

Short Communication

PAH Concentrations Inside a Wood Processing Plant and the Indoor Effects of Outdoor Industrial Emissions

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Abstract

Our study was aimed at assessing the effects of indoor and outdoor emission sources on indoor and outdoor concentrations of ambient particulate matter (PM) and PM-bound polycyclic aromatic hydrocarbons (PAHs) in a small sawmill in Silesia, Poland. The concentrations of total suspended particles (TSP), of their respirable fraction (PM₄), and of 16 PM₄- and TSP-bound PAHs were measured. The indoor PM emission sources (i.e. the saw and other tools for wood processing) did not cause a significant hazard to the sawmill workers. Nonetheless, the concentrations of the 16 PAH mixtures within the sawmill were high, especially indoors. Such high indoor PM-bound PAH concentrations were due to sawdust-adsorbing PAHs coming from industrial PAH sources beyond the sawmill (a cokery).

Keywords: sawmill, particulate matter, respirable dust, health hazard, persistent organic pollutants

Introduction

Until the late 1990s, the basis for the Silesian economy could have been very aptly identified with heavy industry and hard coal excavation [1, 2]. Later, after two decades of Polish economic evolution, these sectors lost their importance in favor of other, less heavy industries, and now small and medium-sized companies from the sectors of commerce, craft, service, construction, transport, and accommodation, etc. are 99% of all the business entities in Silesia Province [3]. This change in the structure of employment thoroughly rearranged the Silesian occupational health hazard inventory.

Usually, the air inside factory production buildings is polluted – with what depends on the factory profile [4-8]. The hazard to the workers depends on the type and concentration of the pollutants [9-11]. The concentrations of some production-related substances at some worksites, e.g. assembly lines, are routinely controlled according to the law [12]. However, in some circumstances foreign pollutants coming from outdoor sources are more hazardous to indoor workers than the production-related substances released inside buildings. Outdoor emissions from the factory neighborhood can then degrade the indoor air more than emissions from production.

The goal of the study was to apportion between outdoor and indoor sources the concentrations of total suspended

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particles (TSP), its respirable sub-fraction of the particles with aerodynamic diameter not greater than 4 μm (PM_{10}), and of some polycyclic aromatic hydrocarbons (PAHs), adsorbed on these particles, in a sawmill. The sawmill was equipped with several wood-processing lines situated in relatively tightly closed halls. It was located in Biskupice, in a heavily polluted quarter of Zabrze, a city in the Upper Silesia Agglomeration. There were some industrial utilities nearby, including a large cokery.

Material and Methods

We selected six sampling points within the sawmill area (Fig. 1). Two points, P1 and P2, were located in building B1, P1 at the saw and P2 at the other end of the building, practically beyond the effect of sawing. Point P3 was located in open shed B2, where wood-sawing occurs for 1 to 3 hours a day. Point P4 was located at sawmill entrance gate G, practically on the factory area border. Points P5 and P6 were located in the main production building B3, P5 at the main sawmill line, and P6 at the control room far from the production utilities.

Two SKC aspirators (Blandford, Dorset, U.K.) were located at each sampling point, at about 1.6 m above ground level – one adjusted to sample PM_{10} , the second to sample TSP. Within 05.03.2014–15.04.2014, at each point, four eight-hour samples of both PM_{10} and TSP were taken according to the Polish Norms [13, 14], which defines the method for making measurements at worksites with the use of an SKC aspirator.

The quartz fiber filters (QMA, $\phi 25$ mm, CAT No. 1851-025; Whatman, GE Healthcare Bio-Sciences Corp.; Piscataway, NJ, USA) were mounted on and taken away from the aspirators in a laminar airflow cabinet. Prior to sampling, the quartz fiber filters were baked at 600°C for at least 6 h to remove any traces of organics. The dust-loaded substrates, right after their weighing, were put into Petri dishes wrapped light-tightly in aluminum foil and stored in a freezer (-18°C) until analysis.

The masses of the samples were determined by weighing the substrates before and after exposure (MYA 5.3Y.F microbalance; RADWAG, Radom, Poland; resolution of 1 μg). They were conditioned in the weighing room (air humidity of 45±5%, air temperature 20±2°C) for 48 hours before each weighing.

