



A Comparison of PAH Emission Sampling Methods (Cyclone, Impactor) in Particulate and Gaseous Phase

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ABSTRACT

Four different domestic heating boilers and four types of fuel (lignite, wet wood, wood pellets and mixed fuel) were tested, and the emissions of the particulate matter (PM) and polycyclic aromatic hydrocarbons (PAHs) were correlated. Dekati low-pressure impactor (DLPI, Dekati) sorting of the PM fractions into PM_{0.1}, PM₁, PM_{2.5} and PM₁₀ was used to determine the emission factors of the PAHs in a dilution tunnel via isokinetic sampling and was compared with a cyclone (Tecora). The 4 PAHs were mostly detected on the fine particles of PM₁ in the DLPI and on the fine particles of PM_{2.5} in the cyclone, and in some cases, they were mainly detected in polyurethane foam (PUF) used for the collection of the gas phase placed behind the DLPI and cyclone. The effectiveness of DLPI sampling was generally comparable or lower than the cyclone sampling of the range 0.01–1.33 mg kg⁻¹.

Keywords: Domestic heating; Particulate matter; PAH sampling; Impactor DLPI; Cyclone.

INTRODUCTION

Residential stationary sources, including fireplaces, stoves, cookers, masonry heaters and small boilers with nominal outputs below 50 kW are one of the major sources of emissions; in particular, they accounted for 68.3% of the benzo[a]pyrene and 51.8% of the total PAH emissions (the sum of 4 PAHs according to EMEP/EEA Guidebook (Kubica, 2007; EEA, 2016)). The PAH concentrations are the highest during winter, most probably due to residential heating as a major PAH source (Cazier *et al.*, 2016).

Polycyclic aromatic hydrocarbons (PAHs) comprise a few hundred organic compounds consisting of 2 or more condensed benzene rings. In general, high molecular weight PAHs (4–6 rings) tend to be more concentrated in particle phase, while the ones with lower molecular weight (2–3 rings) are often concentrated in gas phase (Li *et al.*, 2016). PAHs are formed during the incomplete combustion of organic materials at high temperature. UNECE nomenclature for reporting of air pollutants (EEA, 2013) includes only 4 PAHs (benzo[b]fluoranthene (BbF), benzo[k]fluoranthene

(BkF), benzo[a]pyrene (BaP) and indeno[1,2,3-cd]pyrene (INP)), as mentioned in Table S1. These PAHs are mainly bound to particulate matter. Organic matter can be condensed to form particles either via nucleation-condensation or via condensation on existing particles. As a result, organic matter is present as different particle types with various morphologies (Holoubek, 1996; Ravindra *et al.*, 2008; Lisouza *et al.*, 2013; Torvela *et al.*, 2014; Mikuška *et al.*, 2015; Tiwari *et al.*, 2015).

The sampling of particulate matter (PM) from combustion in residential stationary sources is still challenging. The problems of PM formation include the unstable combustion process, especially in manually fed heating appliances due to changeable fuel uptake, the unstable temperature, the amount of flue gases and the changeable combustion rate. It is appropriate to use a dilution tunnel to achieve isokinetic conditions for sampling. Three methods that address the measurement of PM₁₀ and PM_{2.5} in stacks using impactors, virtual impactors and cyclones have been standardized (Bergmans *et al.*, 2014). Impactors, such as the electrical low-pressure impactor (ELPI), the Dekati Low-Pressure Impactor (DLPI), and the Dekati Gravimetric Impactor (DGI) are suitable devices for measuring fine particles (Dekati, 2017). Cascade impactors are air sampling devices that comprise a series of stages whose flow characteristics separate particles into finer fractions (Galarneau *et al.*, 2017). There are several studies that have used DLPI and

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discussed the PAHs emission from the combustion in boilers such as from a pellet boiler with a nominal output of 25 kW, which included 30 PAHs (Lamberg *et al.*, 2011), from different types of boilers considering a sum of 27 PAHs (Johansson *et al.*, 2004), or from biomass boilers with higher nominal outputs (40–50 kW) (Leskinen *et al.*, 2014; Torvela *et al.*, 2014). The PM and PAH emissions from other residential heating facilities, such as stoves and masonry heaters, that used DLPI have been studied, e.g. by Boman and Lamberg (Boman *et al.*, 2005; Lamberg *et al.*, 2011).

