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EMISSION OF PCDD/FS FROM DOMESTIC COMBUSTION USING VARIOUS WOODS,
BIOFUEL AND COALS

EMISE PCDD/F PŘI SPALOVÁNÍ RŮZNÝCH DRUHŮ DŘEVA, BIOPALIV A UHLÍ V
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Abstract

Lignite, biomass and natural gas was combusted in six different types of boilers. Production of these pollutants was observed: CO, TOC, PAHs, PM, PCBs, NO_x, PCDD/F. It was applied marginal and multivariate statistics for evaluating the effect of various parameters on produced pollutants.

Abstrakt

V šesti různých typech kotlů bylo spalováno uhlí, biomasa a zemní plyn a byly sledovány emise těchto škodlivin: CO, TOC, PAU, PM, PCB, NO_x, PCDD/F. Pomocí marginální a multikriteriální analýzy byl sledován vliv různých parametrů na produkované škodliviny.

1 INTRODUCTION

Biofuels, wood and coal are popular sources of relatively cheap energy, despite their problematic emission of carbon monoxide (CO), nitrogen oxides (NO_x), as well as persistent compounds, like polychlorinated dibenzo-p-dioxins and furans (PCDD/Fs) [1-4], polychlorinated biphenyls (PCBs) [2-5], polycyclic aromatic hydrocarbons (PAHs) [4-5], and their direct precursors, such as polychlorinated phenols (PCPh) [3-4,6], polychlorinated benzenes (PCBz) [3-4,6]. Their emissions are subjected to deeper interest due to increasing emission from domestic sources, even more if they are present as a fuel for co-combustion [7-8]. Some estimates of emission factors for wood, biomass and coal combustion in Czech Republic have recently been published [9-11].

The effect of various parameters within this work were observed from various experiments, using marginal and multivariate statistics [12-13].

2 MATERIALS AND METHODS

2.1 Used burning facilities, regimes, fuel

Experiments were performed in six different types of boilers: automatic over-fire boiler, over-fire boiler, under-fire boiler, down draught boiler, fireplace type stove, and gas boiler.

Detailed experimental set-up and used fuels are given in the presentation [14]. All the tests of the boilers were carried out on the standard instructions as given by the manufacturer of each appliance.

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2.2 Sampling, analysis

With each experiment on solid fuels, a minimum of three burnings were carried out. Each test was performed after an operating period of several hours. The following parameters were continuously recorded during the test:

- ❑ CO, NO_x, SO₂ and TOC – in the part of the chimney, approximately 1 m behind the burning facility, in accordance with the EN 303-5 standard. The CO, NO_x and SO₂ parameters were determined by IR detection system in accordance with following standards: EN 15058 (for CO), ISO 10849 (for NO_x), ISO 7935 (for SO₂), ISO 10396 (standard for sampling),
- ❑ TOC – FID detection, in accordance with EN 12619,
- ❑ particulate matters (PM) were sampled in accordance with ISO 9096,
- ❑ sampling of PCDD/Fs, PCBs and PAHs was done in accordance with EN 1948, by isokinetic regime (well established by dilution tunnel, as described recently [10]). The ratio of dilution was approximately 1:5.

All sampling and testing methods were validated (accredited) according to the ISO 17025 standard. For final analysis of PCDD/Fs, PCBs, PCBz, PCPh an isotopic dilution method using ¹³C-labelled compounds was applied; for PAHs, the analysis by ¹⁰D was used. Analysis was carried out on the GC-MS/MS system (Finnigan); for PCDD/F, appropriated validation to use a high-resolution gas chromatograph with high-resolution mass detection was performed to meet the EN 1948 standard.

2.3 Data analysis

All 46 observations were subjected to exploratory data analysis (EDA) to reveal normality of data based on various graphical diagnosis (e.g. symmetry plot, halfsum plot, Box-and-whisker plot, quantile plot and rankit Q-Q plot while the coefficient of skewness measures the asymmetry of the observations). The Statistica 9.0 CZ™ (StatSoft Inc.®) and QC.Expert™3.1 (TriloByte® Ltd.) were used.

