# COMPARISON OF DIOXINS AND RELATED COMPOUNDS IN THE EMISSION DURING THE START-UP PROCEDURES AT A MUNICIPAL WASTE INCINERATOR

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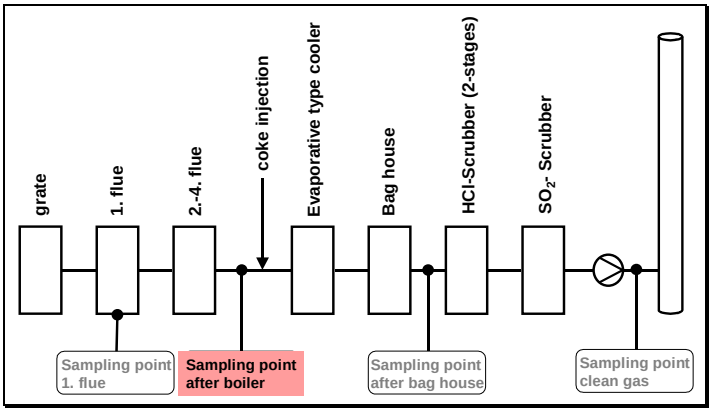
***Introduction***

In 2002/2003 we reported about PCDD/F-emissions during the start-up of a municipal waste incinerator[1]. With primary and secondary measures during the optimization of the cold start-up phase we could show a sustainable reduction of the stack gas emissions of PCDD/F down to the range of normal operation even in the start-up phase[2].
The measurement results of chlorophenols (ClP) and chlorobenzenes (ClB) in the flue gas (sampling point "after boiler", fig.1) during cold-start up procedure of selected campaigns will be discussed in this paper.

***Methods and Materials***

All measurements and sample-extractions were performed according to EN 1948 with the exception that the sampling time was shortened and adjusted to the different phases of the start-up procedure. After clean-up, ClB have been analysed with GC/MS using $^{13}$C-labeled ClB-standards added before extraction. The analytical procedure for ClP comprises alkaline extraction of the Soxhlet-extract, back-extraction of the ClP after derivatisation and GC/MS-analysis using $^{13}$C-labeled ClP-standards added before extraction. The detection limit was 1-10 ng/Nm³ for trichloro- to hexachlorobenzene and trichloro- to pentachlorophenol isomers. mono- and dichloro-congeners have not been investigated. All data are standardized to 273 K and 1013 hPa at 11 % $O_2$ . A detailed plant description can be found in[1].

**Figure 1: plant scheme and sampling locations**




***Results and Discussion***

In Table 1 the results of a total of 11 sampling phases, subdivided into burner start, drying phase, burner phase, waste feed and normal incineration conditions, from three measurement campaigns are summarized.