The aim of this study was to study the particle phase and gas phase emissions of 4 PAHs from domestic heating boilers of old and modern construction commonly used in Central and Eastern Europe via combustion of different types of fuels. The results of the sampling of particulate matter and consequent PAH analysis obtained by the Dekati Low-Pressure Impactor (DLPI) (Dekati, 2017) were compared with a cyclone that was used simultaneously. To our knowledge, there has been no comparative study of the cyclone and DLPI impactor that focused on PAH emissions from domestic hot water boilers.

MATERIAL AND METHODS

The boilers, fuels, test set-up, conditions and the emission measurements are presented briefly in this section and were described in detail in our previous work (Krpec *et al.*, 2016; Horak *et al.*, 2017). Only 11 of those 25 combustion tests are included in this study. This is due to the time coverage of the DLPI, which was higher than 50% of the time coverage of the cyclone.

Boilers and Fuels

The tested combustion devices (Fig. S1) represent the most frequently used boiler designs for domestic heating in the countries of Central and Eastern Europe. They are described in detail in our previous publications (Krpec *et al.*, 2016; Horak *et al.*, 2017), and the designation of the boilers has been retained as described in our previous publications.

The combustion tests were performed with four different fuels: lignite (L1, L2), wood pellets (WP), wet spruce wood logs (WW) and mixed fuel (MF). The mixed fuel was a mixture of lignite (44%), wet spruce logs (34%) and wood chips (9%) placed into polyethylene terephthalate bottles. The wood chips were soaked with used vegetable frying oil (13%) (Krpec *et al.*, 2016). The elementary compositions and calorific values of the fuels were determined prior to the combustion of each fuel (Table S2).

Test Set-up and Emission Measurements

All tests were conducted in an accredited testing laboratory at the Energy Research Center (VŠB-TU Ostrava). The boilers were operated either at nominal output (P_{nom}) or at reduced output (30% of nominal output, P_{min}) according to their operating manuals and according to the requirements of the EN 303-5:2012 standard. A dilution tunnel was operated by considering the AS/NZS-4013:2014

standard and the EPA Method 5G.

The DLPI (Dekati, Fig. S2) was used to determine the PM concentration and mass-size distribution in the dilution tunnel via isokinetic sampling in the middle of the flue gas stream. The sampling was made with regards to the EN 13284-1 (BSI, 2001), ISO 11338-1 (ISO, 2003) and EN ISO 23210 (ISO, 2009) standards, which do not include the sampling of the PM_1 and $PM_{0.1}$ fractions (Drastichová, 2015). The flue gas was cooled down in the dilution tunnel ahead of the DLPI. The DLPI was heated during collection to a temperature of 80°C to prevent condensation of flue gases and to be closer to the temperature of flue gases in the dilution tunnel. Any diluter was applied ahead of the DLPI. The DLPI enables the sorting of the PM into thirteen different sized fractions with diameters of approximately 0.03 μm to 10 μm . The sums of the particle masses on the individual collection substrates provide the distribution of the PM fractions: $PM_{0.1}$ (0–2 stage), PM_1 (0–7 stage), $PM_{2.5}$ (0–9 stage) and PM_{10} (0–13 stage), Table S3. Behind the DLPI was a polyurethane foam (PUF) for the collection of PAHs in the gaseous phase. The use of PUF is meaningful because, for example, for benzo[a]pyrene, the vapor fraction can represent a significant amount of its total concentration. PUF is an efficient sorbent due to its relatively high capacity, low cost and low impedance (Paolini *et al.*, 2016). The correctness of the results from the DLPI was compared in this study with the results from a cyclone (Tecora) that was simultaneously used in parallel to determine the PM concentration and mass-size distribution. The time coverage of the DLPI in comparison with the time coverage of the cyclone is summarized in Table S4. The results of the EF (emission factor) PAHs from the cyclone are presented in detail in our previous work (Horak *et al.*, 2017).

