

František HOPAN*, Michal ŠYC**, Jiří HORÁK***, Milan DEJ, Kamil KRPEC,
Tomáš OCELKA, Tomáš TOMŠEJ, Vladimír PEKÁREK

EMISSION FACTORS OF SELECTED ORGANIC COMPOUNDS FROM DOMESTIC
HARDWOOD COMBUSTION

EMISNÍ FAKTORY VYBRANÝCH ORGANICKÝCH SLOUČENIN ZE SPALOVÁNÍ
TVRDÉHO DŘEVA V MALÝCH SPALOVACÍCH ZAŘÍZENÍCH

Abstract

Emission factors were determined during beech logs combustion in four domestic facilities typical for Central European region households. In flue gases there were determined except basic pollutants (NO_x, CO, PM and OC as TOC) also selected organic pollutants as PCBz, PCPh, PAH, PCB, and PCDD/F. Generally, obtained EF values of selected pollutants were lower for modern combustion facilities than for older ones. However, some differences were found between modern facilities in dependence on their type as well. For better understanding results were also subjected to principal component analysis.

Abstrakt

Emisní faktory (EF) byly stanoveny při spalování bukového dřeva ve čtyřech typech malých spalovacích zařízeních typických pro domácnosti středoevropského regionu. Ve spalinách byly sledovány základní znečišťující látky (NO_x, CO, PM a VOC jako TOC) a také vybrané organické znečišťující látky PCBz, PCPh, PAU, PCB a PCDD/F. Obecně lze konstatovat, že naměřené EF vybraných znečišťujících látek byly nižší při použití moderních typů spalovacích zařízení než na zařízeních starších konstrukcí. Nicméně, jsou také pozorovány rozdíly mezi jednotlivými moderními zařízeními v závislosti na jejich typu. Pro lepší pochopení výsledků byla naměřená data rovněž zpracovaná komponentní analýzou.

1 INTRODUCTION

Emissions from domestic burning facilities significantly participate on total environmental pollution[1]. Their contribution is evident from seasonal changes obtained by long-term monitoring programs[2]. Hence, it is necessary to determine accurate contribution rate for reason of precise emission inventories and source identification.

Emission inventories utilize emission factors (EF) for computation of individual source participation to total emissions. However, emission factor values for domestic burning differ widely. Gullet et al.[3] determined emission factors of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/F), polychlorinated biphenyls (PCB), hexachlorobenzene (HxCBz), polyaromatic hydrocarbons (PAH), and particulate matter (PM) on fireplace and woodstove for two woody fuels (oak and pine). Resulted emission factors ranged from 0.25 to 1.4 ng I-TEQ PCDD/F kg⁻¹ depending on fuel and combustion facility. Dilution tunnel was used for achieving isokinetic sampling conditions. Sig-

* Ing., Energy Research Center, VSB – Technical University of Ostrava, 17.listopadu 15/2172, 708 33 Ostrava, tel. (+420) 59 732 3856, e-mail frantisek.hopan@vsb.cz

** Ing. Ph.D., Institute of Chemical Process Fundamentals, Academy of Sciences of the Czech Republic, v.v.i., Rozvojová 2, 165 02 Prague 6, tel. (+420) 220 390 372, e-mail syc@icpf.cas.cz

*** Ing. Ph.D., Energy Research Center, VSB – Technical University of Ostrava, 17.listopadu 15/2172, 708 33 Ostrava, tel. (+420) 59 732 3866, e-mail jirka.horak@vsb.cz

nificant effect of combustion facility age on emission factor values was reported by Hedman et al.[4] as well as effect of stationary or instationary combustion period phase. PCDD/F emission factors varied from 1.2 to 12 ng WHO-TEQ kg⁻¹ for woody biomass on tested facilities. Dilution tunnel was also used for achieving isokinetic sampling conditions. On the other side, Wevers et al.[5] reported no effect of combustion period or fuel age on determined emission factors from 5 tested stoves. Resulted values were 2–89 ng I-TEQ PCDD/F kg⁻¹, however, effect of facility was not examined. Chimney emissions from 30 households were sampled for determination of „real“ PCDD/F emission factors[6]. Tested combustion facilities included stoves and boilers with wide range of thermal input and age. Computed emission factors were within 0.002–4.5 ng TEQ PCDD/F MJ⁻¹ depending on tested facility, combusted fuel and/or inappropriate operation of certain unit. However, isokinetic sampling was not possible due to low flue gas velocity in chimney. Schatowitz et al.[7] found emission factors for beech logs as fuel 0.23–1.23 ng NATO TEQ PCDD/F kg⁻¹ on combustion facility of thermal output ranged from 6 to 1800 kW. Combustion was operated with regard to CO minimization. However, details about sampling were not reported in this study.

