

Ambient Air Measurement of PCDD/Fs Impacted by Wood Combustion in Germany

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1 Introduction

In Germany, residential wood combustion accounts for approximately 8 % of the emission of particulate matter < 10 μ m (PM₁₀) in the year 2019 (Kessinger et al., 2020). In addition to PM₁₀, other organic pollutants like polychlorinated dibenzodioxins and -furans (PCDD/F) are formed as byproducts. PCDD/F-patterns or profiles are often used to get indications for certain PCDD/F-sources. While PCDD/F-patterns exist for European ambient air monitoring stations (e.g. Kirchner 2020, Dreyer 2021, Piazzalunga 2013) and several industrial or combustion processes, a typical profile for residential wood combustion is not known. Quass et al. (2016) evaluated PCDD/Fs in ambient air and in emission data by multivariate statistical analyses, among others positive matrix factorization (PMF), but a typical PCDD/F-profile for residential wood combustion could not be defined. Knowing about the limited value of test bench measurements due to the large variety of fuels and combustion conditions, Quass et al. (2016) suggested ambient air concentrations measured under strong domestic combustion influence to extract a typical PCDD/F-profile for residential wood combustion. Therefore, in this study PCDD/Fs were investigated in a German region characterized by a high impact of residential wood combustion. This included the analysis of the 2,3,7,8-substituted congeners as well as the tetra- to octachloro PCDD/F homologue group totals. Statistical analysis was used to identify a reference profile for PCDD/F concentrations enabling future source apportionment of ambient air PCDD/F concentrations.

2 Materials and Methods

Study area and measurement sites: With the help of a study on small-scale furnaces in households of the Free State of Saxony (Poppitz, 2019) the city Thalheim/Erzgebirge was chosen as study area. Thalheim/Erzgeb. consists of about 6.000 inhabitants and is situated at around 450 m a.s.l. in the Ore Mountains in Saxony. It is characterized by a high density and high number of small-scale furnaces in households (> 900, approx. 80 % of the total) with a simultaneous low density and low number of other small-scale furnaces in households (approx. 20 %) and was assumed to be not significantly influenced by industrial point sources. Two sites with assumable potentially different PCDD/F profiles were chosen. As the focus was on the profiles, concentrations itself only played a minor role in these considerations. Measurement point 1 (MP 1), located in the center of Thalheim/Erzgeb., should represent a location with large influence of residential wood combustion. Measurement point 2 (MP 2), located in a distance of about 2 km in the vicinity of a waste water treatment plant, should represent a location with less impact of residential wood combustion, but an additional influence on the PCDD/F profile due to a waste water treatment plant.

Target analytes: Main target analytes were the seventeen 2,3,7,8-substituted PCDD/F congeners and the homologue group totals (tetra-PCDD/F to hepta-PCDD/F). To get information on the influence of residential wood combustion at the measurement sites, specific wood combustion parameters were measured as well: PM₁₀, elemental carbon (EC) in PM₁₀, organic carbon (OC) in PM₁₀, equivalent Black carbon (eBC) in PM₁₀, anhydrosaccharides (levoglucosan, mannosan and galactosan) in PM₁₀ and polycyclic aromatic compounds (PAHs, 16 EPA-PAHs plus retene). In addition, meteorological parameters (temperature, wind speed, and wind direction) were measured at MP 2 and partly, when not available, taken from the German Weather Service (DWD).
Temporal resolution of the measurements: Under the assumption of increased wood burning activity over the weekend, 33 ambient air samples at each site were taken from Fridays 3:00 p.m. to Mondays 3:00 a.m. between October 2018 to April 2019. This temporal resolution was taken as a compromise between PCDD/F-detectability against the background of blank values and methodological quantification limits (MQLs) as well as a meteorological variance being as low as possible. In addition to the short-term sampling on weekends, PCDD/F were also determined as monthly averages (7 monthly values from 10/2017 to 04/2018).