**Table 1: results of ClB, ClP and PCDD/PCDF**

| all results in [ng/Nm³] | run 3 | | | run 6 | | | run 7 | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 start oil burning | 2 oil burner | 3 begin waste feed | 1 start oil burning | 2 drying oil-burning with 1 burner | 3 oil-burning with 1 burner | 1 start oil burning | 2 hold-operation oil | 3 oil-burning with 2 burners | 4 start waste feed | 5 normal |
| **chlorobenzenes (ClB)** | | | | | | | | | | | |
| sum trichlorobenzenes | 3450 | 14000 | 6033 | 4663 | 44 | 3336 | 1612 | 567 | 979 | 13101 | 6024 |
| sum tetrachlorobenzenes | 5575 | 23078 | 15045 | 3534 | 30 | 2700 | 1514 | 454 | 808 | 5876 | 3585 |
| pentachlorobenzene | 5590 | 15690 | 13068 | 3753 | 40 | 2720 | 1287 | 465 | 920 | 4163 | 2883 |
| hexachlorobenzene (HCB) | 3290 | 5600 | 7586 | 4133 | 50 | 2590 | 2972 | 757 | 1390 | 3169 | 1985 |
| **Sum tri-hexaClB** | **17905** | **58368** | **41732** | **16083** | **164** | **11346** | **7384** | **2243** | **4097** | **26308** | **14476** |
| **chlorophenoles (ClP)** | | | | | | | | | | | |
| sum trichlorophenoles | 9200 | 18100 | 12350 | 46540 | 167 | 8728 | 5243 | 2818 | 1870 | 5743 | 7423 |
| sum tetrachlorophenoles | 1550 | 9800 | 11400 | 6781 | 43 | 3521 | 403 | 345 | 527 | 2619 | 4934 |
| pentachlorophenol (PCP) | 1530 | 7200 | 4330 | 6548 | 55 | 2441 | 390 | 326 | 635 | 1102 | 1980 |
| **sum tri-pentaClP** | **12280** | **35100** | **28080** | **59869** | **265** | **14690** | **6036** | **3489** | **3033** | **9463** | **14337** |
| **PCDD/PCDF** | | | | | | | | | | | |
| sum PCDD | 2515 | 4116 | 1885 | 860 | 11 | 367 | 79 | 69 | 84 | 364 | 573 |
| sum PCDF | 629 | 1329 | 1234 | 825 | 11 | 347 | 118 | 75 | 85 | 404 | 756 |
| total PCDD+PCDF | 3145 | 5445 | 3118 | 1686 | 21 | 715 | 197 | 144 | 169 | 769 | 1329 |
| **tox. equivalents I-TEQ** | **35.2** | **77.8** | **52.3** | **24.6** | **0.314** | **9.99** | **2.96** | **2.06** | **2.44** | **12.1** | **22.5** |

The level of tri- to pentachlorophenols (sum) and tri- to hexachlorobenzenes (sum) before optimization of the start-up procedure was 12.3–35.1 µg/Nm$^3$ and 17.9 – 58.4 µg/Nm$^3$ respectively. It was reduced to 3.0 – 14.7 µg/Nm$^3$ and 2.2 – 11.3 µg/Nm$^3$ respectively after optimization. These substances showed therewith a similar behavior as the PCDD/PCDF as reported by Gass et.al. [2] (Fig.2). The optimization was achieved through the reduction of the amount of soot formed by the oil burner by the following measures:

- Optimization of the burner for the start-up conditions
- filling the waste feeder with waste to avoid leakage air
- reduction of the primary and secondary air supply
- manual control and regulation of the air and fuel supply by strictly controlling the CO-level [1]

The outstanding high ClP-value at the oil-burning-start of run 6 (6-1) is mainly determined by dichlorophenols. At only slightly elevated CO-level of 100-300 mg/m$^3$, the ratio of triCP to tetraCP+ pentaCP is around >1.

During that phase of the run, an extremely high CO-peak (>> 500 ppm (11 % $O_2$)) was recorded, showing poor incineration conditions, which also lead to higher values for PCDD/F as well as for ClB. In Figure 3 the distribution of the congener groups of ClP and ClB is shown.