To determine the PM_{10} -bound PAH concentrations, all four samples of PM_{10} or TSP from a sampling point were put together to make one cumulative sample of PM_{10} or TSP, respectively. These cumulative samples were extracted and the extracts were chromatographically examined for the presence of naphthalene (Na), acenaphthylene (Acnl), acenaphthene (Acn), fluorene (Flu), phenanthrene (Phen), anthracene (An), fluoranthene (Flt), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Ch), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (IP), dibenzo[ah]anthracene (DahA), and benzo[ghi]perylene (BghiP) (Fig. 1).

The extraction, the chromatography technique, and validation parameters are described in [15, 16].

Four coefficients were computed expressing the hazards from the mixture of the 16 PAHs (ΣPAH): carcinogenic equivalent (CEQ), mutagenic equivalent (MEQ), TCDD-toxic equivalent (TEQ), and the share of the carcinogenic PAHs ($\Sigma\text{PAH}_{\text{carc}}$) in (ΣPAH). The coefficients and the methods for their computing are described in [15].

Results and Discussion

According to the Ordinance of the Minister of Labor and Social Policy, the sawdust contained in the inhalable fraction of ambient dust is the only air contaminant whose ambient concentrations is obligatorily measured at worksites in Polish sawmills. In the meaning of the Ordinance, the inhalable dust fraction is the whole of TSP [12]. However, the hazard from TSP to workers comes mainly from respirable dust, PM_{10} . In the case of the investigated sawmill utilities, the hazard was not great, the PM_{10} and TSP concentrations (both 8-h and averaged) were below the permissible limits at all measuring points (Fig. 1).

The highest concentrations of PM_{10} occurred at P1, P2, P4, and P6, in average 45, 48, 30, and 23 $\mu\text{g}\cdot\text{m}^{-3}$, respectively; except for P4, all in the production halls (Fig. 1). At P3 and P5, the 8-h PM_{10} concentrations varied between 8 and 18 $\mu\text{g}\cdot\text{m}^{-3}$ and the average concentrations were 16 and 13 $\mu\text{g}\cdot\text{m}^{-3}$, respectively.

At P2, P5, and P6 in the production halls, the average concentrations of TSP were 845, 589, and 601 $\mu\text{g}\cdot\text{m}^{-3}$, respectively, and at P5 at the gate to the sawmill: 555 $\mu\text{g}\cdot\text{m}^{-3}$. At P3, in the open shed, and at P1, at the saw for cutting logs into lumber, they were 149 and 161 $\mu\text{g}\cdot\text{m}^{-3}$. At P3 and P1 the PM_{10} mass content of TSP was high compared to other points. At P1 it was highest and varied from 11 to 59%, and its four-measurement average was 28% (Fig. 1). At P3 the average PM_{10} content of TSP was 10%, at the rest of the points it was less than 10%.

Compared to the outdoor points, the wood processing itself appeared not to elevate significantly the indoor sawdust concentrations nor the shares of respirable fraction in TSP. The highest concentrations of PM_{10} were noted at P1, at the main saw, but they were only a little higher than the PM_{10} concentrations at P4 at the gate to the sawmill.

Instead, the PAH concentrations in the sawmill were enormously high (Fig. 1). The highest occurred in building B1 at the saw, at P2, where the TSP-bound ΣPAH concentration reached 1,425 $\text{ng}\cdot\text{m}^{-3}$; the PM_{10} -bound ΣPAH concentrations at P2 was 329 $\text{ng}\cdot\text{m}^{-3}$. Although the TSP-bound ΣPAH concentrations at P3 and P6 were two times lower than at P2, the PM_{10} -bound ΣPAH concentrations at these points, 365 and 335 $\text{ng}\cdot\text{m}^{-3}$, were similar to this at P2. At P1, at the other end of B1, the PM_{10} - and TSP-bound ΣPAH concentrations were lower than at P2. The differences between P1 and P2 in the ΣPAH concentrations were proportional to the differences in the dust concentrations