Sampling and analytical methods: PCDD/F air sampling was conducted by high volume air samplers (weekends) resp. low volume air samplers (monthly averages) on the basis of a German standard on sampling and analyses. Air samples were collected using binder-free glass fiber filters and a cartridge containing polyurethane foam. Separation and detection of target analytes occurred by high resolution gas chromatography coupled to high resolution mass

spectrometry. The wood combustion parameters were sampled over the same time (weekends, 60 hours) according to national and international standards: PM10 (low volume sampling - DIN EN 12341 (2014-08), Gravimetry), EC and OC in PM10 (low volume sampling - DIN EN 12341 (2014-08), thermo-optical measurement DIN EN 16909 2017-06, EUSAAR-2, Sunset Laboratory), eBC in PM10 (low volume sampling - DIN EN 12341 (2014-08), attenuation at wave lengths 370 and 880 nm, Magee Scientific OT21), anhydrosaccharides (low volume sampling - DIN EN 12341 (2014-08), ion chromatography with amperometric detection, VDI 2444 (2020-03)), and PAH (high volume sampling, DIN ISO 12884 (2000-12), high resolution gas chromatography coupled to high resolution mass spectrometry).

3 Results

The averaged values of PCDD/F and wood combustion related parameters at both measurement sites are presented in Table 1. Slightly higher PCDD/F concentrations were measured at MP 2. The detection of the wood burning tracers in each sample suggests a general influence of wood combustion implying a high, but not an extremely high level. The wood tracer compounds have a very similar time course at both sites, with concentrations being similar. A difference t-test – applied separately for each wood combustion tracer and PM10 – showed that the data from both sites were not significantly different ($p < 0.01$). TEQ-values in the short-term samples ranged from about 2 to 71 fg WHO₂₀₀₅-TEQ/m³. Particularly at times of lower temperature, PCDD/F-TEQ-concentration peaks occurred in parallel at both measurement points. At these time points, wood combustion tracer concentrations were also elevated. Significantly higher TEQ-values of approximately 64 and 147 fg WHO₂₀₀₅-TEQ/m³ were obtained on April 30th (sampling time 24-hours only, values not included in mean values in Table 1), which is a special date because traditionally at the evening before May 1st large outdoor fires (“Hexenfeuer”) are burned.

Table 1: Measurement results in ambient air at both measurement points

compound	unit	MP 1	MP 2	averaging time
PCDD/F	fg WHO ₂₀₀₅ -TEQ/m ³	10.7	14.0	mean value of 7 monthly averages (10/2018 – 04/2019)
Σ 2,3,7,8-PCDD/F	fg/m ³	271	298	
Σ PCDD/F-homologue groups (tetra-octa)	fg/m ³	705	884	
PCDD/F	fg WHO ₂₀₀₅ -TEQ/m ³	8	17	mean value of 33 weekend averages (10/2018 – 04/2019)
Σ 2,3,7,8-PCDD/F	fg/m ³	208	324	
Σ PCDD/F-homologue groups (tetra-octa)	fg/m ³	580	1100	
Particulate matter (PM10)	μg/m ³	12.8	12.6	mean value of 33 weekend averages (10/2018 – 04/2019)
Elemental carbon (EC) in PM10	μg/m ³	0.6	0.5	
Organic carbon (OC) in PM10	μg/m ³	3.3	3.0	
Equiv. Black carbon (eBC) in PM10	μg/m ³	0.7	0.7	
Levogluconan in PM10	μg/m ³	0.22	0.24	
Mannosan in PM10	μg/m ³	0.04	0.05	
Galactosan in PM10	μg/m ³	0.01	0.02	
Benzo[a]pyrene in PM10	ng/m ³	0.8	1.0	

The mean values obtained from the congener and homologue group sum profiles were also similar at both sites (Figure 1a). The statistical analysis included so called mass closure profiles (MSP), where the homologue group sum profile is calculated based on so-called reduced (delta (D)-) homologue group sums. For this purpose, the 2,3,7,8-PCDD/F congeners, measured separately as individual substances, are subtracted in the respective formation of the homologue group sums in order to ensure the statistical independence of the homologue group sums from the congeners (Ocd and Ocf were excluded). The mean congener profiles are characterized by high mean congener fractions for octachlorodibenzodioxin (MP 1: approx. 45 %; MP 2: approx. 41 %) followed by 1,2,3,4,6,7,8-heptachlorodibenzodioxin (MP 1: approx. 18 %; MP 2: approx. 17 %), 1,2,3,4,6,7,8-heptachlorodibenzofuran (MP 1: approx. 7 %; MP 2: approx. 8 %) and octachlorodibenzofuran (each approx. 4.5 %), and 2,3,7,8-tetrachlorodibenzofuran (each approx. 5 %). For the mean homologue group sum profiles, highest values were observed for tetrachlorodibenzofurans (each about 32 %), followed by octachlorodibenzodioxin (MP 1: about 16 %; MP 2: about 13 %), pentachlorodibenzofurans (MP 1: about 13 %; MP 2: about 15 %), and heptachlorodibenzodioxins (MP 1: about 11 %; MP 2: about 10 %). Congener and homologue group profiles were very similar to the profiles of the monthly samples. The direct comparison of the profiles of the two measuring points showed no significant differences with mean Aitchison distances between 0.10 and 0.11. This means that a separation of the two measuring points with respect to their PCDD/F profiles was statistically not possible. Thus, the original measurement strategy

