

EMISSION OF PCDD/FS FROM COMMERCIALY AVAILABLE SMALL SCALE APPLIANCES AT COMBUSTION OF VARIOUS OILS

Ocelka T.^{1*}, Horak J.², Tydlitát V.³, Pekárek V.³, Danihelka P.², Grabic R.¹, Obal L.⁴

¹ Institute of Public Health, National reference laboratory for POPs, Partyzánské nám. 7, 702 00, Ostrava, Czech Republic, Tomas.Ocelka@zuova.cz

² VŠB-Technical university Ostrava, Energy Research Center, 17. listopadu 15, 708 33 Ostrava – Poruba, Czech Republic

³ Institute of Chemical Process Fundamentals, Academy of Sciences of the Czech Republic, Rozvojova 2, 165 02 Prague 6 – Suchbát, Czech Republic

⁴ TESO, Ltd, Janáčkova 1020/7, 702 00 Ostrava-Moravská Ostrava, Czech Republic

*To whom correspondence shall be addressed

Introduction

Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) belong to group persistent toxic substances emitted from various thermal processes. Recently, main interest was focused on greatest sources of PCDD/F, like incinerators, metallurgic plants, etc.... However, latest concern is also focused on small burning facilities for domestic purposes that have been postulated as remarkable source of POPs, if considered as a total emission flux.

Group of commonly used burning facilities is represented by oil-burning facilities, where some of them were designed or legally approved for incineration of motor oil after use. This plays important role in accelerating use as a cheap alternative for fossil fuel with acceptable price¹. The lowest price the lower level of treatment of oil prior reuse for incineration is distinctive. Oils have originated from various sources (car repairing services, road transport, etc....). Combustion of oil can result in formation of PCDD/Fs^{1,2}, in particular upon uncontrolled combustion process³.

Main goal of this work was concerned on the study of emission of PCDD/Fs from two general kinds of small burning facilities: *evaporation units* and units fitted with oil burner (*burner units*). In experiments, there were burned various kinds of oils, including oils after use. One of the goals of this study was also comparison with emission limit (0,1ng/m³ TEQ) considered for large sources.

Materials and Methods

Used burning facilities

Evaporation units (10 experiments): boilers AT 500 (29-44 kW) and AT 400 (21-31 kW), manufactured by Thermobile Industries B.V., The Netherlands.

Burner units (17 experiments): boilers Viadrus U22, manufactured by ŽDB Inc. Bohumín, Czech Republic, fitted with Kroll KG2055 burner (35-59 kW).

Used oils

Based on previous experience and results available^{2,3}, various kind of oils were used.

Evaporation units:

- oil after use from diesel lorry transport and heavy-duty machinery – marked as “DH”,
- oil after use from diesel and petrol transport, contaminated by vapex) – marked “DB”,
- light fuel oil with paraffin – marked as “LTOP”,
- light fuel oil – marked “LTO”,
- diesel fuel – marked as “N”.

Burner units:

- oil after use from personal car engines (collection from one brand)
- oil after use from personal car engines (collection from various brands)

Formation, sources and source inventories

- diesel fuel
- oil after use from diesel and petrol transport, contaminated by Vapex)

Sampling, analysis

Fuel characterization: all used oils were sampled and tested on chemical and physicochemical characteristics (metals, PCBs, PAHs, water, viscosity etc.), except of PCDD/Fs.

Emission sampling method:

In general, sampling and analysis were performed in accordance with the EN 1948 standard. All used methods were validated (accredited) according to ISO 17025 standard. For final analysis of PCDD/Fs, an isotopic dilution method was used. Analysis was carried out on GC-MS/MS system (Finnigan).

Results and Discussion

All measured data are very complex, representing megavariable data matrix. More detailed insight is subject of publication. On this paper, results of PCDD/Fs are given only – see Tables 1a) and 1b). All reported concentrations are related to 11% O₂ content.

Table 1a Emission of PCDD/F and CO for Burner units

Experiment	U 22 unit, with various fuels																		
	B1	B2/1	B2/2	B3/1	B3/2	B4/1	B4/2	B4/3	B4/4	B4/5	B4/6	B5/1	B5/2	B5/3	B5/4	B6/1	B6/2	B6/3	B6/4
CO [mg.m ⁻³]	7	175	3	47	1 394	3	2	2	100	132	381	1 111	39	169	75	158	210	152	131
Σ PCDD [ng.m ⁻³]	1.14	1.49	1.42	1.92	0.08	0.12	0.20	0.18	0.19	0.15	2.10	12.9	0.59	0.36	0.20	0.12	0.09	0.04	0.08
Σ PCDF [ng.m ⁻³]	1.30	2.23	2.65	3.73	0.28	0.37	0.46	0.30	0.44	0.67	3.97	10.7	4.91	3.21	0.35	0.23	0.16	0.21	0.26
Σ PCDD/F [ng.m ⁻³]	2.44	3.72	4.07	5.65	0.37	0.49	0.65	0.48	0.64	0.82	6.08	23.6	5.50	3.57	0.55	0.35	0.25	0.25	0.34
I-TEQ PCDD/F [ng.m ⁻³]	0.039	0.067	0.069	0.077	0.005	0.008	0.012	0.009	0.008	0.016	0.017	0.427	0.096	0.048	0.007	0.003	0.006	0.003	0.004
Ratio PCDD/PCDF	0.88	0.67	0.54	0.52	0.29	0.33	0.43	0.61	0.43	0.23	0.53	1.21	0.12	0.11	0.59	0.52	0.55	0.22	0.31