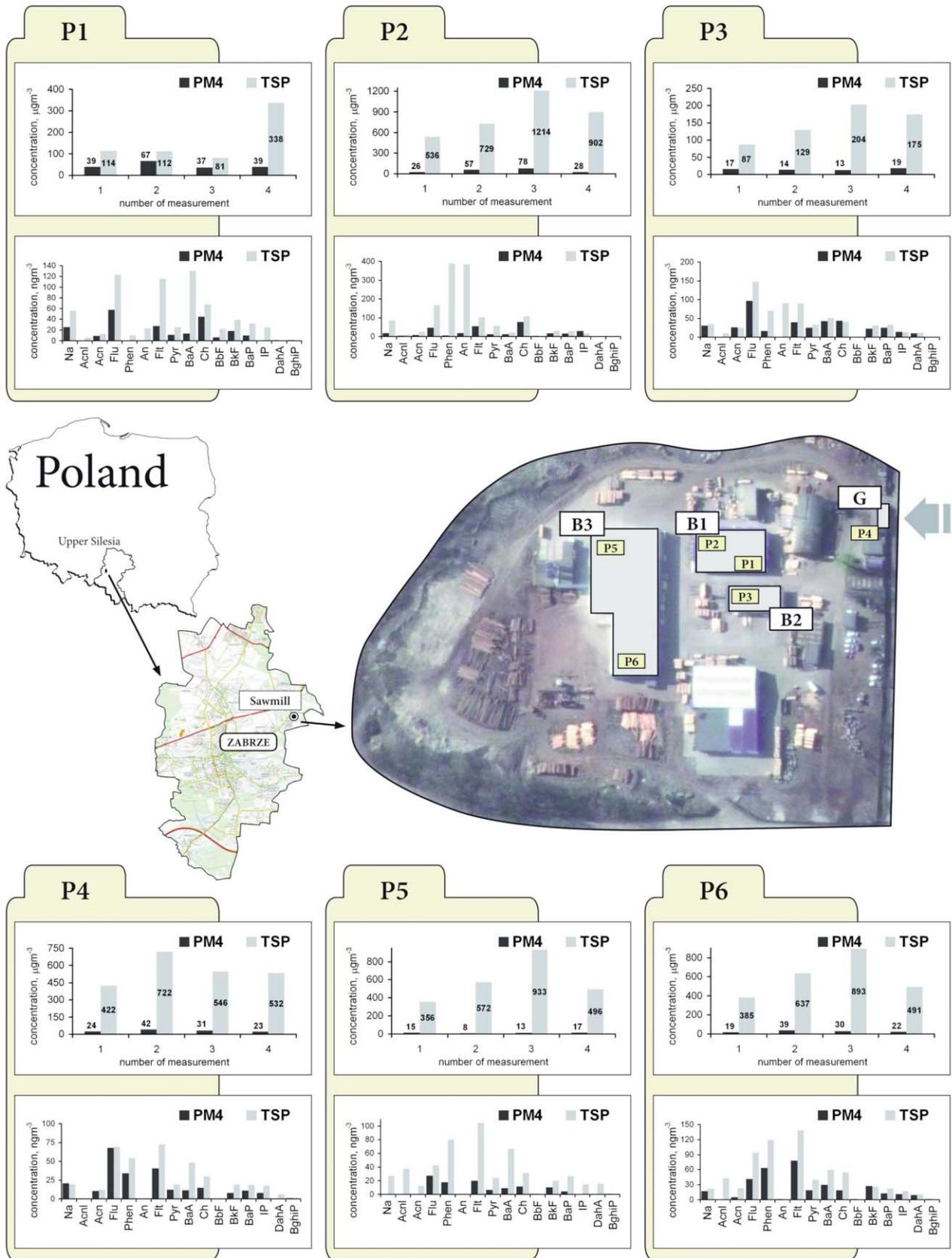


Fig. 1. Location of the sampling points, 8-h concentrations of PM₄ and TSP, and the average concentrations of PM₄- and TSP-bound PAHs in the sawmill.

Table 1. PAH profiles at the six sampling points in the sawmill.