**Figure 2: comparison sum of PCDD/PCDF and chlorobenzenes, chlorophenols**

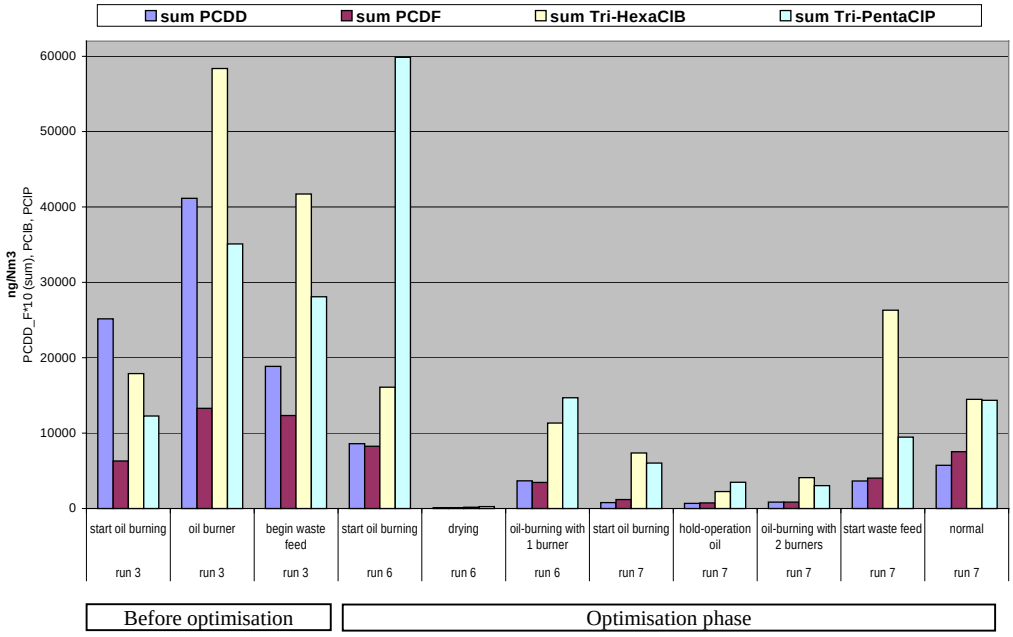
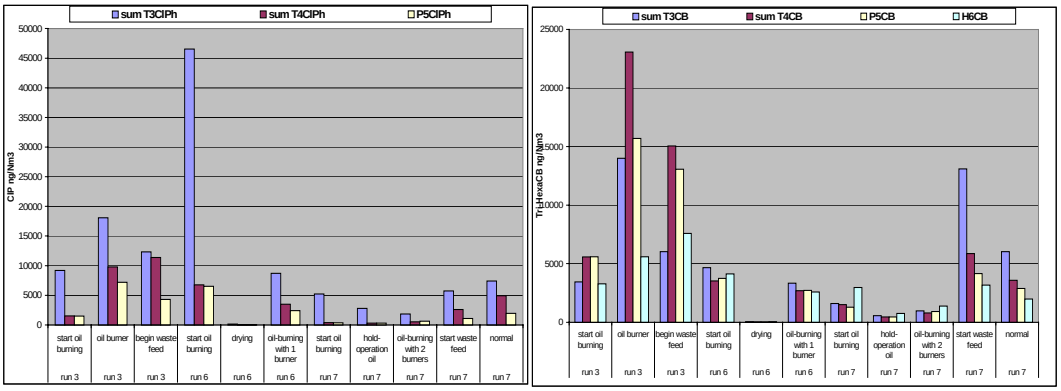


**Figure 3: distribution of the congener groups of Chlorophenols and Chlorobenzenes**




For the evaluation of the correlation between PCDD/PCDF- and ClP/ClB-emissions linear regression has been chosen, whereby correlation is expressed by the correlation coefizient ($R^2$) (Table 2).

If the processes are further differentiated into "oil-burning" and "waste burning" (run3-3 and 7-4, 7-5), the correlation between sum ClP and PCDD/PCDF becomes even better (see Table 2 and Figure 4):

- ClP **:** PCDD for oil-burning $R^2$= 0.80
- ClP **:** PCDF for oil-burning $R^2$= 0,94
- ClP **:** PCDD for waste-burning $R^2 > 0.95$
- ClP **:** PCDF for waste-burning $R^2 > 0.95$

No such effect has been observed for the chlorobenzenes.

