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Article

Release of PAH from Secondary Products Made from End-of-Life Tire Recyclates into 20% Aqueous Ethanol as Assessment of Human Dermal Absorption

Stefan Hoyer [1,*], Lothar Kroll [1], Benny Fischer [2], Kai Pisulla [2] and Albrecht Seidel [2]

[1] Department of Lightweight Structures and Polymer Technology, Chemnitz University of Technology, Reichenhainer Straße 31/33, 09126 Chemnitz, Germany
[2] Biochemical Institute for Environmental Carcinogens (Prof. Dr. Gernot Grimmer-Foundation), 22927 Grosshansdorf, Germany
* Correspondence: stefan.hoyer@mb.tu-chemnitz.de; Tel.: +49-371-531-37814

Abstract: Compliance with the legal limits set at the European level for the content of polycyclic aromatic hydrocarbons (PAH), which are harmful to human health and the environment, is of central importance for the recycling of rubber, particularly end-of-life tires (ELT), into secondary products, e.g., elastic fall protection mats or anti-slip mats for the transport sector. However, different regulations associated with different analytical methods apply to newly produced tires on the one hand and secondary products made from ELT on the other. Given these discrepancies, ELT can potentially contain levels of PAH, which can be problematic when reused in consumer products. The total PAH content, however, is not without doubt a reliable risk indicator, which should ultimately be based primarily on the transfer of the substances from the product into the skin of human beings or their release into the environment. Accordingly, additional studies are required to determine the extent to which migration-based measurements are more suitable for risk assessment and how the PAH content correlates with migration. Complementing the recently published results of PAH content in different types of ELT, this study investigates the release of PAH for a range of typical secondary materials composed entirely or partly of ELT. In the present study, migration tests with 20% aqueous ethanol were applied, a methodology that has been shown in previous investigations by others to reflect human skin exposure well, and the resulting migration rates of PAH are determined.

Keywords: polycyclic aromatic hydrocarbons; migration; extraction; REACH

Citation: Hoyer, S.; Kroll, L.; Fischer, B.; Pisulla, K.; Seidel, A. Release of PAH from Secondary Products Made from End-of-Life Tire Recyclates into 20% Aqueous Ethanol as Assessment of Human Dermal Absorption. *Recycling* **2023**, *8*, 6. https://doi.org/10.3390/recycling8010006

Academic Editor: Marc Marín-Genescà

Received: 20 November 2022
Revised: 21 December 2022
Accepted: 24 December 2022
Published: 30 December 2022

1. Introduction

Polycyclic aromatic hydrocarbons (PAH) are a group of lipophilic compounds that are known to occur as complex mixtures that pose a potential health risk to humans [1,2] or cause ecotoxicological effects when released into the environment [3,4]. Consequently, limit values (REACH) have been established at the European level for the PAH content of accessible parts of consumer goods made of rubber or plastic that come into contact with human skin or the oral cavity on a regular basis or for a prolonged period of time (Regulation (EU) No. 1272/2013). This regulation limits the total content of the eight EU priority PAH [5] to 1 mg/kg each, but for the entire range of baby toys and toddler products, a stricter limit value of 0.5 mg/kg each has been set.

The setting of these maximum PAH levels leads to two straits for the recycling of end-of-life tires (ELT). Firstly, no harmonized analytical method for the PAH content determination has yet been established as European standard. As shown in a recent study [6], the amount of PAH measured is strongly dependent on the extraction method and solvent selected and can vary considerably for different standards. Secondly, new tires are subject to different test methods to limit the PAH content, and the associated measurement methods are primarily designed to address the PAH content of the process oil (Regulation (EC) No. 1907/2006). However, tires also commonly contain high levels of carbon black as reinforcing fillers, which are an additional source of PAH in the rubber. The PAH content of carbon black is not regulated, so ELT may have high PAH content readings, depending on the measurement method selected. This can become a problem for legal reasons when ELT are recycled into consumer products. Examples of such products are elastic fall protection mats, impact sound insulation, anti-slip mats for the transportation sector, or rubber coatings for tool handles. Recently, it was demonstrated [6] that the determined PAH content of ELT can exceed the maximum permissible values for consumer products by more than three times for some PAH compounds when this is determined using a continuous hot extraction with toluene. This methodology is considered by the Joint Research Centre (JRC) to be beneficial for the future development of a European standard [7].