PM fraction, location	16 PAHs ranked by ambient concentrations growing from left to right															
PM ₄ , P1	Acnl	Phen	IP	DahA	BghiP	Pyr	Acn	BaA	BkF	BbF	An	Na	Flt	BaP	Ch	Flu
TSP, P1	BbF	DahA	BghiP	Acnl	IP	BaA	Acn	BaP	BkF	Pyr	Na	Flt	Ch	Flu	An	Phen
PM ₄ , P2	An	DahA	BghiP	Acnl	BbF	Acn	Phen	BaP	IP	Pyr	BkF	Na	Ch	Flt	Flu	BaA
TSP, P2	DahA	BbF	Acnl	Phen	Acn	BghiP	BaA	Pyr	BaP	BkF	An	Na	IP	Flu	Flt	Ch
PM ₄ , P3	Acnl	BbF	BghiP	DahA	IP	Phen	BkF	BaP	Acn	Na	Pyr	Flt	BaA	Ch	An	Flu
TSP, P3	Acnl	An	BbF	DahA	BghiP	BkF	IP	Acn	BaP	BaA	Pyr	Ch	Na	Phen	Flt	Flu
PM ₄ , P4	An	BbF	BghiP	Acnl	DahA	IP	Acn	Pyr	BkF	BaP	Na	Ch	BaA	Phen	Flt	Flu
TSP, P4	Acnl	An	BbF	BghiP	DahA	Acn	IP	BaP	Na	Pyr	BkF	Ch	BaA	Phen	Flu	Flt
PM ₄ , P5	Na	Acnl	Acn	An	BbF	IP	DahA	BghiP	BaP	Pyr	BaA	BkF	Ch	Phen	Flt	Flu
TSP, P5	Acnl	An	BbF	BghiP	DahA	BaP	IP	Na	Acn	BkF	Pyr	Ch	BaA	Flu	Phen	Flt
PM ₄ , P6	An	BbF	BghiP	Acn	IP	DahA	BkF	Pyr	Na	BaP	Ch	Acnl	Flu	BaA	Phen	Flt
TSP, P6	An	BbF	Acn	BghiP	DahA	IP	Na	Ch	Pyr	BaP	BkF	BaA	Flu	Acnl	Phen	Flt

between these points. At gate G, beyond the sawmill installations, the PM₄- and TSP-bound Σ PAH concentrations were 240 ng·m⁻³ and 387 ng·m⁻³. They were low compared to the concentrations at other points, but still high compared to the concentrations in the region [17, 18].

Table 2. PAH diagnostic ratios for the six sampling points in the sawmill.

PM fraction, location	Flt/(Flt+Pyr)	BaA/(BaA+Ch)	BaP/BghiP
Coal/coke [20, 22-24]	0.53	0.5	>1.25
Coke in Upper Silesia [8]	0.54 (0.5-0.6)	0.47 (0.40-0.51)	3.9 (1.37-12.18)
Wood burning [20, 22-26]	>0.5	0.86	0.9-6.6
PM ₄ , P1	0.71	0.23	75.06
TSP, P1	0.64	0.17	58.00
PM ₄ , P2	0.82	0.66	4.23
TSP, P2	0.82	0.14	1.94
PM ₄ , P3	0.55	0.49	252.65
TSP, P3	0.77	0.44	36.72
PM ₄ , P4	0.78	0.57	25.97
TSP, P4	0.79	0.62	3.31
PM ₄ , P5	0.76	0.44	33.69
TSP, P5	0.78	0.52	55.84
PM ₄ , P6	0.81	0.68	3.41
TSP, P6	0.80	0.62	3.78

Practically, there was no dependence between the dust concentrations and the Σ PAH concentrations (linear correlation coefficient was $R^2=0.52$). Neither were the concentrations of particular PAHs correlated linearly with the dust concentrations ($R^2<0.35$). Such correlations would occur if the dust and its PAH content were of common provenance.

The PAH profiles at different points differed (Table 1). However, among the 16 PAHs, at almost each sampling point, Ch, Flt, BaA, BkF, and Pyr, the PAHs typical of the emissions from hard coal combustion or coking [19-21], had the highest concentrations. Additionally, the profile of PM₄-bound PAHs was similar to the profile of TSP-bound PAHs at each point, and at P3 and P4 in the open air very similar, making common origin of the PM₄- and the TSP-bound PAHs highly probable.