PAH Analysis

The PAH analysis was performed in the laboratory in the Nanotechnology Centre (VŠB-TU of Ostrava). The purification of PUF before analysis was performed in a Soxhlet extraction apparatus. The quantification of the PAHs was performed via gas chromatography in connection with a mass spectrometer (GC/MS) Trace GC Ultra/TSQ Quantum XLS from Thermo Scientific in simple ion monitoring (SIM) mode. The system was calibrated with a diluted standard solution of PAHs (Absolute Standard, Inc., Part 10017, 2000 $\mu\text{g mL}^{-1}$ in dichloromethane). The blank samples were analyzed together with the samples, and no detectable PAHs were identified in those blanks (in the purified PUFs, aluminum foils, in the solvents or in the extractor vessels). The aluminum foils were analyzed in groups from different DLPI runs from the same combustion tests. The limits of detection were determined to be in the range of < 0.15 to < 1.0 $\text{mg}_{\text{PAH}}/\text{kg}_{\text{fuel}}$. The uncertainty of the PAH analysis was determined to be 23%. The uncertainty of sampling during the combustion tests was defined as 20%; thus, the total uncertainty of the measurement was 30%.

Emission factors (EFs) of the PAHs were used to calculate the participation of individual PAHs in the total PAH emissions.

RESULTS AND DISCUSSION

The EFs of the 4 PAHs as defined by UNECE nomenclature for reporting of air pollutants (EEA, 2013) were discussed in detail. First, the distribution of the 4 PAHs in the PM fractions and PUF was discussed. Furthermore, the overall EFs Σ 4 PAHs from 11 combustion tests were summarized.

Comparison of PAH Emissions from the DLPI and the Cyclone

A comparison of the EF PM from the cyclone and the DLPI was described in our previous study (Krpac et al., 2016). The DLPI enabled sorting of PM fractions into $PM_{0.1}$, PM_1 , $PM_{2.5}$ and PM_{10} , whereas the cyclone enabled sorting of PM into $PM_{2.5}$ and PM_{10} . Particle size is perhaps the most important property that determines particles behavior in a gas (Kantová et al., 2017). The distribution of the 4 PAHs in the particular PM fractions captured by the DLPI is shown in Fig. 1. They can be separated into 4 groups: a) PAHs in $PM_{0.1}$, b) PAHs in $PM_{0.1-1}$, c) PAHs in $PM_{1-2.5}$, and d) PAHs in $PM_{2.5-10}$ (Table S4). Only the time coverage via DLPI sampling that was higher than 50% of the time coverage via cyclone was considered for further discussion (Table S4). Finally, only 11 of the 25 combustion tests were included in this study, and the designation of combustion tests remained as reported in Horak (Horak et al., 2017).

It was reported in the literature (Sahu et al., 2008; Lisouza et al., 2013) that PAHs with a higher molecular weight ($MW > 228 \text{ g mol}^{-1}$) preferentially segregate into

fine particles. The DLPI data showed that 4 PAHs with $MW > 228 \text{ g mol}^{-1}$ were primarily detected (more than 50%) on PM_1 except for tests no. 4, 20, 24 and 25, in which the 4 PAHs were mainly (more than 50%) detected in the gas phase (PUF), and for test no. 3, in which the 4 PAHs were also detected on larger PM and in PUF (Fig. 1, Table S4). The cyclone data showed that 4 PAHs were mostly detected on $PM_{2.5}$, except for test no. 18 in which the 4 PAHs were mainly detected in PUF (Fig. 2, Table S5).

Because in several tests the distribution of the 4 PAHs was comparable or higher in polyurethane foam (PUF) than in the PM of DLPI and its distribution was not negligible (Figs. 1 and 2), the 4 PAHs were further considered as the sum in $PM_{10} + \text{PUF}$.

The effectiveness of the DLPI capture (EFs Σ 4 PAHs in PM_{10}) was mainly lower than or comparable with the cyclone capture (EFs Σ 4 PAHs in PM_{10}), except for the tests no. 1 and 18 (Figs. 3 and 4).