Nevertheless, the German Federal Institute for Risk Assessment (BfR) stated in 2009 [8] that it is not so much the PAH content in a product that is relevant for assessing the health risk, but rather the quantities that are released on contact with the skin and absorbed by the consumer (migration). However, at the time the PAH content limits were introduced, there were no reliable migration methods available to determine the PAH released from these products. In contrast, however, there were already suitable analytical methods available for the PAH content determination in such articles. This made it possible to enforce the restriction on the basis of a content limitation, but without prescribing a specific measurement procedure to date. However, Annex XVII of Regulation (EC) No 1907/2006 (REACH), point 50, column 2, paragraph 8 points out that further scientific knowledge on the migration of PAH from articles is needed to potentially adapt the relevant regulations to the actual hazard potentials. In the meantime, the methods for measuring the migration of PAH from products have been further developed, so that their transfer into a liquid simulant mimics the migration into human skin as realistically as possible [9,10].

In this context, Bartsch et al. [9] investigated the migration of PAH from consumer products into aqueous sweat simulant and aqueous ethanol in comparison to the results for the amount of benzo[*a*]pyrene (B[*a*]P) permeating human test skin in the Franz cell chamber. They found that 20% aqueous ethanol at 37 °C and horizontal circling motion (hereafter referred to as BfR method) was an even better predictive model than other commonly used skin models applicable in the Franz cell chamber (EpiDerm™, Strat-M™ or porcine skin). In conclusion, the application of this test method gives results “in good agreement to the actual exposure of human skin against B[*a*]P migrating out of contaminated products” [9].

In 2018, the Directorate General Joint Research Centre (DG JRC) published a report on the STANPAH project [11] (hereafter referred to as JRC report) to provide scientific support for the implementation and possible modification of the restriction on PAH, particularly in relation to paragraphs 5 and 6 of entry 50 of Annex XVII of REACH. The objective was to gain a better understanding of the migration behavior of PAH from plastic and rubber components and to develop a reliable methodology for the determination of PAH migration from these matrices upon dermal contact. In this context, the BfR method was also applied to determine the release of the eight EU priority PAH. It was assessed that this method might be considered a good basis for a harmonized method after appropriate validation. In addition, the following conclusions were drawn:

- Migration increases under dynamic conditions (linear shaking) by a factor of up to 20. Therefore, dynamic conditions were selected for subsequent tests.
- Under the same migration conditions, the relative migration of PAH depends on the molecular weight and shape of each substance, its content, the matrix, and the specific surface area of the test specimens.
- The results indicate that extender oil has the greatest influence on the release, and the PAH it contains appear to migrate more easily than those in the carbon black.
- Carbon black may have the ability to reabsorb released PAH, with this effect potentially increasing with increasing specific surface area of the carbon black.

- After an initial increase for PAH released over time, the trend for some materials indicates that migration tends to reach a plateau. However, in other cases, a decrease in released PAH has been observed after the passing of a maximum, which is associated with reuptake.
- For end-of-life tire granulates, a potential barrier effect of a polyurethane coating was found, whereas migration from coated granulates was up to three times lower.

The objective of this study was an exploratory characterization of the migration of PAH from blended materials consisting of substantial amounts of ELT (hereafter referred to as blends) into 20% aqueous ethanol under dynamic conditions at 40 °C, as conducted by JRC [11]. In line with the findings of the JRC report, that the relative migration of PAH also depends on the matrix, migration tests were performed for a range of potentially relevant matrix materials. Absolute as well as relative (PAH content related) migration rates of five blends, with ELT contents ranging from 36 to 100%, are presented. Extending the scope of the STANPAH project [11], a broader range of 26 different PAH compounds were analyzed, including the eight EU priority PAH (REACH) [5], the 16 U.S. EPA priority PAH [12], and the 22 environmentally relevant PAH in Germany (established as monitoring list by the German Federal Environmental Agency (UBA) [13]).

2. Results

2.1. PAH Content

The PAH content was determined analytically for two selected blends (NR_36 and PUR_36 according to Table 2) by means of hot extraction with toluene (Grimmer method). The results are summarized in form of bar graphs in Figure 1. The sorting of the PAH compounds is performed from top to bottom with increasing retention time. In the second and third columns, the eight EU PAH as well as the 16 U.S. EPA PAH are marked with an "x". Detailed measurement results can be found in Table A1 (Appendix A).