Usually, fine and coarse particles come from different sources and their PAH contents (PAH profiles) entirely differ [19, 20, 22]. The similarity of the profiles would not be surprising if the PM₄ mass shares in TSP were very high, but in the sawmill they were not, except for PM at P1.

The residual doubts were removed by computing the values of diagnostic ratios (proportions of particular PAH concentrations [8, 20, 22-26]), which matched the values of such ratios for PAHs from coal combustion and coking (Table 2).

The three ratios assumed values close to those for PAHs from coking and coal combustion. The Flt/(Flt+Pyr) were slightly higher than those for coking (Table 2), so besides coal combustion and coking the combustion of wood in ovens (neighboring houses and allotment gardens) might be a source of PAHs in the sawmill [27]. Within the sawmill itself, there were no PAH sources – neither wood nor fossil fuels were burnt, and all the tools in use were electric. Wood burning caused by the process of sawing (dull or

Table 3. Concentrations of Σ PAH and BaP and the values of the indicators of the exposure to the PAH mixture (CEQ, MEQ, TEQ, and Σ PAH_{carc}/ Σ PAH) for PM₄- and TSP-bound PAHs at the sampling points in the sawmill (present study) and selected locations in Upper Silesia (literature).

PM fraction, location	BaP	CEQ ^{a)}	MEQ ^{b)}	TEQ ^{c)}	Σ PAH _{carc} / Σ PAH ^{d)}
	ng·m ⁻³			pg·m ⁻³	
PM ₄ , P1	9.97	14.38	15.48	116.06	0.42
TSP, P1	32.23	55.01	61.39	293.66	0.46
PM ₄ , P2	16.41	23.79	30.75	145.32	0.47
TSP, P2	29.01	41.55	40.87	193.16	0.14
PM ₄ , P3	25.56	86.79	39.72	166.60	0.40
TSP, P3	33.31	102.76	49.03	206.50	0.26
PM ₄ , P4	11.01	14.07	15.53	53.36	0.22
TSP, P4	18.41	56.27	32.23	138.07	0.36
PM ₄ , P5	4.45	6.59	6.53	53.47	0.33
TSP, P5	26.92	114.98	44.26	160.48	0.35
PM ₄ , P6	13.05	68.91	25.08	171.01	0.33
TSP, P6	22.72	86.28	39.69	183.84	0.28
Złoty Potok, winter, regional background [15]	4.03	5.85	4.87	7.36	0.52
Katowice, winter, urban background [15]	12.48	18.46	20.47	91.95	0.56
Katowice, winter, highway [15]	14.27	106	29.54	147.79	0.63
Złoty Potok, summer, regional background [15]	2.46	4.50	4.29	13.8	0.5
Katowice, summer, urban background [15]	2.97	5.29	4.23	13.71	0.59
Katowice, summer, highway [15]	4.73	15.46	6.45	20.42	0.55
Zabrze, summer, crossroads [16]	1.1	1.48	1.9	10.29	0.48
Ruda Śląska, summer, road [16]	0.3	1.57	0.87	6.62	0.84
Zabrze, winter, urban background [18]	16.09	25.04	25.24	116.03	0.66

^{a)} carcinogenic equivalent CEQ=0.001×[Na]+[Acn]+[Acn]+[Flu]+[Phen]+[Flt]+[Pyr]+0.01×([An]+[Ch]+[BghiP])+0.1×([BaA]+[BbF]+[BkF]+[IP])+1×[BaP]+5×[DahA]; values of 0.001, 0.01, 0.1, and 1 are the so-called toxic equivalence factors (TEF) for specific PAHs, taken from the [30];

^{b)} mutagenic equivalent MEQ=0.00056×[Acn]+0.082×[BaA]+0.017×[Ch]+0.25×[BbF]+0.11×[BkF]+1×[BaP]+0.31×[IP]+0.29×[DahA]+0.19×[BghiP]; values of 0.00056, 0.082, 0.017, 0.25, 0.11, 1, 0.31, 0.29, 0.19, and 0.01 are the so-called minimum mutagenic concentrations (MMC) for specific PAHs, taken from the study [31];

