



Polycyclic aromatic hydrocarbons in particulate matter emitted from coke oven battery



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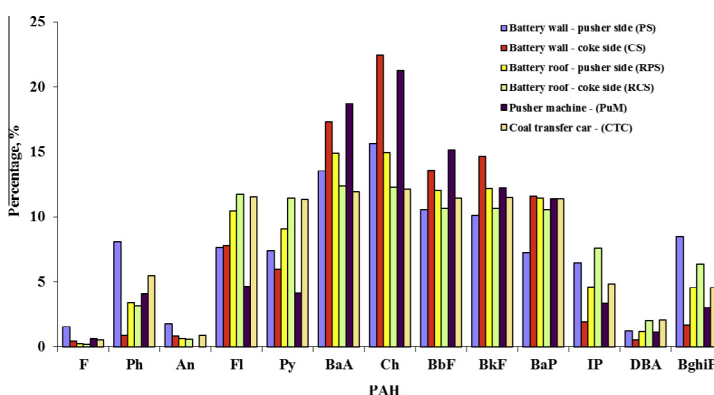
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HIGHLIGHTS

- Determination of 13 PAHs in dust captured in a close neighborhood of coke oven battery has been done.
- Characteristic for coking process ratios of selected pairs as well as PAH's profiles in TSP were determined.
- Investigation was carried out on a plant fulfilling all BAT requirements.
- PAHs analyzes were done with use of gas chromatography techniques.

GRAPHICAL ABSTRACT

Average percentage of individual PAHs in total PAHs bounded with TSP of the coke oven battery sampling zones.



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ABSTRACT

Coke oven battery is one of the main sources of fugitive total suspended particles (TSP) and polycyclic aromatic hydrocarbons (PAHs) in coke plants. In this study the content of selected PAHs associated with the TSP in the immediate vicinity of the coke oven battery Radlin (Poland) was investigated. TSP collection places were located on battery wall, battery roof, pusher machine and coal transfer car. Revealed TSP concentrations were within the range of 0.50–5.15 mg/m³, the total content of PAHs within wide range of 216.6–28018.9 µg/g. Regardless of the concentration level of PAHs connected with the TSP in the coke oven battery surrounding, it was found that four rings PAHs are the main fraction (50–70%). The high average concentrations of benzo[a]pyrene (BaP) and Toxicity Equivalent BaP (BaPeq) reaching 1.29 and 2.63 µg/m³ respectively in the immediate vicinity of coke oven battery, could pose a serious threat to the health of a coking plant workers. Calculated diagnostic ratios BaA/(BaA + Ch), Fl/(Fl + Py), BaP/(BaP + Ch), BbF/BkF, BaP/BghiP, BaA/Ch are characteristic for the coking process.

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1. Introduction

Coke production is found to be the crucial environmental nuisance. This is caused by the fact, that it is not possible to make such process fully hermetic.

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The greatest total dust and gases emission source in the coking industry is the coke oven battery. Among emitted pollutants polycyclic aromatic hydrocarbons (PAHs) are present. The recent interest in emission of PAHs from national coke industry is caused by its high production potential (10 mln Mg/a) which results in its significant share in PAHs emission established at the level of 20 Mg/a, including benzo[a]pyrene – 8 Mg/a. It must be emphasized that, polish coke plants meet all the requirements of European emission standards. The determination of the coke plant impact on the environment mostly is done using emission factors. The estimated emission factors for total PAHs as well as for individual ones are different depending on place and measurement procedures e.g. in studies carried out in 1978–1989 by Bjorseth, Eisenhut, Tonelaar and Duiser the total PAHs emission factors were in range of 2.5–15 g/Mg [1–4]. Despite significant differences in values some similarities also can be found. One is the concentration of particular PAHs group, which is the greatest for lighter, 3–4 rings PAHs (from 74 to 84 wt.%), and then for 5–6 rings PAHs (from 16 to 26 wt.%). It is also found that among 3-ring PAHs share of phenanthrene is very high and reaches up to 45.9% [5]. Further studies carried out by Bendrowski in 1995 allowed to established obligatory emission factors of benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene and indeno[1,2,3-cd]pyrene as both, single compounds and their sum – $\Sigma 4$ PAHs [6].