In addition, boxplots are presented in Figure 1, which contain the four quartiles of the measurement series of Hoyer et al. [6] in a modified form, indicating the expected range of values for the PAH content of the two blends for the ELT content of 36%. These are results from a two-year analysis of the PAH content of truck tire recyclates (2017-19, 36 tests of monthly samples). The recyclates used for the blends studied here are from the same source and period. To derive the boxplots, each individual measurement was corrected by a factor of 0.36, and thus normalized for the ELT content. The objective is to compare the expected range of PAH content (boxplot) based on the ELT content of the blends with the actual measurements (bar graph). However, it must be taken into account that additional PAH were added to the NR_36 blend by the carbon black of the matrix material.

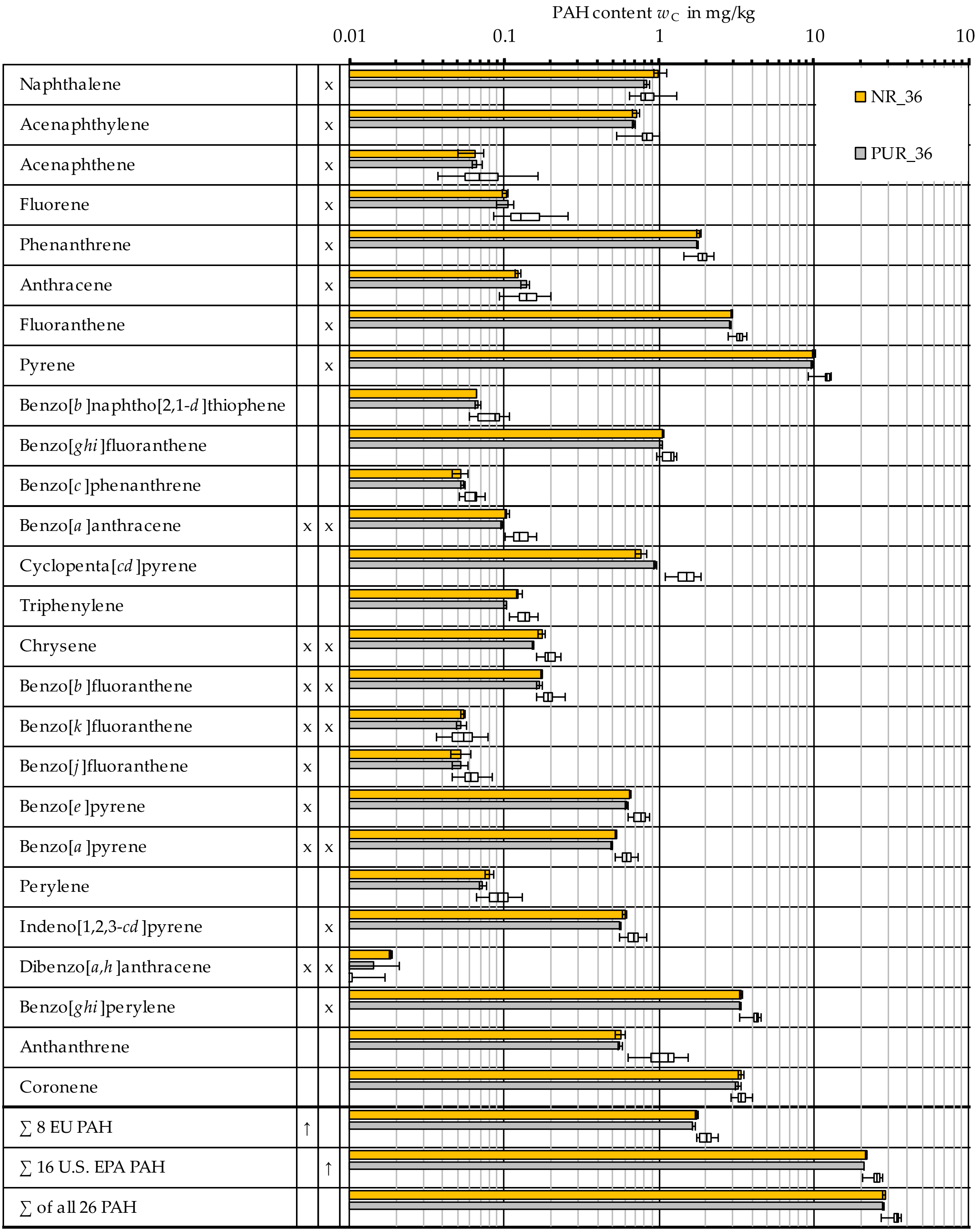

Figure 1. Arithmetic mean as well as minimum and maximum of the triple measurement of the PAH content for PUR_36 and NR_36 (bar graph). Expected value range of the PAH content based on the ELT content of 36% (boxplot). In the second and third columns, the compounds belonging to the sum values are marked with an "x", the arrow indicates the relevant column.