Large variation of emission factor values for woody biomass combustion is obvious from above mentioned studies. Detailed description of sampling method, tested facilities and combustion operation conditions are characterized insufficiently in some cases. Moreover, precursors of PCDD/F formation like polychlorinated phenols (PCPh), and polychlorinated benzenes (PCBz) were analyzed rarely. Therefore, the main aims of this work were to find representative emission factors on four combustion facilities typical for Central European region and to analyzed PCDD/F and their formation precursors (PCBz, PCPh) and PAH. Furthermore, the next aim was to identify possible effect of combustion facility type on obtained results.

2 MATERIALS AND METHODS

Beech logs (length 30 cm) as a hardwood representative were used as a fuel for all combustion tests. Results of ultimate and proximate fuel analyses are shown in Tab 1. Low ash content below 1 wt. % in burned beech logs is typical for woody biomass. Relatively low fuel humidity indicates that beech logs were aged and stored in dry condition. Tested fuel has very low content of chlorine at level 58 mg/kg.

Tab 1 Results of ultimate and proximate analyses

Beech logs			
Proximate analysis		Ultimate analysis	
Water (wt. %)	9.6	C (wt. %)	45.5
Ash (wt. %)	0.8	H (wt. %)	5.6
Combustibles (wt. %)	89.6	N (wt. %)	0.1
Ash ^d (wt. %)	0.9	O (wt. %)	47.7
Volatiles ^d (wt. %)	99.1	S (wt. %)	0.24
LHV (MJ/kg)	15.7	Cl (mg/kg)	58

^d - dry matter; LHV - lower heating value

Twelve combustion tests were realized in three different types of domestic boilers and in one fireplace type stove typical for the Czech Republic and Central European region. More details about tested facilities are shown in Tab 2.

Tab 2 Overview of tested combustion facilities

	Type	Thermal output ² (kW)	Run	Fuel consumption ³ (kg/h)	Temperature at chimney inlet ³ (°C)
Boiler A	Old type boiler - burn up	23.5	A1–A3	6.9	220±50
Boiler B	Old type boiler - burn down	24	B1–B3	6.2	160±20
Boiler C	Modern type boiler - gasification	17–25 ¹	C1–C3	9.8	260±30
Stove D	Modern fireplace type stove	8	D1–D3	2.3	300±40

¹ - based on combusted fuel; ² - data from producer; ³ - data obtained during tests

Boilers and stove were tested at domestic combustion testing facility consisting of balance, tested boiler or stove, isolated chimney system (height 3 m) exhausting to a dilution tunnel hood, dilution tunnel and fan. More details about testing facility and all advantages of dilution tunnel application were presented elsewhere before[8].

Fuel charge rates and charges period of all tested facilities were realized according to directions of producer. Flue gas samplings were started after achieving steady state regime of combustion, i.e. ca 2 hours after ignition. Whole testing facility (chimney, dilution tunnel, etc.) was cleaned after three subsequent runs with same tested combustor but not between each single run.

Flue gas sampling and selected organic compounds analyses were performed in accordance with the European standard EN 1948.

All results in Tab 3 and Tab 4 are averages of three tests on the same facility. Levels of some PCBz, PCB and PCDD/F congeners were below the detection limit; in this case detection limit values were used as a representative.