The determination of qualitative and quantitative composition of PAHs emitted from a given technological process and their appearance in gaseous and solid phases enables to specify PAHs emission source. In case of coke industry, profiles of PAH groups differ in number of rings in the particle or characteristic PAHs ratios (values of mass ratios of individual PAHs and PAH groups present in the dust) and thus are convenient to establish coke oven battery fingerprints and tracers. According to Khalili 89.8% share of naphthalene and 9.4% share of 3-ring PAHs in total amount of 20 determined PAHs can be stated as fingerprint of coke plant [7]. Fluorene present in the air is one of the coke plant tracers [8]. Harrison et al. found that common appearance of particular PAHs was the emission source marker. Hence, chrysene and benzo[k]fluoranthene are coal combustion markers, coronene and phenanthrene are combustion engines emission markers, pyrene, fluoranthene and phenanthrene are waste incineration plant markers, while heating oil combustion results in emission of fluorene, fluoranthene and pyrene together with benzo[b]fluoranthene and indeno[1,2,3-cd]pyrene [9]. In order to determine the share of emission source in PAHs concentration in air, the comparison of PAHs profiles mainly presented in TSP is made [10,11]. Comparing the results obtained in Belgium [12] it was found that ambient air close to steelworks contained anthracene, pyrene, benzo[g,h,i]perylene and chrysene what could be caused by emission from coke oven batteries. Analyses and measurements of PAHs concentration in both, gaseous and solid phases of air samples collected 100 m away from coke oven battery revealed that profiles of PAHs in ambient air significantly depended on wind direction and presence of other sources [13]. PAHs ratios in atmospheric particles have different values depending on emission source. The analysis of coke plant dust performed by Khalili and Simcik revealed characteristic, higher than 5 ratio of BaP/BghiP, 0.79 ratio of Ph/An, 0.7 ratio of BaA/Ch and 2.5 ratio of BeP/BaP [7,8]. In this case values of BaP/BgP or Py/BaP ratios, indicated cars with combustion engines as the main emission source [14–16].

PAHs appear in either gaseous or solid phases or in both of them. Distribution of PAHs between gas and solid phase depends on environmental conditions i.e. ambient temperature, air humidity, particles concentration and PAHs properties i.e. molecular weight, vapor pressure, particles size, surface area and the nature of particulate [17–20], photochemical degradation and radical reactions [21,22]. Airborne PAHs with less than three aromatic

rings (mol wt. 128–178) are gaseous, whereas PAHs with five or more rings (mol wt. >228) occur in the solid phase [23–25]. Lee et al. established the level of PAHs bound to airborne particulates in ambient air around the traffic source in the range 28.3–67.3% (46.1% in average). Simultaneously, the mean particle phase distribution of total PAHs in the urban and rural atmospheres was only 18.7% and 20.6%, respectively [17]. Ravindra et al. indicated that concentration of PAHs in gaseous phase was 10 times higher than in particles of dust present in analyzed samples. However, the share of PAHs stated as hazardous reaches ca. 55% in solid phase, while in gaseous phase it is only 2% [12].

2. Experimental

The study was based on a modern coke oven battery in Radlin Coke Plant fulfilling best available technique (BAT) requirements, and it comprises determination of PAHs concentration in TSP in direct proximity to coke oven battery, investigation of PAHs profiles and characterization of their composition to indicate emission source markers. The battery was built in 2009, it contains 2 blocks which comprise 43 coking chambers of dimensions (mm) 15900 × 5000 × 500 each, its coke production capacity reaches 750 thousand Mg/a. The charging of chambers is done using stamp method, while coke quenching by means of wet method. The pneumatic sealing of ascension pipes closure is applied. For limitation of pollutants emissions during chambers discharging coke transfer machine is equipped with integrated suction hood followed by dedusting installation. The dedusting process is carried out in 2 devices arranged in series i.e. cyclone and bag filter [26].

Points, where air polluted with gases and dust emitted from the battery in unorganized manner were sampled, had been determined considering different phases and conditions of coking process.

TSP samples were collected in the nearest surrounding of coke oven battery (Fig. 1). This manner of samples collection reduces the possible PAHs transformations, caused by chemical reactions i.e. oxidation, phototransformation and interaction with other compounds as well as influence of others PAHs sources to minimum.

TSP samples were collected on 17th and 18th of September 2009 by Staplex® TFIA Series High Volume Air Samplers (The Staplex® Company, New York, USA). Sampler was equipped with SH 810 Filter Holder Assemblies. During the measurements, the weather conditions were as follows: temperature 15–16 °C, absence of rain, wind velocity below 3 m/s and pressure 973 hPa.

The mass of the sampled dust was determined gravimetrically (Sartorius balance, resolution 0.01 g). Before each weighing, the filters were conditioned for at least 48 h at the air temperature of 20 ± 1 °C and air relative humidity of $50 \pm 5\%$ in the weighing room.

The sampling was carried out for 1 h, the volumetric air flow was greater than 50 dm³/min and the volume of collected air reached about 3.5 m³.

2.1. Sample preparation and analysis of PAHs

Samples of TSP was extracted from filters in ultrasonic bath with dichloromethane (CH₂Cl₂). The extract was percolated, washed and dried in helium atmosphere. The dry residue was diluted in propanol-2 (CH₃CH(OH)CH₃) and next distilled water was added to receive alcohol/water volume ratio 15/85. For selective purification, the obtained samples were solidified (SPE) via extraction in columns filled with octadecylsilane – C-18, (Supelclear™ ENVI-18 Tubes, Supelco USA). PAHs were eluted with the use of dichloromethane. The extract of PAHs was thickened by helium atmosphere to volume of 0.5 cm³.

A Perkin Elmer Clarus 500 gas chromatograph equipped with a flame ionization detector (FID) was used. An RTX-5 (Restek)

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