of extracting a PCDD/F profile for wood combustion by statistical analysis of two different measurement points (MP 1 – wood combustion hotspot and MP 2 – characterized by further source processes) had to be discarded. Accordingly, the overall methodological concept of the statistical analyses was adapted, and the two measurement points were considered together to obtain statistically more reliable results.

By cluster analysis, a group of samples could be identified, which were simultaneously characterized by elevated levels of the wood combustion tracers levoglucosan, OC, EC, eBC, and benzo[a]pyrene. The mean PCDD/F profile of this cluster in comparison to the profile of the remaining samples showed significantly lower levels of lowly chlorinated congeners (2,3,7,8-tetrachlorodibenzodioxin: 0,2 % vs. 0,5 %, 2,3,7,8-tetrachlorodibenzofuran: 2,5 % vs. 6,5 %, 1,2,3,7,8-pentachlorodibenzofuran: 1,5 % vs. 2,9 %, and 2,3,4,7,8-pentachlorodibenzofuran: 3,0 % vs. 5,5 %) and significantly higher levels of highly chlorinated homologue group totals (octachlorodibenzodioxin: 24,7 % vs. 12,0 %, and octachlorodibenzofuran: 2,4 % vs. 1,2 %) (Figure 1b).

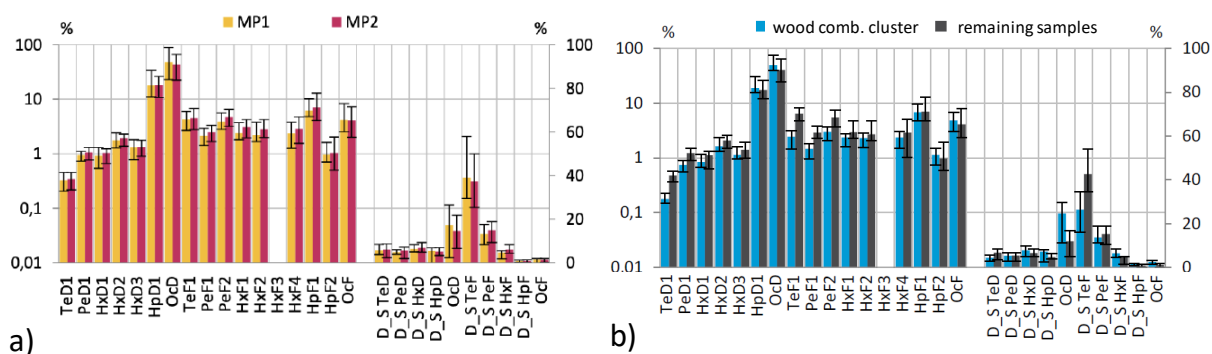


Figure 1: a) Comparison of the mass closure profiles of both measurement points in Thalheim/Erzgeb. (columns: mean values; black lines: 10th and 90th percentiles), b) Comparison between the wood combustion cluster to the average of the remaining samples identified by cluster analysis.