The reasons for the lower DLPI effectiveness are as follows:

i) Any diluter was applied ahead of the DLPI; thus, it was impossible to cover the entire combustion period using one DLPI (column DLPI coverage, Table S4). The two available impactors were used sequentially during the combustion tests with a time delay due to their cleaning, reassembly and pre-heating. The average values measured in the adjacent collections were used to calculate the EFs. The number of used DLPIs is mentioned in Table S4. It is recommended to increase the dilution ratio to cover the entire period of sampling by the DLPI to avoid filling the DLPI or use a diluter ahead of the DLPI.

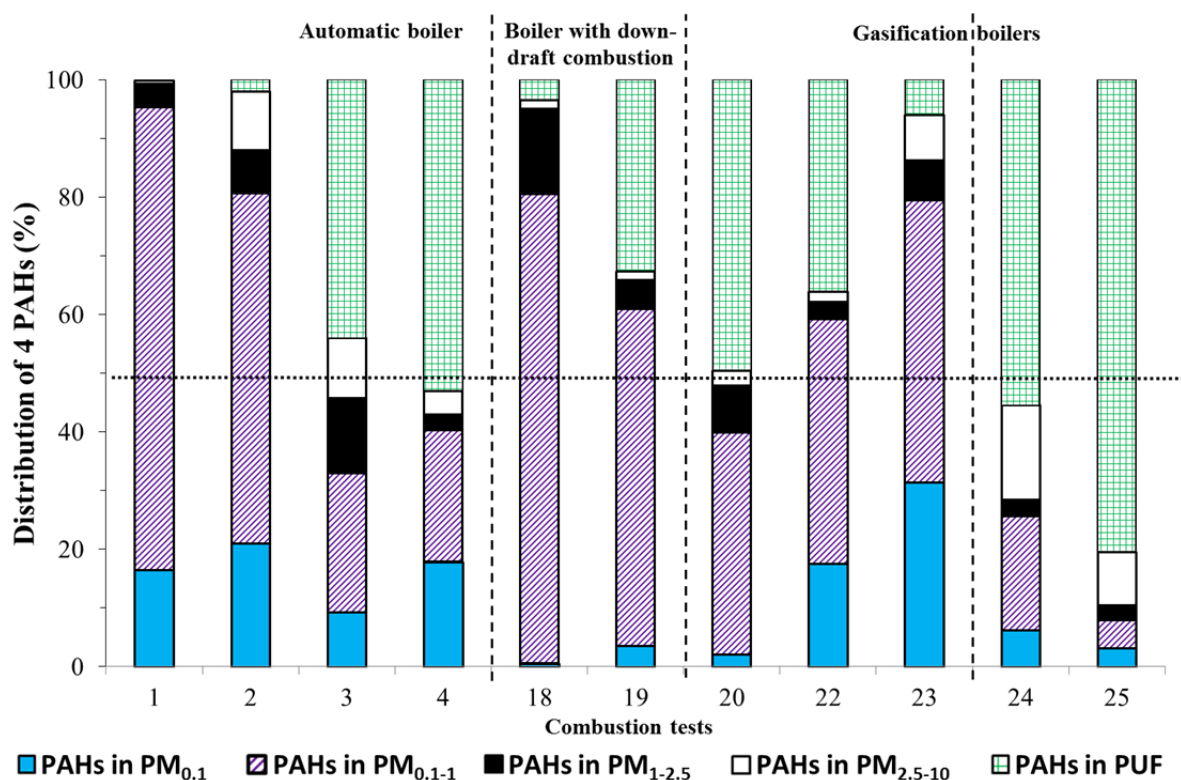


Fig. 1. Distribution of the 4 PAHs in the particulate matter of DLPI and in PUF.