The Jarque-Berra test ($\alpha = 0.05$) was preliminary used to test the normality of concentration distribution within each parameter. This revealed a lack of normal distribution, together with moments of skewness and kurtosis describing how the shapes of sample frequency distribution curves differed from the ideal Gaussian curves. Due to lack of normality, original data were then transformed to improve the symmetry of data distribution and variance stabilization. The Box-Cox [15-16] transformation was selected. The effect of transformation (as the example for the sum of PCDD) is given on the Fig.1.

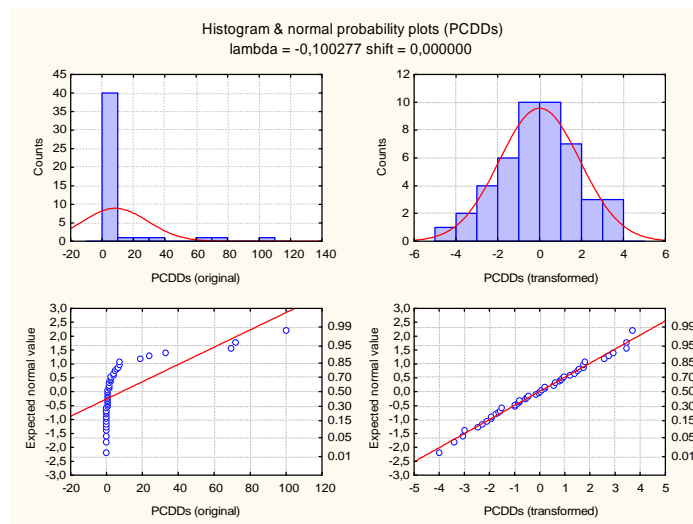


Fig. 1 The effect of data transformation (Box-Cox transformation)

The correlation matrix (CM) was then created from the values of 9 parameters of all 46 experiments to identify the relationship. Pearson's product moment correlation coefficient was used. The correlation matrix was used for construction of the projection of variables and observations by the PCA technique.

Principal component analysis (PCA) was carried out to reduce the number of original variables (11 element contents) through their linear combinations (principal components) and to discover further dependencies among the original variables. Normal distribution of each metal was previously checked, since the PCA procedures are based on linear combinations of the variables and their correlations. PCA was based on the correlation matrix, with no factor rotation. PCA was therefore applied to the correlation matrix for this study, and each variable is normalized to unit variance and therefore contributes equally.

A contingency table was used as a base for graphical representation of categorical data, namely used fuels, boilers, and isomeric pattern of PCDD/Fs, as average values from observations (mostly from 3 cases), based on observations that compare well, as given on the PCA scatter plot.

The parameters are as follows: PAHs is the sum of 10 polyaromatic 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. PCBs is the sum of PCB No. 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, 170, 180, and 189. TEQ PCBs was calculated based on WHO-TEFs 2005. PCDD/Fs is the sum of Tetra- to OctaCDD/Fs, TEQ PCDD/Fs was calculated based on TEFs according to EN 1948.

3 RESULTS AND DISCUSSION

The PCA model of variables, explaining 71.5% of total variance is given in Figure 2 and 3. There is an apparent strong correlation between CO and PAHs, resulting in the formation of PAHs mainly directed by CO. The correlation is positive, thus, the more CO is formed, the more PAHs are in the exhaust. The same direction is for TOC, however the vector does not reach the value of both parameters (CO and PAHs), so that the relationship is not so tight. As for total particulate matter (PM), the parameters are between PAHs and those chlorinated compounds, in closer proximity to PAHs than to PCBs and PCDD/Fs. The PCDDs and PCDFs exhibits strong mutual correlation that can be attributed to similar reaction principles, besides PCBs. No strong relationship was found for SO₂ and the NO_x influence to POPs formation.

Detailed insight of conducted experiments reveals the PCA plot of observation, as given in Fig.3.

