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Automobile Tires—A Potential Source of Highly Carcinogenic Dibenzopyrenes to the Environment

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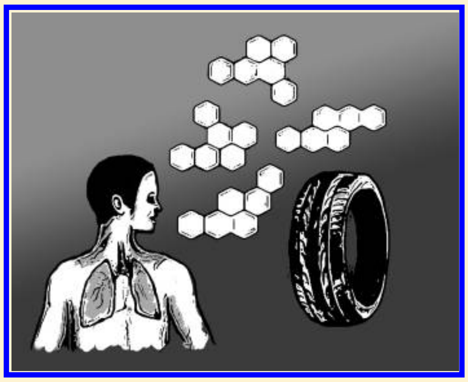
Supporting Information



ABSTRACT: Eight tires were analyzed for 15 high molecular weight (HMW) polycyclic aromatic hydrocarbons (PAH), using pressurized fluid extraction. The variability of the PAH concentrations determined between different tires was large; a factor of 22.6 between the lowest and the highest. The relative abundance of the analytes was quite similar regardless of tire. Almost all (92.3%) of the total extractable PAH content was attributed to five PAHs: benzo[*ghi*]perylene, coronene, indeno[1,2,3-*cd*]pyrene, benzo[e]pyrene, and benzo[a]pyrene. The difference in the measured PAH content between summer and winter tires varied substantially across manufacturers, making estimates of total vehicle fleet emissions very uncertain. However, when comparing different types of tires from the same manufacturer they had significantly ($p = 0.05$) different PAH content. Previously, there have been no data available for carcinogenic dibenzopyrene isomers in automobile tires. In this study, the four dibenzopyrene isomers dibenzo[*a*,*l*]pyrene, dibenzo[*a*,*e*]pyrene, dibenzo[*a*,*i*]pyrene, and dibenzo[*a*,*h*]pyrene constituted <2% of the sum of the 15 analyzed HMW PAHs. These findings show that automobile tires may be a potential previously unknown source of carcinogenic dibenzopyrenes to the environment.

INTRODUCTION

Technological improvements and regulatory requirements regarding exhaust emissions derived from road traffic have led to a significant decrease in particles from tail pipe emissions.[1] However, traffic related nonexhaust particles remain largely unchanged, making these emissions increasingly significant contributors to the environmental burden of particles as exhaust particle emissions decrease. Sources of nonexhaust particles associated with vehicles include: brake lining, tire and road-surface wear, and resuspension of road dust.[1] It has been suggested that nonexhaust sources constitute a substantial part of vehicle-derived particle emissions.[2−5] Using emission-factor models, 50−85% of traffic-generated PM_{10} (particles measuring 10 μm or less) were attributed to nonexhaust sources.[4] Experimentally determined emission factors for traffic-generated PM_{10}, measured in a street canyon, showed that up to 60% by weight of the total traffic related particles had a nonexhaust origin.[2] Resuspension of road dust has been recognized as the predominant source of PM_{10} in urban air.[3,5] Road dust is a chemically complicated mixture with a multitude of sources, including natural sources (e.g., soil, plant fragments and other biological materials) and traffic-related sources.[6]

In general, particles from nonexhaust sources have larger aerodynamic diameters than do particles originating from tail-pipe emissions.[7] However, Dahl and co-workers found in 2006 that a significant amount of submicrometer particles were produced at the road-tire interface.[8] Some studies indicate that most of the particles produced from wear of tire treads and road surfaces are deposited on the road surface;[9] however, some become airborne, either through direct emission or resuspension, and could constitute as much as 5% by weight of the total suspended particles in inner-city air.[10] It has been suggested that airborne tire-debris particles have a bimodal size-distribution that could constitute as much as >90% by weight of particles with an aerodynamic diameter below 1 μm, with the remaining part made up by particles with an aerodynamic diameter larger than 10 μm.[10] This would mean that a significant fraction could be deposited deep into the respiratory system when inhaled and that tire-tread-wear particles could be transported far from their sources of emission.[10] On the basis of measurements of molecular markers for tire debris in cities in Japan it was estimated that tire-tread-wear particles, collected at a rooftop, contributed to approximately 0.8% of the total PM_{10} concentration.[11] The largest tire-tread-wear particles will deposit in the direct vicinity of the source of emission. However, urban runoff and wind erosion may transport these particles to other environmental compartments, such as sediments, soils, and sewage sludge.[9] Nevertheless, there are still large gaps in our knowledge regarding both the total

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amount and the size distribution of particulate tire-wear emissions.

Automobile tire rubber is composed of 40−60% rubber polymers, 20−35% reinforcing agents/fillers such as carbon black or silica, and 15−20% mineral oils such as extender oils/softeners.[12] The composition of the rubber depends on where in the tire the rubber is used.[12] The less abundant components include vulcanization agents, vulcanization activators, vulcanization accelerators, protective agents, and processing aids.[12] Highly aromatic (HA) oils used as extender oils or softeners in the tire-manufacturing process are rich in PAHs, many of which are classified as carcinogenic/mutagenic environmental toxins with the potential to cause negative long-term effects both in humans and in the aquatic environment.[13,14] The PAH concentration in these oils ranges between 10 to 30%.[15] Owing to the potential hazard of HA oil usage, their use has been regulated by EU Directive 2005/69/EC,[13] which forbids HA oils in rubber manufacturing as a measure to phase out these PAH-rich oils and replace them with low-PAH alternatives such as mild extracted solvates (MES) and treated distillate aromatic extracts (TDAEs). Any new tire or tire tread used for retreading manufactured after first January 2010 may not contain any extender oil with more than 1 mg kg^{-1} benzo[*a*]pyrene (B[*a*]P) or more than 10 mg kg^{-1} of the sum of the eight PAHs: B[*a*]P, benzo[*e*]pyrene (B[*e*]P), benzo[*a*]anthracene (B[*a*]A), chrysene (CHR), benzo[*b*]fluoranthene (B[*b*]F), benzo[*j*]fluoranthene (B[*j*]F), benzo[*k*]fluoranthene (B[*k*]F), and dibenz[*a,h*]anthracene (DB[*a,h*]A).[13] Tires that were manufactured prior to this date are not covered by these threshold values and may still be sold on the market. It has been estimated that the replacement of HA-oils will reduce the PAH emission originating from tire-tread-wear by 98%.[16] Another material known to contain PAHs used in tire manufacturing is carbon black.[17,18] Carbon black is a form of elemental carbon used as reinforcement material in the tire rubber to give the tire its desired properties in abrasion resistance and tensile strength.[17]