2.2. PAH Migration

2.2.1. Specific Migration of PAH into 20% Aqueous Ethanol

Figure 2 (left) presents the results for the specific migration of PAH per area of test specimen into 20% aqueous ethanol at 40 °C and linear shaking for 24 h. In Figure 2 (right), the measurement results are normalized by the ELT content w_{ELT} of the respective blends. Table 1 presents statistical indicators. In both cases, only those PAH compounds that were measurable, i.e., above the limit of quantification (LOQ, see Table A2), are presented. Among the measurable PAH, in five cases individual measured values were below the limit of quantification (see Table 1, footnotes 1 to 3). Here, the LOQ was taken as the measured value. This means that, in these cases, the migration w_{M} of this specific PAH will be slightly overestimated.

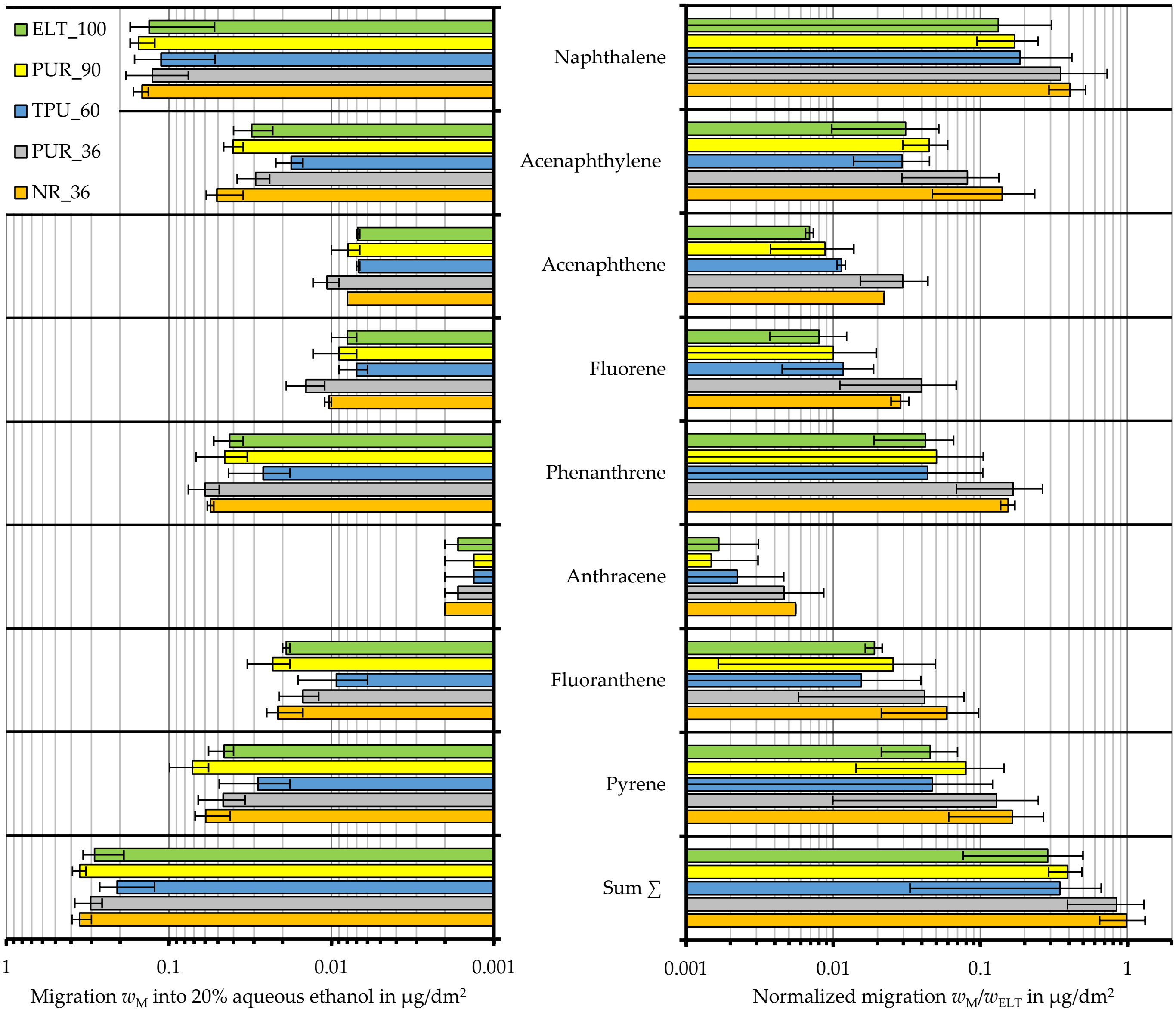

Figure 2. Results (average, min, max) for the specific migration w_{M} of PAH into 20% aqueous ethanol µg/dm² (**left**). Normalized results (average and confidence interval for α = 0.05) for $w_{\mathrm{M}}/w_{\mathrm{ELT}}$ obtained by dividing the results for w_{M} by the respective ELT content w_{ELT} of the samples (**right**).