Positive Matrix Factorization (PMF) was able to extract two factors (Figure 2) whose PCDD/F profiles were significantly different from each other. The mean Aitchison distances of 0.78-0.90 demonstrate that the PCDD/F profiles of the two factors should be considered as being statistically dissimilar. Multivariate regression analysis revealed that factor 1 correlated primarily with benzo[a]pyrene and factor 2 correlated with the wood combustion tracer levoglucosan as well as with benzo[a]pyrene. We suggest that Factor 1 may represent a mixture of other sources. A comparison of both PCDD/F PMF-factor profiles revealed a good similarity between the PCDD/F profile of factor 2 and the average PCDD/F profile of the wood combustion cluster. In the congener profile, factor 1 showed significantly higher levels of 2,3,7,8-tetrachlorodibenzodioxin (0.7 % vs. 0.1 %), 2,3,7,8-tetrachlorodibenzofuran (10.3 % vs. 1.3 %), 1,2,3,7,8-pentachlorodibenzofuran (4.3 % vs. 1.3 %) and 2,3,4,7,8-pentachlorodibenzofuran (7.8 % vs. 2.9 %), and lower proportions of 1,2,3,4,7,8,9-heptachlorodibenzofuran (0.8 % vs. 1.4 %) and octachlorodibenzofuran (2.9 % vs. 5.4 %). For homologue group totals, the proportions are higher for factor 1 for D₋ sum of tetrachlorodibenzodioxins (7.8 % vs. 2.2 %) and D₋ sum tetrachlorodibenzofurans (49.7 % vs. 18.3 %) than for factor 2. The homologue group totals D₋ sum hexachlorodibenzofurans (0.4 % vs. 2.3 %) and octachlorodibenzodioxin (7.9 % vs. 23.8 %) are significantly lower in factor 1 than in factor 2.

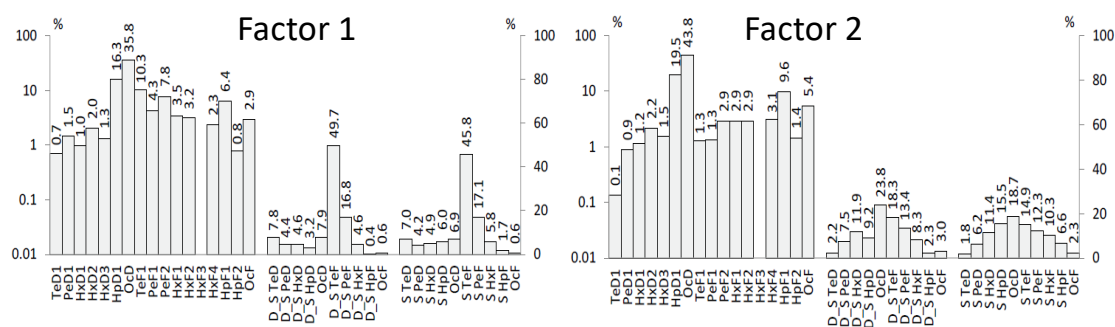


Figure 2: PCDD/F congener and homologue group profiles of factor 1 (left) and factor 2 (right) extracted by Positive Matrix Factorization (PMF).

4 Discussion

PCDD/F concentrations at both measurement points in Thalheim/Erzgeb. were higher than those of German or Alpine background stations (<5 fg WHO₂₀₀₅-TEQ/m³) (Kirchner et al. 2020, Dreyer 2021), but significantly lower than two measurement points in northern Italy (89 resp. 66 fg WHO₂₀₀₅-TEQ/m³) (Piazzalunga et al. 2013).