The Swedish National Chemicals Inspectorate estimated that 10 × 10^6 kg of tire rubber is worn and released into the environment annually in Sweden, giving a rough estimate of annual emission of 60 kg of B[*a*]P.[12] The annual tire-tread-wear emission in other countries has been estimated to the following: Italy, 50 × 10^6 kg;[19] USA, 500 × 10^6 kg;[20] Germany, 60 × 10^6 kg;[21] Denmark, 7.3 × 10^6 kg;[10] Australia, 20 × 10^6 kg.[22] Tire-tread-wear has been pointed out as an important anthropogenic source of PAHs in road dust.[23−25] However, other studies have emphasized the importance of other sources, such as road-surface wear,[26] automobile exhaust,[27] and leaking engine oil.[28]

Previous measurements of PAHs in tires have demonstrated that the sum of PAHs analyzed differs widely and is ranging between 16.1 to 226 μg g^{-1}.[6,11,23−27,29] The past studies include different PAHs in their analyses and a few of them report data on >252 Da PAHs. Many of these earlier studies recognize pyrene (PYR) as the predominant PAH in tires, with a relative abundance ranging between 23.9−49.1%.[6,11,23,25,29] Benzo[*ghi*]perylene (B[*ghi*]P) has been recognized as the second or third most abundant PAH in a few of these past studies.[23,25,29]

There has not so far, to our knowledge, been any data reported on the mutagenic/carcinogenic dibenzopyrenes; dibenzo[*a,l*]pyrene (DB[*a,l*]P), dibenzo[*a,i*]pyrene (DB[*a,i*]P) and dibenzo[*a,h*]pyrene (DB[*a,h*]P) in automobile tires, and the literature regarding B[*a*]P is scarce. Dibenzo[a,e]pyrene (DB[*a,e*]P) have previously been determined in recycled tire rubber granulates used in artificial-turf playing fields,[30] data for the other dibenzopyrene isomers were however not reported. B[*a*]P, being the most well-studied individual PAH, is commonly used as a surrogate PAH to assess the mutagenicity and carcinogenicity of a PAH mixture.[14] Dibenzopyrene isomers have been suggested to be even more mutagenic/carcinogenic than B[*a*]P,[14] which might lead to an underestimation of the carcinogenicity of a PAH-containing matrix if solely the B[*a*]P concentration is taken into account.[31] Data available of dibenzopyrenes in other urban emission sources are diesel[32,33] and gasoline particulate emissions.[33] The reported concentrations vary, however, depending on vehicle and driving conditions.[33]

The aim of the present study was to determine dibenzopyrenes in tires in order to evaluate the importance of automobile tires as a source of dibenzopyrenes to the environment using a previously developed method for the 15 HMW (>252 Da) PAHs; B[*b*]F, B[*k*]F, B[*e*]P, B[*a*]P, perylene (Per), indeno[1,2,3-*cd*]fluoranthene (Ind[1,2,3-*cd*]F), indeno[1,2,3-*cd*]pyrene (Ind[1,2,3-*cd*]P), DB[*a,h*]A, picene (Pic), B[*ghi*]P, coronene (Cor), DB[*a,l*]P, DB[*a,e*]P, DB[*a,i*]P and DB[*a,h*]P.

■ EXPERIMENTAL SECTION

Chemicals and Solvents. The solvents hexane, toluene, methyl-*tert*-butyl ether (MTBE), and methanol were of HPLC grade and were purchased from Rathburn Chemicals Ltd., U.K. Ethanol (absolute, Ph. Eur.) was from VWR International S.A.S Fontenay-sous-Bois, France. PAH standard compounds used in this study were as follows: perdeuterated benzo[*a*]pyrene (B[*a*]P-D$_{12}$) (98%, Larodan Fine Chemicals AB, Sweden), perdeuterated coronene (Cor-D$_{12}$) (98%, Chiron AS, Norway), perdeuterated dibenzo[*a,i*]pyrene (DB[*a,i*]P-D$_{14}$) (98%, LGC Promochem, Sweden), B[*b*]F and B[*k*]F (99% and 98% respectively, Chem Service, West Chester, PA, U.S.A.), B[*j*]F (Larodan Fine Chemicals AB, Sweden), B[*e*]P (98%, Sigma-Aldrich, St. Louis, MO, U.S.A.), B[*a*]P (98%, Sigma-Aldrich), Per (>99.5%, Sigma-Aldrich, Ind[1,2,3-*cd*]F (98%, Radiant Dyes, Wermelskirchen, Germany), Ind[1,2,3-*cd*]P (98%, AccuStandard Inc., New Haven, CT, U.S.A.), DB[*a,h*]A (99%, Fluka AG, Switzerland), Pic (99.5%, Larodan Fine Chemicals AB), B[*ghi*]P (98%, Janssen Chimica, Belgium), Anthanthrene (ANTH) (L. Light & Co., Colnbrook, England), Cor (>99.5%, Janssen Chimica), DB[*a,l*]P (96%, Accustandard Inc.), DB[*a,e*]P (98%, LGC Promochem), DB[*a,i*]P (96%, Sigma-Aldrich), and DB[*a,h*]P (>99.5%, Koch-Light Laboratories LTD, England). Concentrations of calibration standards and internal standard solutions were corrected with respect to neat-compound purity.