3 Results and Discussion

Emission factors of major flue gases pollutants are shown in Tab 3. CO emission factor values are nearly the same for all three tested boilers (A, B, C) while for tested stove (D) the EF value is approximately half. Same values of 1 300 mg/kg for EF of particulate matter (PM) were found for boilers A and B. Lower emission factors of PM at level 880 mg/kg and 830 mg/kg were determined for boiler C and for stove D respectively. Lower PM emission factor values from gasification type boiler C are expected due to flue gas flow pattern inside a boiler. Similar findings as for PM emission factors can be reported for EF of total organic carbon (TOC), so the highest values were found for boilers A and B, lower for boiler C and the lowest values for stove D. On the contrary, opposite results were obtained for NO_x emission factor values, the EFs decreased in following order: stove D > boiler C > boiler B > boiler A.

Tab 3 Emission factors of major flue gas pollutants (all in mg/kg)

	A	B	C	D
CO	62 000±2 000	59 000±12 000	62 000±9 000	31 000±6 000
NO _x	850±90	940±80	1 400±100	1 600±100
TOC	12 000±1 000	11 000±3 300	6 200±2 700	1 400±200
PM	1 300±200	1 300±100	880±100	830±150

Calculated emission factors of all analyzed organic compounds are summarized in Tab 4.

Tab 4 Emission factors of selected organic compounds

	A	B	C	D
PCPh ($\mu\text{g}/\text{kg}$)	- ^e	- ^e	- ^e	7.2 ± 1.1
PCBz (ng/kg) ^a	50 ± 3	58 ± 4	130 ± 20	110 ± 10
PAH (mg/kg) ^b	27 ± 3	16 ± 4	6.5 ± 0.4	1.5 ± 0.3
PCB (ng/kg) ^c	27 ± 7	62 ± 30	12 ± 4	23 ± 5
I-TEQ PCB (pg/kg)	16 ± 3	19 ± 4	6.9 ± 0.4	12 ± 1
PCDD/F (ng/kg) ^d	5.0 ± 1.4	5.8 ± 0.8	3.5 ± 0.2	7.7 ± 2.1
I-TEQ PCDD/F (pg/kg)	150 ± 10	340 ± 40	130 ± 20	200 ± 30

^a - sum of tetra- to hexa-CBz; ^b - sum of 10 polycyclic aromatic hydrocarbons (fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(g,h,i)perylene, dibenzo(a,h)anthracene, indeno(1,2,3-cd)pyrene); ^c - sum of 14 PCB congeners with TEQ values; ^d - sum of tetra- to octa-CDD/F; ^e - not determined.

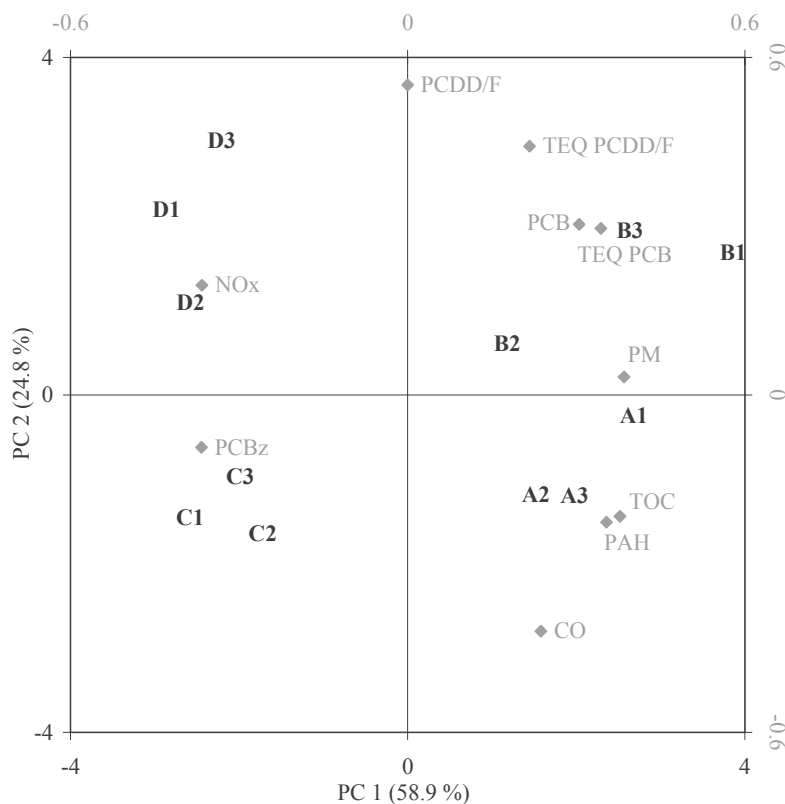


Fig 1 Biplot

Emission factors of selected organic compounds (Tab 4) did not show any evident patterns as major pollutants. Therefore, obtained results were subjected to principal component analysis (PCA). A two component model that characterized 83.7 % of total variance was obtained. The biplot from