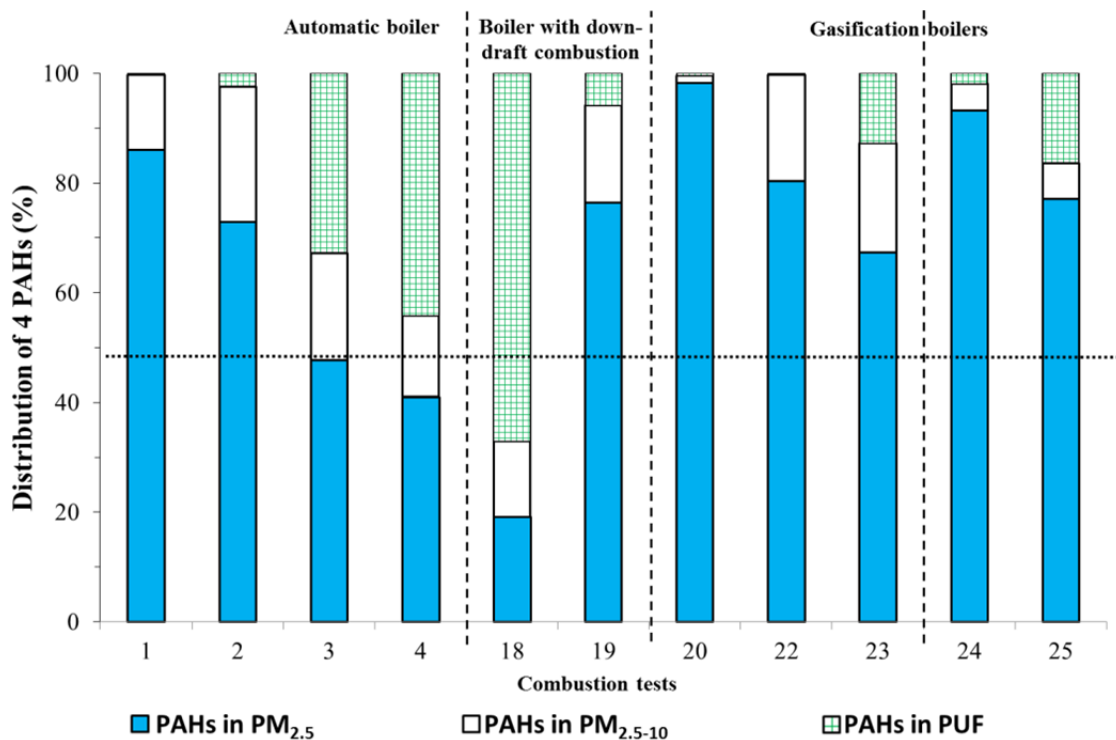


Fig. 2. Distribution of the 4 PAHs in the particulate matter of cyclone and in PUF.