Tire Samples. Eight makes of tire from four different manufacturers were used in this study. The analyzed tires consisted of three summer tires, two nonstudded winter tires and three studded winter tires. One make of tire was from AGI, two makes of the tires were from Bridgestone, two makes of the tires were from Michelin and three makes of tires were from Nokian, a more detailed description of the analyzed tires is given in Table S1 of the Supporting Information, SI. Two tires of each make were analyzed in triplicate. The tire treads were abraded using a coarse stainless steel file at between two and four different locations on each tire. The tire samples were obtained from VTI (the Swedish National Road and Transport Research Institute) where they had previously been used in road simulation studies.[34] All of the analyzed tires were manufactured before the first of January 2010.

Tire-Particle Extraction and Sample Preparation. Between 10 and 30 mg of tire particles were weighed on a circular, glass microfiber filter (Ø = 25 mm, Whatman International Ltd., England) on a Mettler Toledo XP6 microbalance, d = 1 μg (Mettler-Toledo International Inc., Greifensee, Switzerland). The amount of tire particles needed was determined by an initial screening of the different makes of tires. The glass microfiber filters were wrapped in larger microfiber filters (Ø = 47 mm, Whatman International Ltd., England) to reduce the amount of fine tire-particles in the extracts. The filters were inserted into 5 mL ASE 200 extraction cells. B[*a*]P-D_{12}, Cor-D_{12}, and DB[*a,i*]P-D_{14} were added as surrogate standards.

The tire particles were extracted with toluene and methanol (9:1 v/v) at 200 °C and 3000 psi using an ASE 200 accelerated solvent extraction system (Dionex Corporation, Sunnyvale, CA, U.S.A.). Detailed analytical extraction operating conditions have been presented elsewhere.[35] The tire particles were analyzed batch-wise with one procedural blank per batch. The extraction cells were dissembled and cleaned between each batch. The cell bodies and end-caps were cleaned using ultrasonication (Sonicor SC-100−22, Sonicor Instrument Corporation, Copiague, NY, U.S.A.) in ethanol; frits and polyether ether ketone (PEEK) seals were cleaned using ultrasonication in hexane. The polytetrafluoroethylene (PTFE) O-rings for extraction-cell end-caps was changed between each batch to minimize the risk of cross-contamination and leakage.

The extracts were evaporated using a TurboVap LV evaporator (Zymark Corp., Hopkinton, MA, U.S.A.) at 60 °C under a gentle stream of nitrogen to a volume of less than 15 mL and transferred into disposable test tubes. Extracts were evaporated to a volume of approximately 0.5 mL and added to preconditioned (with 4 mL hexane) 100 mg silica solid-phase extraction (SPE) cartridges (Isolute IST, Biotage AB, Uppsala, Sweden). The walls of the test tubes were rinsed with 0.5 mL hexane and the rinsate was added to the corresponding SPE cartridge. The nonpolar fraction, containing the targeted analytes, was eluted with 2 mL hexane and collected in disposable test tubes. The eluate was evaporated to approximately 0.3 mL and transferred into a microinjection vial for instrumental analysis. In samples where the PAH concentrations were anticipated to be low the extract was further concentrated in the microinjection vial to a volume of approximately 0.1 mL. The recovery rate for the SPE cleanup has been published elsewhere.[36]

The extraction efficiency was determined by performing three subsequent analytical extractions, using the above-mentioned instrumental parameters on one tire sample. Cor-D_{12} was added as a volumetric internal standard prior to instrumental analysis. The analysis was carried out with a procedural blank and in triplicate.

The procedural blanks showed amounts less than 1% of the individual determined amounts for most of the targeted PAHs. However, in some batches the PAHs Ind[1,2,3-*cd*]F and Pic in the blank samples amounted to 7% and 8%, respectively, of that of the analyzed tire in the same batch. The source of this is not known; but small tire particles, which escape the glass microfiber filters, tend to get stuck in the metallic frits of the ASE cells as a result of the high operating pressure. Ind[1,2,3-*cd*]F and Pic were not highly abundant in the analyzed tires, making it unlikely that Ind[1,2,3-*cd*]F and Pic, and not all PAHs are showing elevated concentrations, thus cross-contamination is not the cause. However, Ind[1,2,3-*cd*]F and Pic made only a minor contribution to the total PAH contents.

Online High Performance Liquid Chromatography (HPLC)−Gas Chromatography (GC)−Mass Spectrometer (MS) Analysis of PAH. The online HPLC−GC−MS system was a Varian 9012 Inert solvent delivery system (Varian Inc., Palo Alto, CA, U.S.A.) with a CMA/200 microsampler (CMA Microdialysis AB, Sweden) coupled to an Agilent 6890N gas chromatograph (Agilent Technologies, Palo Alto, CA, U.S.A.) equipped with an Agilent 5973N MSD system (Agilent Technologies). The system setup and workings have been described in detail elsewhere.[36,37]

The selected PAHs were separated from alkanes and lower molecular weight PAHs using back-flush HPLC. The separation was carried out on a 125 × 4.00 mm i.d. Five μm particle-size, nitrophenyl-propyl silica column (Phenomenex, Torrance, CA, U.S.A.) with a C8 Guard-PAK HPLC-precolumn from Waters (Millipore Corp., Milford, MA, USA) using MTBE:hexane (1:1, v/v) as the mobile phase. The back-flush peak containing the targeted analytes was introduced into the programmable-temperature vaporizer−equipped gas chromatograph.