PCA is shown in Fig 1. Variables could be divided into three major clusters. First cluster is oriented to right lower part of biplot and consists of TOC, PAH and CO, i.e. products of incomplete combustion with no relation to chlorination. Second cluster is formed by I-TEQ PCB, PCB, I-TEQ PCDD/F and PCDD/F and is located in the right upper part of biplot or close to PC 2 (PCDD/F). This cluster characterizes chlorinated products of incomplete combustion. Between these two clusters on the PC 1 lays single point of PM; the placement of PM in biplot is expectable, because major part of above mentioned products of incomplete combustion is deposited on solid phase of flue gases - particulate matter. On the left side of biplot there are NO_x and PCBz.

Relatively high EF values of PCPh were obtained for stove D, however for boilers PCPh were not analyzed. High PCPh EFs values are not unexpected due to phenolic character of lignin structure of wood. Moreover, these high values could be also given by the fact that also lowchlorinated congeners of PCPh were obtained, because dichlorinated congeners were absolutely predominant.

The above mentioned results of PCA also confirm expected fact that EF values from modern combustion facilities are lower than that from older-type ones. The lowest EFs of PCDD/F and PCB were obtained for modern boiler C with gasification concept of wood burning. The highest quality of combustion and thus the lowest EFs of CO, TOC, and PAH were determined for fireplace type stove, which works at the highest temperatures of compared facilities (see Tab 2). However, EFs of chlorinated compounds are in some cases higher for stove D than for old-type boilers (A, B). Possible explanation of this fact could be in flue gases temperature at stove outlet which is achieving 300 °C in our tests, i.e. temperature inside the “temperature window” (300–350 °C) proper for de novo synthetic formation of PCDD/F. It means extension of reaction zone of PCDD/F formation to chimney and also prolongation of reaction time suitable for formation of these compounds. This fact occurred just on stove D, flue gases temperature outlets at all tested boilers were below the “temperature window”.

Acknowledgements

This work could not have been realized without financial support of the Ministry of the Environment of the Czech Republic - Project SP/1A2/116/07 and Ministry of Education, Youth and Sports (programme Health and life quality, project WARMES 2B08048).

REFERENCES

- [1] HORÁK J., MACHÁLEK P., HOPAN F., KRPEC K., DEJ M., PEKÁREK V., ŠYC M., OCELKA T., TOMŠEJ T. *Ochrana ovzduší*, 2008, 5–6:38. (in Czech)
- [2] KLÁNOVÁ J., KOHOUTEK J., HAMPLOVÁ L., URBANOVÁ P., HOLOUBEK I. *Environmental Pollution*, 2006, 144:393.
- [3] GULLETT B.K., TOUATI A., HAYS M.D. *Environ. Sci. Technol.*, 2003, 37:1758.
- [4] HEDMAN B., NASLUND M., MARKLUND S. *Environ. Sci. Technol.*, 2006, 40:4968.
- [5] WEVERS M., DE FRÉ R., VANERMEN G. *Organohalogen Compounds*, 2003, 63:21.
- [6] HÜBNER C., BOOS R., PREY T. *Chemosphere*, 2005, 58:367.
- [7] SCHATOWITZ B., BRANDT G., GAFNER F., SCHLUMP E., BUHLER R., HASLER P., NUSSBAUMER T. *Chemosphere*, 2005, 58:367.
- [8] HORÁK J., HOPAN F., KRPEC K., DEJ M., KUBAČKA M., PEKÁREK V., ŠYC M., OCELKA T., TOMŠEJ T., MACHÁLEK P. *Organohalogen Compounds*, 2008, 70:2470.