Table 1b Emission of PCDD/F and CO for Evaporation units

Evaporation units	AT 500						AT400			
	1	2	7	29	6	5	27	28	26	25
Experiment										
Fuel	DH1/1	DH1/2	DH2	DH4	DB	LTOP	DH3/1	DH3/2	LTO	N
CO [mg.m ⁻³]	25	14	634	72	79	593	164	13	86	4
Σ PCDD [ng.m ⁻³]	0.31	0.21	5.14	0.41	4.79	1.04	1.80	1.35	0.05	0.03
Σ PCDF [ng.m ⁻³]	0.22	0.21	6.60	2.02	5.10	1.17	10.7	7.89	0.07	0.06
Σ PCDD/F [ng.m ⁻³]	0.53	0.42	11.7	2.43	9.89	2.21	12.5	9.24	0.12	0.09
I-TEQ PCDD/F [ng.m ⁻³]	0.003	0.002	0.212	0.029	0.157	0.041	0.149	0.123	0.002	0.002
Ratio PCDD/PCDF	1.39	0.98	0.78	0.20	0.94	0.88	0.17	0.17	0.72	0.54

Experimental results showed that CO emission concentration is very sensitive indicator of controlled combustion process. During repeated combustion of DH3 oil (DH3/1 and DH3/2) fault controls of combustion process in experiment DH3/1 were detected. It led to different values of emission CO and PCDD/Fs. There were apparent that personal factor in the term of maintenance and control seems to be important, especially for evaporation units. This aspect was underlined using oil with paraffin content in result badly combustible constituent.

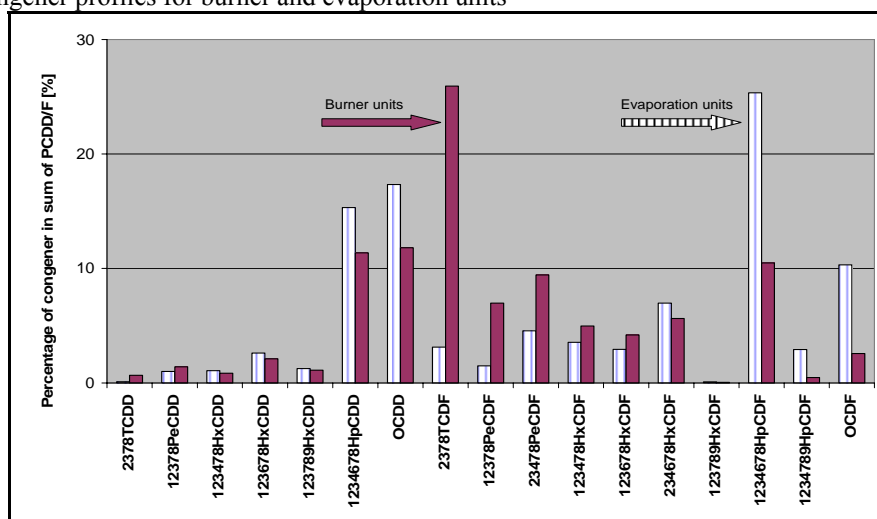
A PCDD/PCDF ratio in emission for evaporation unit was within a range of 0,17-1,4 (mean 0,68). The PCDD/PCDF ratio for burner boilers was within a range of 0,11-1,21 (mean 0,48). These values are different compared to municipal and hazardous waste incinerators, revealing different way of PCDD/Fs formation, apart from recent results². High values of PCDD/PCDF ratio were postulated in experiments with denovo-synthetic reactions at laboratory conditions in case of short reaction period⁴. It is known that PCDD can originate very fast

and easy from chlorinated phenols, which are considered as PCDD precursors by way of various reaction mechanisms⁵.

Relative congener profiles of PCDD/Fs (obtained as a *mean* value for each congener through all realized experiments for burner and evaporation unit) are given in Figure 1. In *burner units* PCDF predominated over PCDD and from TEQ point of view, there were 30% accounted for PCDD and 70% for PCDF. Dominant congener was 2,3,7,8-TCDF.