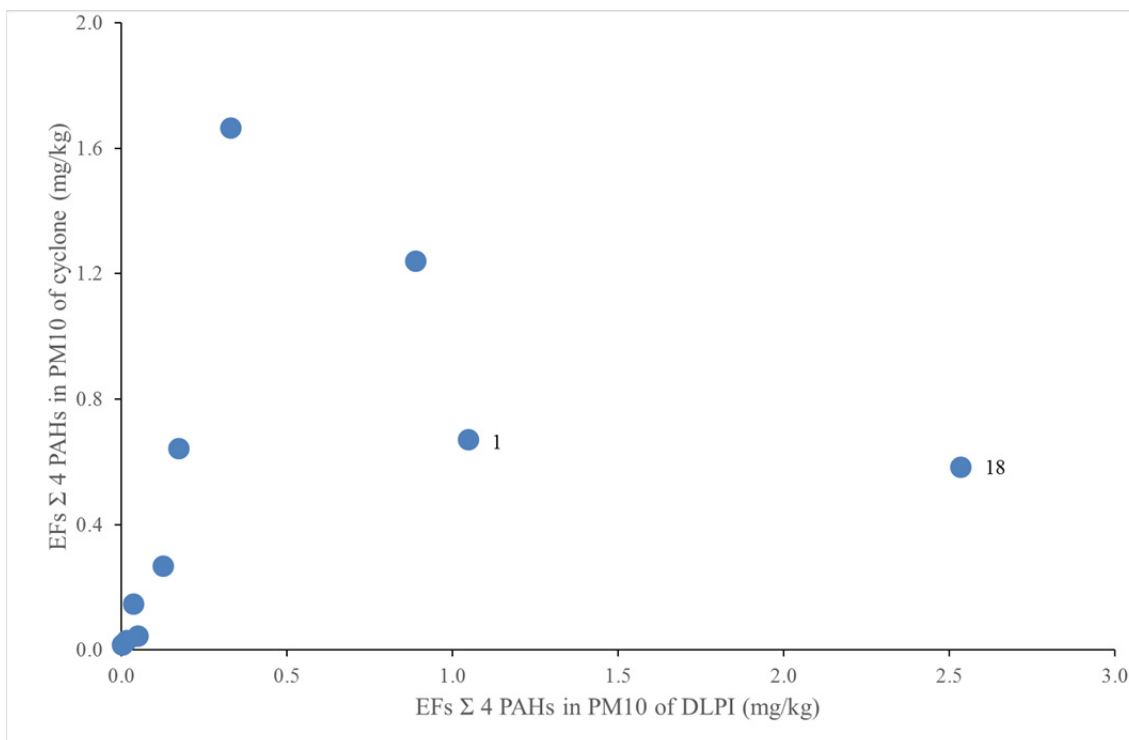


Fig. 3. Dependency graph of EF Σ 4 PAHs in PM₁₀ of the cyclone on the EF Σ 4 PAHs in PM₁₀ of the DLPI.

ii) A decrease of pressure below the 8th stage in the DLPI (< 0.4 bar) could cause desorption of PAHs, especially from the PM₁ fraction, and hence lower the EF Σ 4 PAHs in PM₁₀ that were measured via the DLPI (Hays et al., 2003). A solution could be the use of less stages in the DLPI so the pressure would not be that low and

the pressure would be comparable with the pressure in the dilution tunnel.

The effectiveness of the DLPI and cyclone should be compared by including the rinsing of the DLPI, especially in the case of lighter PAHs; however, the DLPI was rinsed only in tests no. 3 and 4 (not included in Fig. 4).