**Table 2: Correlation between concentration of ClB/ClP and PCDD/PCDF**

| **Correlation** *correlation coefizient* | PCDD $R^2$ | PCDF $R^2$ |
|---|---|---|
| **chlorobenzenes (ClB)** | | |
| sum trichlorobenzenes | 0.37 | 0.46 |
| sum tetrachlorobenzenes | 0.80 | 0.76 |
| pentachlorobenzenes | 0.80 | 0.83 |
| hexachlorobenzene (HCB) | 0.47 | 0.76 |
| sum tri-hexaClB | 0.74 | 0.80 |
| **chlorophenoles (ClP)** | | |
| sum trichlorophenoles | 0.79 *) | 0.86 *) |
| sum tetrachlorophenoles | 0.45/0.96 **) | 0.90 |
| pentachlorophenoles | 0.75 *) | 0.84 *) |
| sum tri-pentaClP | 0.72 *) | 0.93 *) |

*) outlier 6-1 eliminated

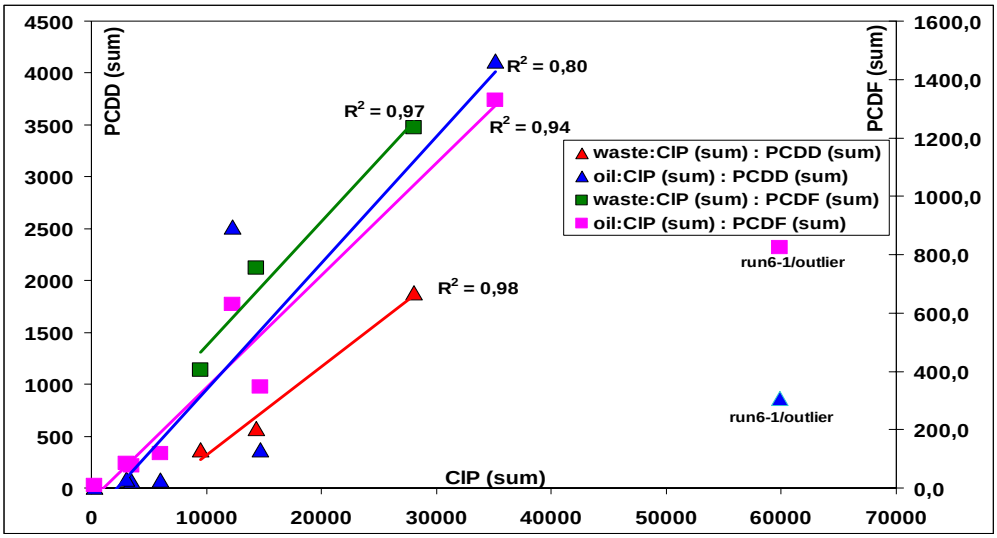
**) outlier 3-1,3-2 eliminated

As already stated, at the oil-burning-start of run 6-1 high CO-level could be observed, leading to very high ClP-emissions. The results of this sampling phase (6-1) was determined as outlier for the calculation of the correlation coefficients (see Table 2).

***Conclusions***

Emission behaviour during combustion processes of PCDD/PCDF and ClB / ClP are comparable, poor combustion conditions connected with an evaluated CO-level are leading to high concentrations of these compounds [2,3,4,5].

**Figure 4: Correlation between concentration of ClB/ClP and PCDD/PCDF [ng/m$^3$]**




If the CO-level is extremely high (>>500 mg/m$^3$), the concentration of chlorophenols is exceedingly elevated (60 µg/Nm$^3$), especially the trichlorophenols (triCP) are formed (46 µg/Nm$^3$). The normal concentration of the chlorophenols in the fluegas after optimizing the combustion procedure was around 3-15µg/Nm$^3$.

It can be stated, that for the operation procedure during the 3 hours period shortly after start of waste feed as well as for the cold-start-up procedure main attention has to be paid to the control of the CO-level. If during the optimized cold-start-up procedure the mean CO-level is below 100 mg/m$^3$, in connection with the gas-cleaning system, it is possible to comply with the limit values especially for the PCDD/PCDF.

***Acknowledgement***

The authors would like to thank MVB staff for providing the necessary data.

***References***

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