The overall PCDD/F profile of Thalheim/Erzgeb. is statistically very similar to the background PCDD/F profiles of Germany (UBA background monitoring stations Waldhof and Schmücke; mean Aitchison distances of 0.25 for the MCP). The PCDD/F profile of Factor 2, initially identified as wood-fired embossed, is still similar to the background profiles at the German background stations Waldhof and Schmücke (mean Aitchison distances of 0.40 - 0.62), but appears more dissimilar than the overall profile from Thalheim/Erzgeb. Differences between factor 2 and the background profiles are lower TeD1 and TeF1 proportions in the congener profile and Σ TeD and Σ TeF proportions in the HGSP, and higher proportions of the Σ PeD, Σ HeD, Σ HxF, and Σ HpF in factor 2 compared to the background profiles. A similar profile could be extracted by Quass et al. (2016) from the modeling of ambient air data of rural sites in Hesse (rural area, Hünfelden and Riedstadt, measurements until 2006). These modeled profiles also showed an increased OCDD content in winter, showing striking similarities to factor 2 profile in Thalheim/Erzgeb. (mean Aitchison distances of 0.31 - 0.41). Factor 1 and 2 profiles revealed no similarities to emission profiles measured at small-scale furnaces or other wood-burning facilities, confirming the diversity of published emission factors and profiles for wood combustion and thus the inapplicability of individual profiles to wood combustion studies. Since Thalheim/Erzgeb. should be clearly dominated by wood combustion, the observed similarity of PCDD/F profiles between Thalheim/Erzgeb. and the German background indicates that wood combustion in Thalheim/Erzgeb. either has no influence on PCDD/F patterns in the outdoor air (otherwise the profiles in Thalheim/Erzgeb. would have to differ from those of the background) or that wood combustion has such an extensive effect on the supra-regional background that the PCDD/F pattern of the background is determined by the wood combustion. Small combustion plants typically do not have flue gas cleaning, so the amount of small combustion plants could significantly influence a background profile. That domestic combustion has an impact on the PCDD/F contamination of the background is suggested by measurement series of the Waldhof and Schmücke monitoring stations, which show significantly higher PCDD/F concentrations in the winter months than in the summer months. If it is assumed that the PCDD/F profile in the background resulted predominantly from wood combustion, then the sample clusters and factors initially identified as characteristic of wood combustion must be interpreted in a more differentiated manner. Thus, the PCDD/F profiles of the individual factors could perhaps describe more specific types of wood burning, e.g., open fires (such as the Hexenfeuer, garden fire, forest fire), wood burning in small combustion plants, by-firing of chlorinated waste wood, or the like. In this case, the PCDD/F profile of PMF factor 1 would also describe a wood combustion, one that was influenced by emission events not presented by factor 2. Since factor 2 has a >70 % contribution in the Hexenfeuer-samples, factor 2 could show potential open fire influences on the PCDD/F profile. It is noticeable that factor 2 is significantly reduced in the fraction of tetrachlorodibenzofurans. In summary, it must be stated that although correlations and PCDD/F profiles were extractable by statistical methods in this project, the reliable identification of a typical profile for wood burning from small combustion plants remains unclear.

5 Conclusions

Although correlations and PCDD/F profiles were extractable by statistical methods, the reliable identification of a typical profile for residential wood combustion remains unclear. The observed similarity of PCDD/F profiles between Thalheim/Erzgeb. and the German background indicates that wood combustion in Thalheim/Erzgeb. either has no influence on PCDD/F patterns in ambient air or that wood combustion has such an extensive effect on the supra-regional background that the PCDD/F pattern of the background is determined by wood combustion. Additionally, different types of wood combustion like open fires or garden fires have an effect on the PCDD/F profiles. The impact of the potential source waste water treatment at MP 2 was too small to measurably influence the profile. In future studies, additionally measurement points could help to distinguish between sources.

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7 References

1. Dreyer, A. (2021): Polychlorierte Dibenzodioxine und -furane (PCDD/F) und polychlorierte Biphenyle (PCB) in der Außenluft und Deposition im ländlichen Hintergrund von Deutschland. In: Umweltbundesamt, Texte 75/2020, Dessau-Roßlau.
2. Kessinger, S., Minkos, A., Dauert, U., Feigenspan, S. (2021): Air Quality 2020, Preliminary Evaluation. In: Umweltbundesamt: German Environment Agency, Dessau-Roßlau, p. 22.

4. Kirchner, M., et al. (2020): Air concentrations and deposition of chlorinated dioxins and furans (PCDD/F) at three high alpine monitoring stations: Trends and dependence on air masses. In: *Atmospheric Environment*, 2020, 223.
5. Piazzalunga, A., et al. (2013): Contribution of wood combustion to PAH and PCDD/F concentrations in two urban sites in Northern Italy. In: *Journal of Aerosol Science*, 2013, 56, 30-40.
6. Poppitz, W., et al. (2019): Kleinf Feuerungsanlagen in Sachsen - Anlagenbestand und Emissionen von Kleinf Feuerungsanlagen in Sachsen. In: Sächsisches Landesamt für Umwelt, Landwirtschaft und Geologie (LfULG), Dresden.
7. Quass, U., Meyer, J., Kuhlbusch, T. (2016): Zuordnung und Quantifizierung der Dioxineinträge auf dem Luftpfad mittels Betrachtung der emissionsseitigen und immissionsseitigen Kongenerenmuster. In: Umweltbundesamt, Texte 23/2016, Dessau-Roßlau.