Gas chromatographic separation was performed on a DB-17MS capillary column (J & W Scientific, Folsom, CA, U.S.A.) of dimensions 60 m × 0.25 mm i.d. with 0.15 μm film thickness equipped with a 5 m × 0.25 mm guard column (J & W Scientific). Helium was used as the carrier gas with a flow of 1.0 mL min^{-1} operating in constant-flow mode. The temperature program was as follows: an initial temperature of 80 °C which was held for 8.50 min, a 40 °C min^{-1} ramp to 200 °C, followed by a second 10 °C min^{-1} ramp to a final temperature of 315 °C, which was held for 67 min, giving a total run time of 90 min.

Data acquisition and processing was done with MSD Chemstation D.02.00.275 (Agilent Technologies). Peak identity was assigned according to compound-specific molecular ion m/z values along with the relative retention time for each compound. In ambiguous cases (e.g., DB[*a,l*]P and DB[*a,i*]P), standard addition was used to identify the correct peak. Native PAHs were quantified using single-point calibration.

DB[*a,i*]P was not fully baseline-resolved from another 302 m/z solute, and as the gas chromatographic column wore out through extensive use the peak resolution tended to decrease (Figure S1, available as SI). This was also observed for DB[*a,l*]P where this isomer began to coelute with another solute. Additionally, the peaks of DB[*a,h*]A and Ind[1,2,3-*cd*]P, normally not separated on a new column, drifted apart as the column wore down. This has been observed for other matrices such as urban air and diesel particulate matter.[38] The chromatogram in Figure S1 of the SI reveals additional peaks that were identified as PAHs through their mass spectra, (Figure S2 of the SI). Peak A was identified as a 252 Da PAH and peaks B and C were identified as 276 Da PAHs. These peaks were observed in selected ion monitoring (SIM) mode in all of the analyzed samples. Peak A, was positively identified as B[*j*]F comparing the retention time and mass spectra with an authentic standard. Peak C was identified in the same fashion as ANTH. The identity of Peak B still remains unknown. B[*j*]F and ANTH were not included in the calibration standard and are not quantified in any of the analyzed tire samples.

RESULTS AND DISCUSSION

Evaluation of the Extraction Efficiency of Tire Rubber Matrix. Pressurized fluid extraction has previously been

Table 1. Measured PAH Concentrations $(\mu g\ g^{-1})$ in the Analyzed Tires[a]

	tire 1A summer $n = 6$	tire 2B studded winter $n = 6$	tire 3B summer $n = 6$[b]	tire 4C winter $n = 6$[c]	tire 5C studded winter $n = 6$	tire 6D studded winter $n = 6$	tire 7D summer $n = 6$	tire 8D winter $n = 6$	average for all tires $n = 48$[d]
B[*b*]F	1.88 ± 0.21	1.54 ± 0.39	3.18 ± 0.38	0.166 ± 0.069	0.196 ± 0.081	2.94 ± 0.71	0.727 ± 0.100	2.35 ± 0.37	1.62 ± 1.16
B[*k*]F	0.321 ± 0.058	0.403 ± 0.088	0.589 ± 0.121	0.0216 ± 0.0089	0.0367 ± 0.0215	1.02 ± 0.29	0.222 ± 0.034	0.833 ± 0.134	0.430 ± 0.360
B[*e*]P	7.29 ± 0.90	4.53 ± 0.80	6.66 ± 0.69	0.611 ± 0.123	0.865 ± 0.197	5.74 ± 1.00	1.59 ± 0.20	4.79 ± 0.76	4.01 ± 2.58
B[*a*]P	6.41 ± 0.67	7.06 ± 1.75	4.02 ± 0.46	0.269 ± 0.049	0.550 ± 0.090	10.1 ± 1.7	2.33 ± 0.30	8.50 ± 1.31	4.91 ± 3.60
per	1.08 ± 0.56	0.709 ± 0.162	1.09 ± 0.11	0.104 ± 0.070	0.200 ± 0.140	1.11 ± 0.24	0.294 ± 0.036	0.895 ± 0.142	0.685 ± 4.78
Ind[1,2,3-*cd*]F	0.0189± ± 0.0026	0.0513 ± 0.0269	0.0907 ± 0.0179	0.00121 ± 0.00079	0.00479 ± 0.00168	0.102 ± 0.039	0.0226 ± 0.0026	0.0814 ± 0.0082	0.0476 ± 0.0416
DB[*a.h*]A	0.0990 ± 0.0170	0.0915 ± 0.0245	0.0949 ± 0.0066	0.00586 ± 0.00293	0.0136 ± 0.0027	0.146 ± 0.029	0.0368 ± 0.0043	0.115 ± 0.012	0.0752 ± 0.0498
Ind[1,2,3-*cd*]P	8.08 ± 1.07	9.23 ± 2.30	6.48 ± 0.69	0.373 ± 0.121	0.877 ± 0.253	14.0 ± 2.5	3.38 ± 0.42	11.1 ± 1.3	6.70 ± 4.78
pic	0.140 ± 0.027	0.0370 ± 0.0083	0.538 ± 0.045	0.0324 ± 0.00861	0.0343 ± 0.0080	0.0366 ± 0.0070	0.0229 ± 0.0035	0.0559 ± 0.0065	0.112 ± 0.168
B[*ghi*]P	33.1 ± 3.8	26.4 ± 4.1	17.0 ± 1.7	1.24 ± 0.24	3.23 ± 1.05	31.2 ± 3.4	7.67 ± 0.92	24.6 ± 3.1	18.1 ± 12.2
DB[*a,l*]P	0.0105 ± 0.0016	0.0126 ± 0.0059	0.0307 ± 0.0042	0.00223 ± 0.00105	0.000929 ± 0.000200	0.0187 ± 0.0032	0.00575 ± 0.00075	0.0192 ± 0.0034	0.0124 ± 0.0096
DB[*a,e*]P	0.154 ± 0.013	0.150 ± 0.050	0.392 ± 0.029	0.0120 ± 0.0047	0.0155 ± 0.0032	0.264 ± 0.033	0.0764 ± 0.0048	0.208 ± 0.015	0.159 ± 0.124
cor	26.4 ± 2.2	17.2 ± 2.7	12.5 ± 1.1	0.936 ± 0.106	1.56 ± 0.07	18.2 ± 2.6	4.25 ± 0.51	13.5 ± 0.7	11.8 ± 8.7
DB[*a,i*]P	0.160 ± 0.100	0.334 ± 0.099	0.511 ± 0.049	0.0164 ± 0.0041	0.0212 ± 0.0077	0.709 ± 0.154	0.0938 ± 0.0159	0.720 ± 0.113	0.321 ± 0.289
DB[*a,h*]P	0.0281 ± 0.0095	0.0242 ± 0.0095	0.0675 ± 0.0053	0.00392 ± 0.00205	0.00380 ± 0.00067	0.0665 ± 0.0110	0.0168 ± 0.0023	0.0594 ± 0.0033	0.0338 ± 0.0262
total PAH	85.2 ± 7.5	67.7 ± 12.4	53.2 ± 5.1	3.79 ± 0.54	7.61 ± 1.44	85.7 ± 12.7	20.7 ± 2.5	67.9 ± 7.6	49.0 ± 32.6