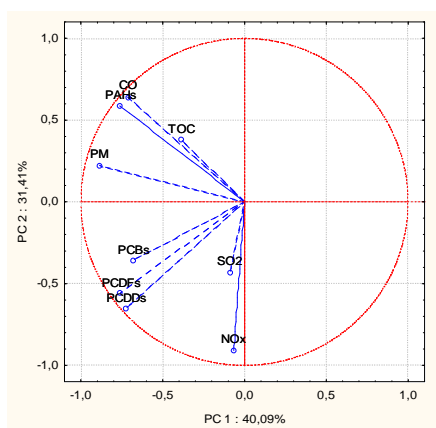


Fig. 2 PCA of selected variables

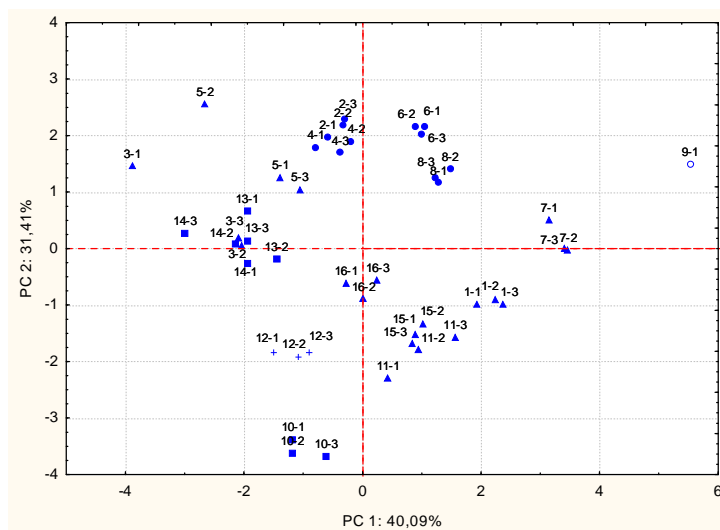


Fig. 3 PCA pattern of all experiments: ○ natural gas, ▲ Lignite, ● Hardwood, + Biomass

Fig.3 shows good agreement among repeated experiments (denote as X-1 up to X-3, where X is number of experiment); only a few of them exhibit small outlying character, like 3-1 and 5-2, which is most probably attributed to the non-homogeneity of used fuel (lignite), when compared with data for other experiments for the given burning facility. (For a more rigid evaluation, e.g. by analysis of variance, it was not possible to perform due to the asymmetry of the data matrix). The outlying experiment 9-1, denoted to natural gas, is not surprising. The scattering among quadrants are more distinctive for used fuels than for used appliances. For example, if there are used 3 different appliances for runs from 2 to 8, they are well clustered for hardwood (full circle). Apart from for lignite, clusters are scattered into two quadrants with remarkable distance.

Strong influence of the construction on the emission, particularly on PCDD/Fs is given in the contingency graph, revealing differences in formation in using different kinds of fuels and appliances (numbers in X axis are denoted as identification of performed runs).

For simplicity, experiments were gathered according to the average value among individual measurements, as a result of the good agreement stated above. With regard to the isomeric pattern of PCDD/Fs, the worst results were obtained using biomass (corn stalk pellets) and bituminous coal. PCDF isomers are more dominating than PCDD. The relative ratio of PCDF/PCDD is characteristic of the use of biomass and bituminous coal for the automatic under-fire boiler, apart from lignite. If the kind of boiler is taken into consideration, changes not only in total quantitative, but also qualitative (isomer) profiles are apparent. The lowest values of PCDD/F were found using hardwood and natural gas. Those results are presented in compatible interpretation of reaction mechanism with and without toxic equivalency factors (TEFs). Complex evaluation in respect to toxicity is outreach of this paper.