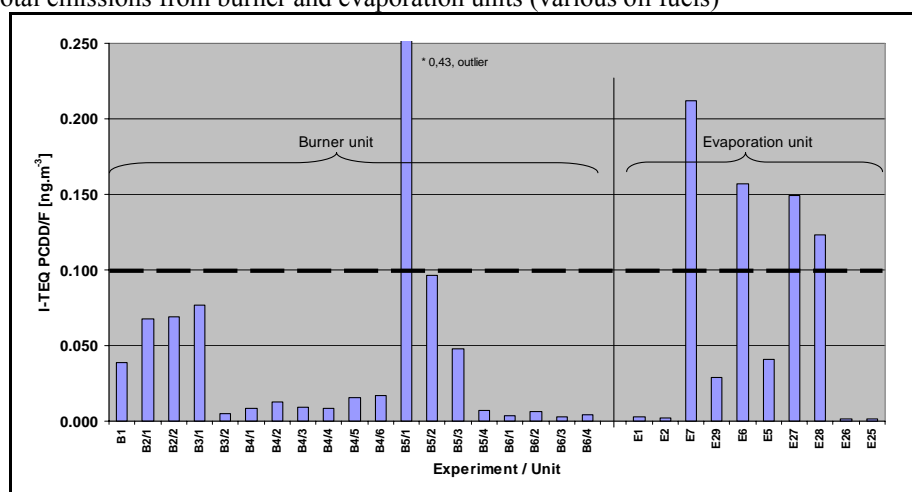
Congener profile from *evaporation units* is partly same and partly different compared to *burner units*. This profile exhibits high HpCDF content. Content of HpCDD, OCDD and low chlorinated CDD were comparable in both kinds of units. From a TEQ point of view, *evaporation units* exhibit 39% PCDD and 61% PCDF, which was roughly comparable to *burner units*.

Figure 1 Congener profiles for burner and evaporation units



It is evident from the Figure 2 that limit 0,1 ng TEQ/m³ is exceeded in four of ten experiments (*evaporation units*). The average concentration all of experiments was 0,07 ng TEQ/m³. However, due to total emission flux exceeding levels does not seem to be critical for environmental contamination. In comparison, emission from *burner units* was found lower than for *evaporation units*. Mean value of all experiments was 0,03 ng I-TEQ/m³ (0,003-0,096). Extreme result of 0,43 ng I-TEQ/m³ is distinctive for uncontrolled burning conditions.

Figure 2 Total emissions from burner and evaporation units (various oil fuels)



Conclusions

Experiments showed probable different PCDD/Fs formation in burner and evaporation units, as given in congener profiles.

1. The PCDD/PCDF ratio indicates different combustion process compared to municipal and hazardous waste incinerators (PCDF dominant, within the range 60-70%).
2. Combustion of oil in burner units indicates lower emission of PCDD/Fs compared to evaporation units. In any case, environmental contamination is not critical due to low emission factor of these facilities.
3. PCDD/F emission from evaporation units is strongly dependent on their maintenance. Uncontrolled burning is mainly caused by impurities concentrated in evaporation pan.
4. In complete risk assessment, possible danger from transportation of oil after use must be taken into account.
5. These conclusions are relevant for liquid fuel combustion including waste oil combustion in vaporizing boilers of 21-44 kW power.

Acknowledgements

This work was by supported by Grant Agency of the Czech Republic, No. 101/01/0830 and 101/06/P262.

References

1. Grabic, R., Danihelka, P., Ocelka, T., Dej, M.; Emmission of POPs from combustion of used oils in heat sources to 30kW and 233 kW power at presence of heavy metals; Proc. Dioxin 99, Krakow, Poland, 1999
2. Brodsky, E.S., Klyuev, N.A., Razapov, A.Z.; Dioxin emission from combustion of waste automobile oils as fuel for small heating furnaces; Organohalogen Compounds, 40 (1999)
3. Danihelka P., Ocelka T., Tydlitát V., Krpec K., Adamčíková L.: "Problematika spalování odpadních olejů v kotlích malých výkonů", Konference : Spalování a životní prostředí, VŠB v Ostravě, 17.-18.června 2003. Sborník ISBN80-248-0394-1
4. Grabic R., Pekárek V., Ullrich J., Punčochář M., Fišerová E., Karban J., Šebestová M.: Effect of reaction time on PCDD and PCDF formation by de novo synthetic reactions under oxygen deficient and rich atmosphere. *Chemosphere* 49, 691-696, 2002
5. Weber R., Dissertation: Synthese, Toxikologie und Vorkommen fluoriertes und chloriert-fluoriertes Dibenzodioxine, Dibenzofurane and Biphenyls, Fakultät für Chemie und Pharmazie, Eberhard-Karls-Universität Tübingen (1996)