^{c)} TCDD-toxic equivalent TEQ= 0.000025×[BaA]+0.00020×[Ch]+0.000354×[BaP]+0.00110×[IP]+0.00203×[DahA]+0.00253×[BbF]+0.00487×[BkF]; values of 0.000025, 0.00020, 0.000354, 0.00110, 0.00203, 0.00253, and 0.00487 are the so-called TCDD-TEF, i.e., toxic equivalency factor relative to 2,3,7,8-tetrachlorodibenzo-p-dioxin TCDD (for TCDD, TEF = 1.0) for specific PAHs, taken from the study [32];

^{d)} the share of the carcinogenic PAHs (Σ PAH_{carc}; [33]) in (Σ PAH) Σ PAH_{carc}/ Σ PAH=(BaA+BaP+BbF+BkF+Ch+DahA+IP)/([Acn]+[Acn]+[Flu]+[Phen]+[An]+[Flt]+[Pyr]+[BaA]+[Ch]+[BbF]+[BkF]+[BaP]+[DahA]+[BghiP]+[IP]).

dirty blade, warped blade, etc.) was not observed in the sampling period. Usually, even if such malfunction occurs, it is handled rather instantly and cannot be considered a significant source of PAHs.

Because there were no PAH sources within the sawmill, municipal emissions (from heating) were negligible because the sampling period was rather hot, and one of the biggest Silesian cokeries was about 200 m north of the sawmill, the hard coal coking was assumed to account for

such enormously high PM-bound PAH concentrations in the sawmill. The high indoor PAH concentrations can be accounted for by PAH absorption and accumulation in sawdust, a very efficient sorbent of gaseous substances [28, 29]. Elsewhere in Zabrze, in the open air, they are lower [18, 25], probably because they naturally propagate in the atmosphere [20]. Accordingly, at the outdoor P4 (at the sawmill gate) they were the lowest among the PAH concentrations in the sawmill.

Therefore, the sawmill workers are exposed to hazard from high indoor PAH concentrations. The CEQ for the PM₄-bound 16 PAH mixture was from 6.59 to 86.79 ng·m⁻³, and for the TSP-bound from 41.55 to 114.98 ng·m⁻³, depending on the sampling point. They were high, elsewhere in Silesia they are much lower (Table 3). Such high values of CEQ were noted only at a highway in Katowice, the capital of Silesia, in winter. The MEQ and TEQ in the sawmill were also high, such that their values were noted in Silesian cities (Zabrze, Katowice) only in winter (Table 3). However, the share of $\sum\text{PAH}_{\text{carc}}$ in $\sum\text{PAH}$ (i.e. $\sum\text{PAH}_{\text{carc}}/\sum\text{PAH}$) was not higher than 47% at any point; in other regions of Silesia it happens to be higher.

This resemblance of the mixture PAH hazard coefficients in the sawmill to the coefficients in big cities in winter ensures that the PAHs in the sawmill came from a high-temperature processing of hard coal (combustion or/and coking).

Conclusions

The pilot research shows that the concentrations of PM₄ and TSP within the sawmill are not so high as to be hazardous. The mass shares of potentially hazardous PM₄ in TSP at the main saw and other wood processing equipment were higher than elsewhere in the sawmill, but the differences were not great.

The real hazard to the indoor workers came from the PM-bound PAHs. The indoor concentrations of PM-bound $\sum\text{PAH}$ in the sawmill were very high. The PAH profiles at the sampling sites and the values of the diagnostic ratios suggest that the PAHs came from hard coal coking or combustion (of coal or wood). Because there is no such PAH source within the sawmill, the PAHs were assumed to come from the nearby coking plant. Less than half of the 16 PAHs were heavier BaA, BaP, BbF, BkF, Ch, DahA, or IP (carcinogens); this and the PAH profiles suggest that the majority of the mass of PAHs to be found in the sawmill were light gaseous PAHs adsorbed on the developed surface of sawdust particles. The intense PAH emissions from the cokery and the high adsorption capacity of the sawdust combine to cumulate PAH in amounts sufficient to cause indoor PAH concentrations in the sawmill comparable to PAH concentrations along a highway in winter.

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