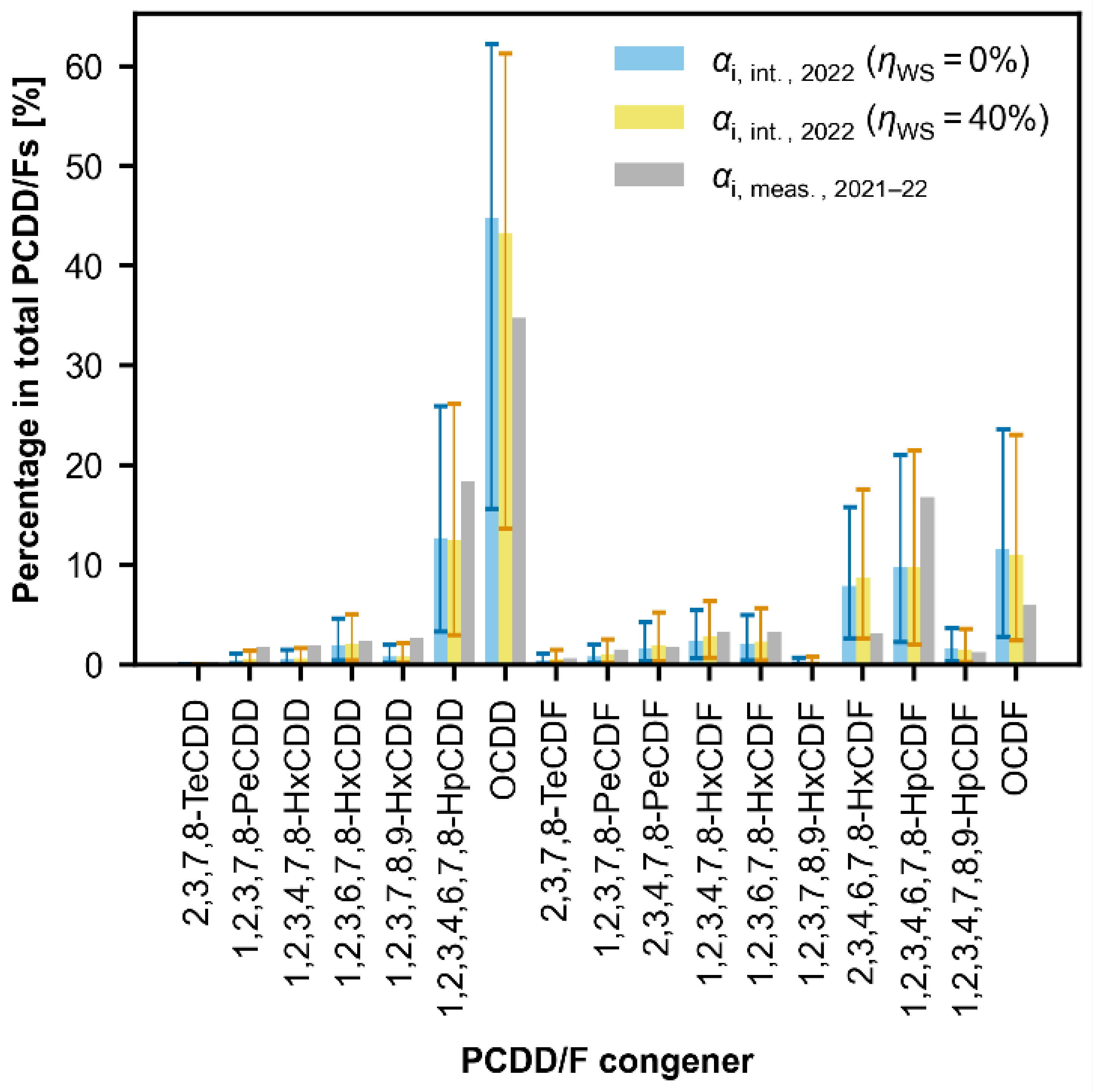

**Figure 5**

Model-derived soil profile in 2022 (blue and yellow bars) and measurement-derived soil profile in 2021–2022 (gray bars) for the Vallon MSWI pollution case. Soil profile simulated for two WS efficiency scenarios on PCDD/Fs total emissions (($\eta_{WS}$= 0%, blue bars and = 40%, yellow bars). Indicative uncertainty bars correspond to the 2.5% and 97.5% quantiles of the fractions obtained by simulations (*n* = 1,000,000) with random sampling on the PCDD/Fs congener’s soil half-life range from −50% to +100% of the reference half-life value