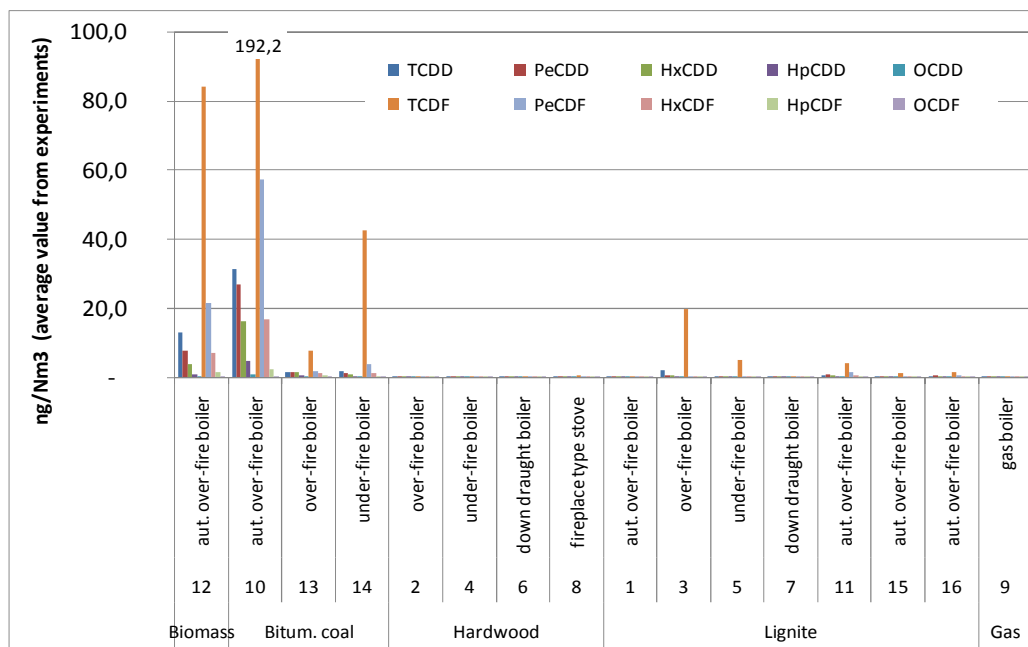


Fig. 4 Contingency data of PCDD/Fs related to fuel / experiments(numbers) / boiler construction

4 CONCLUSIONS

It was shown that data from the presented emission experiment do not fulfill normal distribution that result in using proper transformation before any conclusion based on data analysis is made (if not robust methods are not used, this step is omitted). If estimation of emission factor of PCDD/Fs is made, the fuel used is more critical for taking into account than the boiler used. The worst emission (related to both reaction mechanism in absolute units and with EFs) are expected if different biomass and bituminous coal is used, but this does not apply to different lignite. The hardwood and natural gas is expected to have the best results in terms of the lowest EFs.

5 ACKNOWLEDGEMENTS

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REFERENCES

- [1] Lavric, E. D., Konnov, A. A. and Ruyck, J. D., *Biomass and Bioenergy*, 2004, 26, 115-145.
- [2] Moon, D. H., Hwang, T. W., Park, K. J., et al., *Organohalogen Compounds*, 2006, 68, 2280-2282.
- [3] Jansson, S., Fick, J., Tysklind, M., et al., *Chemosphere*, 2009, 76, 818-825.
- [4] Launhardt, T. and Thoma, H., *Chemosphere*, 40, 1149-1157.
- [5] Dyke, P. H., Foan, C. and Fiedler, H., *Chemosphere*, 2003, 50, 469-480.
- [6] Vierle, O., Launhardt, T., Strehler, A., et al., *Analytica Chimica Acta*, 1999, 393, 131-140.
- [7] Hedman, B., Burvall, J., Nilsson, C., et al., *Waste Management*, 2005, 25, 311-321.
- [8] Pandelova, M., Stanev, I., Henkelmann, B., et al., *Chemosphere*, 2009, 75, 685-691.
- [9] Hopan, F., Horák, J., Dej, M., et al., *Organohalogen Compounds*, 2009, 71, 699-702.

- [10] Horák, J., Hopan, F., Krpec, K., et al., *Organohalogen Compounds*, 2008, 70, 2470-2473.
- [11] Šyc, M., Horák, J., Hopan, F., et al., *Organohalogen Compounds*, 2009, 71, 148-151.
- [12] Meloun, M., Militký, J. and Forina, M., *Chemometrics for analytical chemistry. Volume 1: PC-aided statistical data analysis*, Ellis Horwood, Chichester 1992, 1992.
- [13] Meloun, M., Militký, J. and Forina, M., *Chemometrics for analytical chemistry. Volume 2: PC-aided regression and related methods*, Ellis Horwood, Chichester 1992, 1994.
- [14] Šyc, M., Horák, J., Krpec, K., et al., *Organohalogen Compounds*, 2010, In Press.
- [15] Meloun, M., Hill, M., Militký, J., et al., *Clinical Chemistry and Laboratory Medicine*, 2000, 38, 553-559.
- [16] Meloun, M., Sanka, M., Nemeč, P., et al., *Environmental Pollution*, 2005, 137, 273-280.