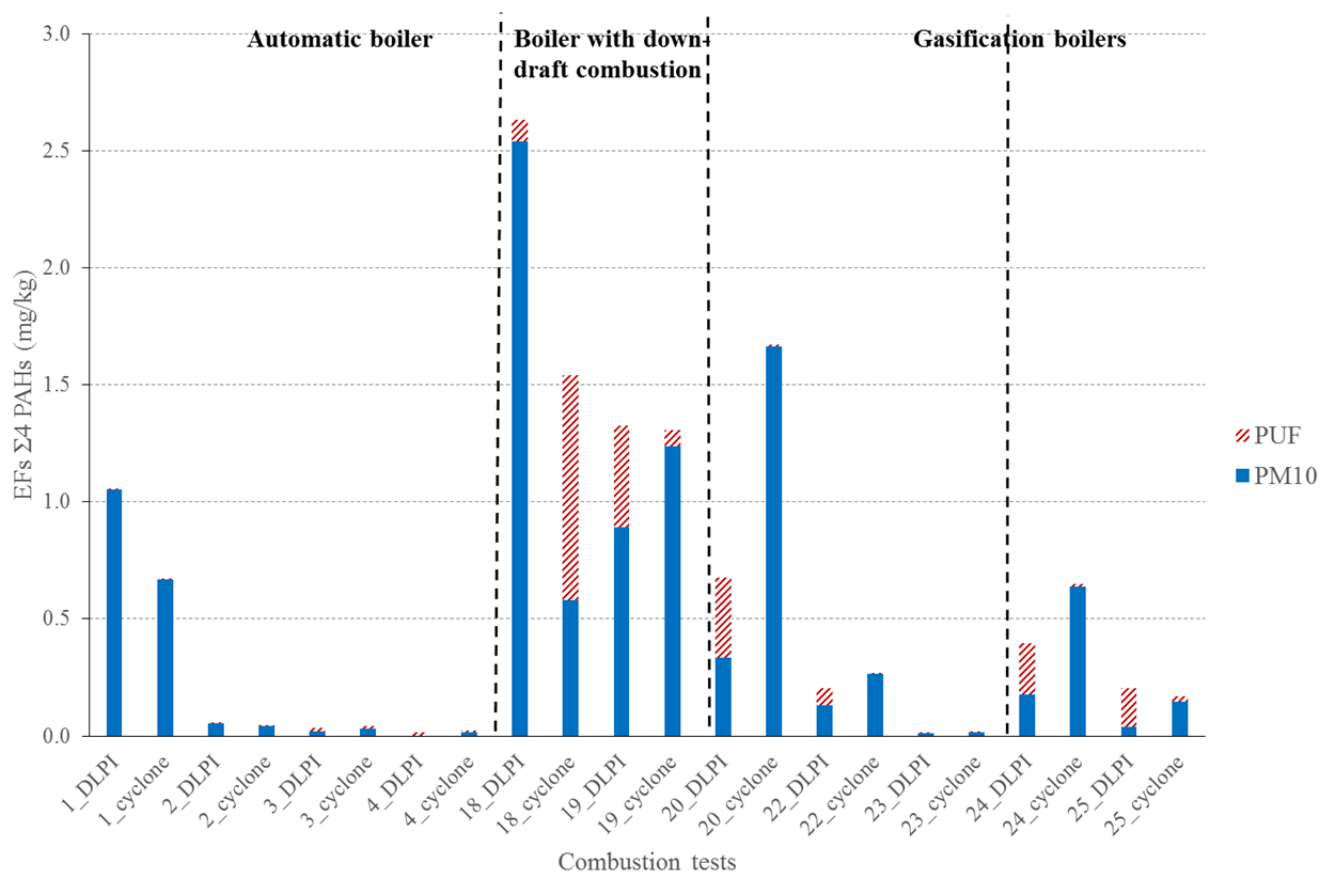


Fig. 4. Comparison of the EF Σ 4 PAHs in the DLPI vs. the cyclone.

The highest EFs of 4 PAHs were observed in the old-type boiler (B3) by comparison of the same fuel and the same conditions of combustion, see Table S4 and Fig. 4. It was confirmed that the efficient combustion at P_{nom} generated lower emissions of 4 PAHs and PM (for all fractions) as compared for B1, B4 and B5 boilers which was reported as well in other studies (Kubica, 2007; Ravindra, 2008).

CONCLUSIONS

One old-designed and three modern domestic heating boilers were tested, and their emissions of particulate matter (PM) and polycyclic aromatic hydrocarbons (PAHs) were compared. A Dekati Low-Pressure Impactor (DLPI, Dekati) sorting of the PM fractions into $PM_{0.1}$, PM_1 , $PM_{2.5}$ and PM_{10} was used to determine the EFs of the 4 PAHs in the dilution tunnel via isokinetic sampling, which was compared with a cyclone. The 4 PAHs were mostly detected in the fine particles of PM_1 in the DLPI, whereas they were detected on the fine particles of $PM_{2.5}$ in the cyclone, and in some cases, they were mainly detected in the PUF used for the collection of the gas phase. The effectiveness of DLPI sampling was generally comparable or lower than the cyclone sampling. This is because one DLPI could not cover the entire duration of combustion tests and had to be replaced several times and PAHs could desorb especially from the PM_1 fraction due to the low pressure in the DLPI. Sampling by the DLPI can possibly be improved by

increasing the dilution ratio in the dilution tunnel to cover the entire period of sampling by the DLPI or by using a diluter ahead of the DLPI.

SUPPLEMENTARY MATERIAL

The results described in the main text of the article are presented in graphs and tables in the Supplementary Material. The schematic diagrams of the tested combustion devices are shown in Fig. S1. The photo of the Dekati Low-Pressure Impactor (DLPI, Dekati) is presented in Fig. S2.

The characteristics of the 4 PAHs are summarized in Table S1. The extensive experimental data are shown in Tables S2 (the specifications of used fuels), S3 (the summary of particulate matter), S4 (EF Σ 4 PAHs in the DLPI fractions) and S5 (EF Σ 4 PAHs in the cyclone fractions).

Supplementary data associated with this article can be found in the online version at <http://www.aaqr.org>.

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