[a] The values presented are the mean and standard deviation of two different individual tires of the same make. The letters A–D indicate different manufacturer. [b] $n = 5$ for DB[*a,l*]P. [c] $n = 5$ for Ind[1,2,3-*cd*]F and DB[*a,l*]P. [d] $n = 47$ for Ind[1,2,3-*cd*]F and $n = 46$ for DB[*a,l*]P.

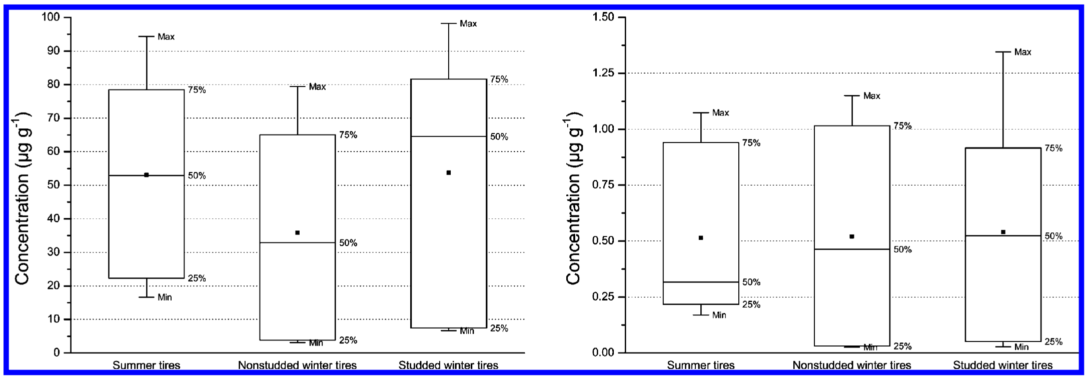

Figure 1. Box plots showing the total PAH content (left) and the sum of dibenzopyrenes (right) in the different types of tires. Values indicated are as follows: maximum, minimum, 75th and 25th percentiles, median (50%) and mean (line with black square).

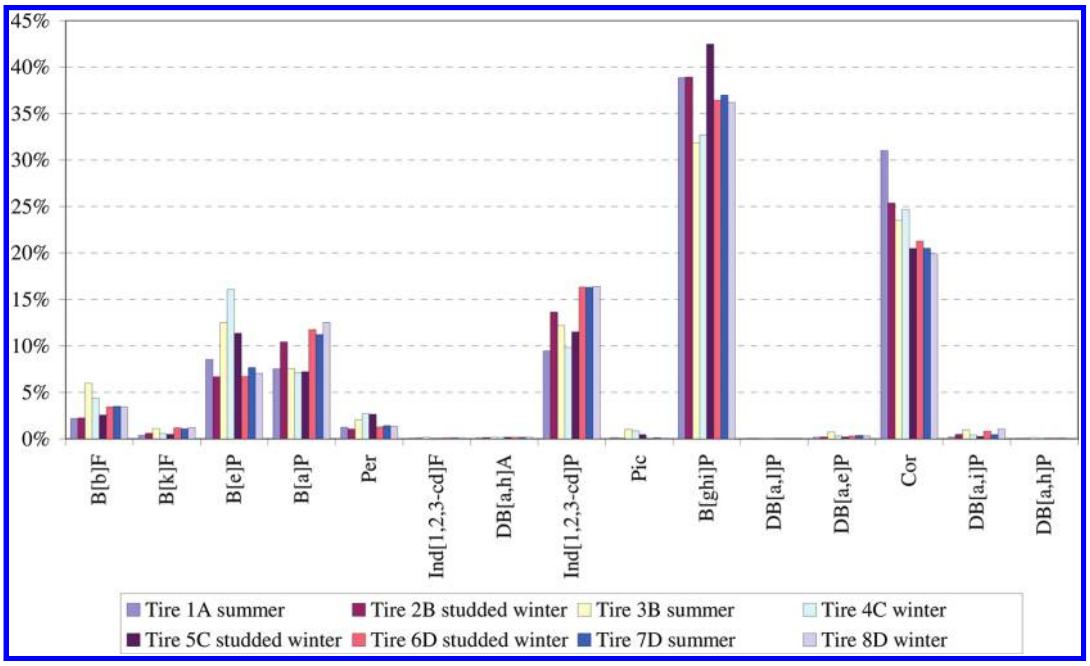

Figure 2. Mean relative abundance of the quantified PAHs in each make of tire.

demonstrated to be highly efficient for extracting the PAHs considered in this study from diesel particulate matter,[38] which is a difficult extraction matrix.[39,40] A mixture of toluene and methanol (9:1, v/v) was used as the extraction solvent in this present study, which has been shown to increase the amount of B[*a*]P extracted from the standard reference material, SRM 2975 Diesel Particulate Matter, compared to the certified value assigned by NIST.[35] Table S2 of the SI shows the recoveries for the native PAHs and the surrogate standards B[*a*]P-D_{12} and DB[*a*,*i*]P-D_{14}, calculated as the percentage recovery at each analytical extraction step of the total quantified amount of all analytical extractions combined. Each targeted PAH was quantified against the added volumetric internal standard Cor-D_{12}. This extraction procedure recovered 88.7−98.8% of the native PAHs in the first analytical extraction step, leading to the conclusion that one analytical extraction is sufficient for an exhaustive extraction of the selected PAHs. The surrogate standards were also more readily extracted compared to their native analogues, 98.8% and 99.7% for DB[*a*,*i*]P-D_{14} and B[*a*]P-D_{12}, respectively, presumably as a result of not being incorporated into the rubber matrix.

HWM PAHs in Tires. The PAH content varied significantly across the different tires (Table 1). The total dibenzopyrene and B[*a*]P concentrations differed by a factor of up to approximately 31 and 38, respectively, between the lowest and highest measured concentration. The total PAH content (sum of 15 HMW PAHs) differed by a factor of up to 23 between different tires. The median total PAH contents of all summer (53 μg g^{-1}), nonstudded (33 μg g^{-1}) and studded (65 μg g^{-1}) winter tires (Figure 1), irrespective of manufacturer, did not differ significantly using a Kruskal−Wallis test at 5% significance level. Likewise for the sum of all dibenzopyrene isomers (Figure 1), no significant difference was found in the median contents of the summer and winter tires.

For the dibenzopyrene isomer that is considered to be most toxic, DB[*a*,*l*]P,[14] the mean contents were 16, 11, and 11 ng g^{-1} (median: 10, 14, and 11 ng g^{-1}) for summer, nonstudded, and studded tires, respectively. Summer tires had a lower PAH content than did studded and nonstudded winter tires from the same manufacturer (Table 1). This was probably a result of different raw materials, but could also have been because of different manufacturing processes. The total PAH content of tire 8D winter was more than 300% higher than that of Tire 7D

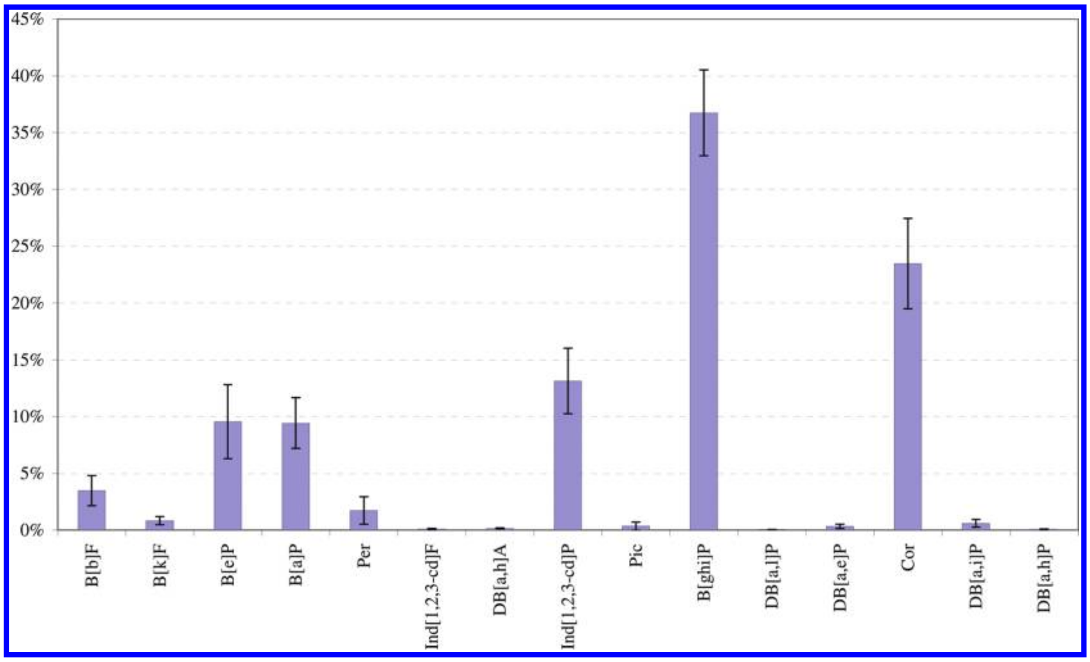

Figure 3. Mean relative abundance in all of the analyzed tires; error bars show one standard deviation from the mean value. Mean and standard deviation were calculated from the concentration determined in all samples of all analyzed tires (n = 48, except for Ind[1,2,3-*cd*]F: n = 47 and DB[*a*,*l*]P: n = 46).

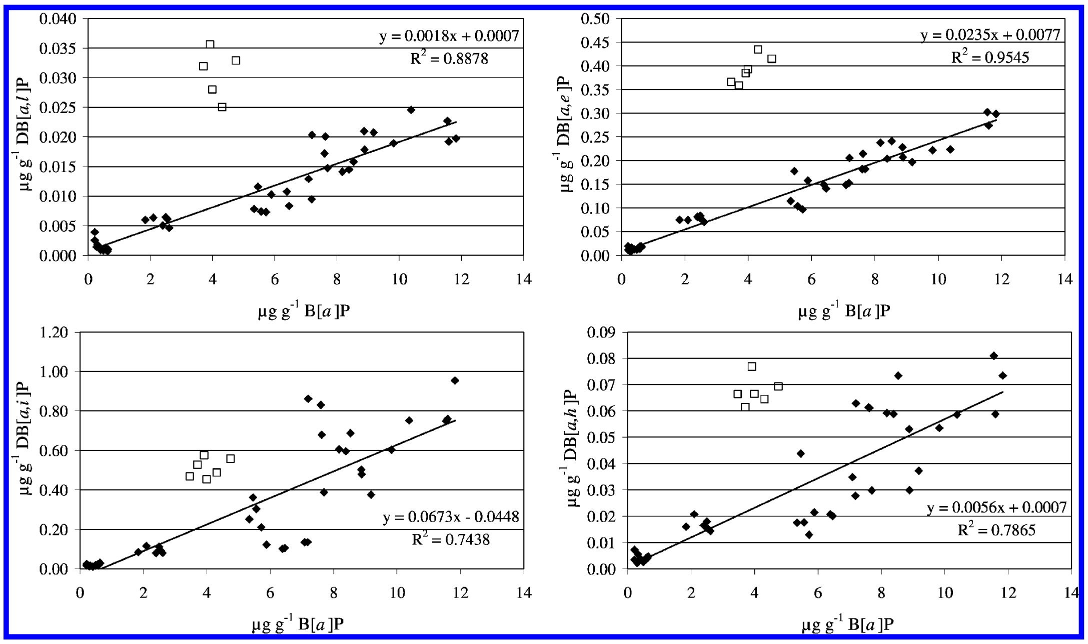

Figure 4. Measured DB[*a*,*l*]P (upper left), DB[*a*,*e*]P (upper right), DB[*a*,*i*]P (lower left) and DB[*a*,*h*]P (lower right) concentrations plotted against measured B[*a*]P concentrations. The black diamonds represents an individual tire sample, the hollowed squares represent data for Tire 3B summer, which is not included in the linear regression and correlation.

summer. The PAH content of Tire 2B studded winter was about 27% higher than that of Tire 3B summer. The B[*a*]P and dibenzopyrene content of winter tires was higher than that of summer tires from the same manufacturer. Statistically significant difference between Tire 8D winter and Tire 7D summer as well as between Tire 2B studded winter and Tire 3B summer was found at 5% significance level using a Mann–Whitney U test for the total PAH, B[*a*]P and the sum of dibenzopyrene content.

There were some similarities in the mean relative PAH abundance in the analyzed tires (Figure 2) regardless of make, type, or manufacturer, suggesting that they shared a common source of PAHs. B[*ghi*]P was the most abundant of the analyzed PAHs in all of the tires, ranging between 32–43%, of the sum of the 15 analyzed HMW PAHs followed by Cor (20–31%). The relative abundance of B[*a*]P ranged between 7–13% for the analyzed tires, making B[*a*]P the fourth to fifth most abundant of the targeted PAHs depending on the make of the tire. 92.3% of the total PAH content could be attributed to the five PAHs: B[*ghi*]P (36.7 ± 3.8%), Cor (23.5 ± 4.0%), Ind[1,2,3-*cd*]P (13.1 ± 2.9%), B[*e*]P (9.6 ± 3.3%), and B[*a*]P (9.4 ± 2.2%) (Figure 3). The standard deviation of the most

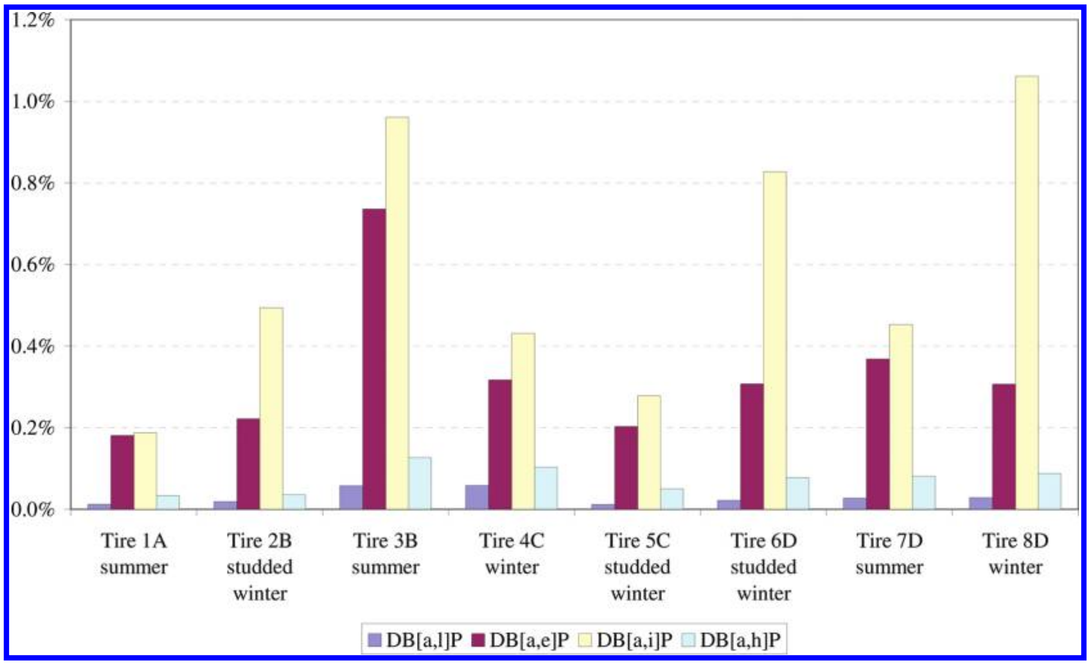

Figure 5. Mean relative abundance of the analyzed dibenzopyrene isomers; DB[*a,l*]P, DB[*a,e*]P, DB[*a,i*]P, and DB[*a,h*]P.

abundant above-mentioned PAHs indicates that there was a consistency in the relative PAH abundance in the analyzed tires, however, the lesser abundant PAHs (e.g., the dibenzopyrene isomers, Per, Ind[1,2,3-*cd*]F, and Pic) had a relative standard deviation greater than 50% across all of the analyzed tires. Further research is needed to determine whether tires in general have a similar PAH profile or if the PAH profile differs at different manufacturing locations, intended for certain markets (e.g., Europe, North America, Asia etc.) and year of manufacture.

Including all data, poor correlation, but statistically significant at 98.2% level, was found between the measured concentration of B[*a*]P and the sum of the four dibenzopyrenes. However, excluding the data from Tire 3D summer, the correlation increased, especially for DB[*a,l*]P (R^2 = 0.89) and DB[*a,e*]P (R^2 = 0.95) (Figure 4). On the basis of the linear regression, it is possible to roughly estimate the dibenzopyrene content in tires, if the B[*a*]P content is known.

Since no PAHs with MW < 252 Da were analyzed in this present study, it is difficult to accurately determine what fraction of the total PAH constitutes of PAHs with >252 Da. By comparing the relative abundance of B[*a*]P (4.4%, average across tires, not market share weighted mean) from Kumata et al.,[11] where several >252 Da PAHs were included along with the low MW PAHs; phenanthrene, anthracene, fluoranthene, PYR, B[*a*]A and CHR, with the relative abundance of 9.4% B[*a*]P from the present study, a very rough estimate that the HMW PAHs; (B[*b*]F, B[*k*]F, B[*a*]P, B[*e*]P, Per, Ind[1,2,3-*cd*]P, Per, B[*ghi*]P and Cor) accounts for approximately 40% of the total PAH content in the tires analyzed in the present study.

DB[*a,i*]P was consistently the most abundant dibenzopyrene isomer, followed closely by DB[*a,e*]P (Figure 5). DB[*a,l*]P and DB[*a,h*]P were in general, present only in minute amounts in all of the analyzed tires. The concentrations varied between 0.001 $\mu g\ g^{-1}$ (DB[*a,l*]P) and 0.82 $\mu g\ g^{-1}$ (DB[*a,i*]P). The mean concentration of all dibenzopyrenes for all tires was 0.53 $\mu g\ g^{-1}$, corresponding to less than 2% of the total PAH content (range: 0.4−1.9%). Using the Swedish Chemical Inspectorate estimate for tire-tread-wear emission of 10 × 10^6 kg annually (valid for 1994) in Sweden[12] and the mean values, calculated from all tires, of B[*a*]P and dibenzopyrenes (Table 1) gives an annual emission of 49 kg B[*a*]P and 5.3 kg dibenzopyrenes, respectively. Using the median values, the corresponding annual emissions are estimated to be 50 kg B[*a*]P and 3.6 kg dibenzopyrenes, respectively. Comparing these estimates with that of the Swedish Chemical Inspectorate estimated annual emission of 60 kg B[*a*]P[12] suggests that the present estimated annual emission of dibenzopyrenes in Sweden is plausible. This indicates that tire-tread-wear may be a potential source to dibenzopyrenes to the environment. The annual emission of B[*a*]P, in Sweden in 1994, from other sources has been estimated; where gasoline vehicle exhaust contributed with 450 kg (passenger cars and light-duty trucks with and without catalytic converter), diesel vehicle exhaust: 20 kg, wood burning: 430 kg and residential oil heating: < 1 kg.[14] This suggests that tire-tread-wear could be a larger contributor of B[*a*]P to the environment than diesel vehicle exhaust and residential oil heating. An annual emission of dibenzopyrenes from these sources is currently not available in the literature. However, the total mean dibenzopyrene content measured in the tires is low compared to reported concentrations in other urban sources i.e., diesel and gasoline particulate exhausts. The mean sum of the dibenzopyrene content in diesel exhaust particles varies between a factor of 6.6,[32] and 0.90−15.6 (mean of two vehicles, urban driving cycle and motorway driving cycle)[33] higher than the determined content in tires. Gasoline vehicle exhaust particles contain a factor of 2.3−285 (mean of two vehicles, urban driving cycle, and motorway driving cycle), more dibenzopyrenes than tires.[33] But it should be noted that the particle size of the emissions differ drastically between the sources and this is crucial for the impact on the environment, population exposure, and potential health effects. Particles emitted from incomplete combustion are <1 μm, whereas the mass particle size distribution of tire-tread-wear may be much larger, but is much less known.

The tires that were analyzed in this present study were all manufactured prior to the ban of HA-oils in tire rubber, which makes it reasonable to anticipate that there will be a decline of PAH emissions originating from tire-tread-wear in the future. It is however necessary to investigate what significance carbon black has to the PAH content in a tire. By replacing HA-oils with alternative extender oils, carbon black may well become a relatively more important source to PAHs than the extender oil used in the tire manufacturing. Because of the substantial variation in the dibenzopyrene content across the analyzed tires, further research is necessary to determine the distribution of tires in a real-world vehicle fleet, taking into consideration the market share of tires from different manufacturers and the age of the tires in operation. It is also necessary to fill the gaps in our knowledge regarding tire-particle generation and distribution in the environment in order to assess the implications to human health and our environment.

It has been estimated that Europe, the U.S., and Japan together generate 5×10^9 kg of scrap tires annually.[41] Through the release of PAHs from stockpiled scrap tires,[41] PAH emissions from pyrolysis of scrap tires[42] or leaching of PAHs from recycled tire rubber material,[30] tires are a source of environmental pollution of PAHs throughout their entire lifecycle.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Table with additional information on the analyzed automobile tires. Table with PAH extraction recoveries. GC−MS chromatogram from a tire particle extract. Mass spectra of tentatively identified PAHs. This information is available free of charge via the Internet at http://pubs.acs.org

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Notes

The authors declare no competing financial interest.

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