Table 1. Statistical indicators for the specific migration w_M of PAH into 20% aqueous ethanol in µg/dm^2.

Material	Parameter	Naphthalene	Acenaphthylene	Acenaphthene	Fluorene	Phenanthrene	Anthracene	Fluoranthene	Pyrene	Sum $\sum$
ELT_100	Arithmetic mean $\bar{x}$	0.132 [1]	0.031	0.007 [2]	0.008	0.042	0.002	0.019	0.046	0.267
	Margin of error e	0.172 [1]	0.021	0.000 [2]	0.004	0.023	0.001	0.002	0.024	0.295
	Standard deviation s	0.069 [1]	0.009	0.000 [2]	0.002	0.009	0.001	0.001	0.010	0.119
	Maximum value	0.173	0.040	0.007	0.010	0.053	0.002	0.020	0.057	0.337
PUR_90	Arithmetic mean $\bar{x}$	0.154	0.040	0.008 [2]	0.009	0.045	0.001	0.023	0.072	0.350
	Margin of error e	0.069	0.014	0.005 [2]	0.009	0.049	0.001	0.022	0.059	0.097
	Standard deviation s	0.028	0.006	0.002 [2]	0.003	0.020	0.001	0.009	0.024	0.039
	Maximum value	0.173	0.046	0.010	0.013	0.068	0.002	0.033	0.099	0.393
TPU_60	Arithmetic mean $\bar{x}$	0.112	0.018	0.007 [3]	0.007	0.026	0.001	0.009	0.028	0.204
	Margin of error e	0.139	0.009	0.000 [3]	0.004	0.036	0.001	0.014	0.044	0.195
	Standard deviation s	0.056	0.004	0.000 [3]	0.002	0.014	0.001	0.006	0.018	0.079
	Maximum value	0.163	0.022	0.007	0.009	0.043	0.002	0.016	0.049	0.267
PUR_36	Arithmetic mean $\bar{x}$	0.126	0.029	0.011	0.014	0.060	0.002	0.015	0.046	0.304
	Margin of error e	0.135	0.019	0.005	0.010	0.035	0.001	0.013	0.043	0.163
	Standard deviation s	0.054	0.008	0.002	0.004	0.014	0.001	0.005	0.017	0.066
	Maximum value	0.184	0.038	0.013	0.019	0.076	0.002	0.021	0.066	0.379
NR_36	Arithmetic mean $\bar{x}$	0.146	0.051	0.008	0.010	0.056	0.002	0.021	0.059	0.354
	Margin of error e	0.041	0.034	0.000	0.001	0.006	0.000	0.014	0.037	0.121
	Standard deviation s	0.016	0.014	0.000	0.001	0.003	0.000	0.006	0.015	0.049
	Maximum value	0.165	0.059	0.008	0.011	0.058	0.002	0.025	0.069	0.395

[1] One of three results was below the LOQ of 0.0524 µg/dm^2 (LOQ is considered as reading); [2] One of three results was below the LOQ of 0.0067 µg/dm^2 (LOQ is considered as reading); [3] Two of three results were below the LOQ of 0.0067 µg/dm^2 (LOQ is considered as reading).

2.2.2. Migration of PAH Relative to Their Content

The relative migration rate w_{RM} is determined by relating the absolute amount of migrated PAH m_E to the amount of PAH contained in the test specimens m_C (see Section 4.5.4). Figure 3 presents the results for the blends whose PAH content was determined analytically (see Section 2.1). Figure 4 displays the results for the blends whose PAH content was estimated based on their ELT content. Detailed results can be found in Table A3 (Appendix C).

For all PAH compounds for which migration was not detectable, the LOQ of the specific migration w_M (Table A2) is considered for the calculation of the maximum values (right error bar) for each PAH compound and the sum parameters. This provides an estimation for the uncertainty resulting from the limit of quantification.

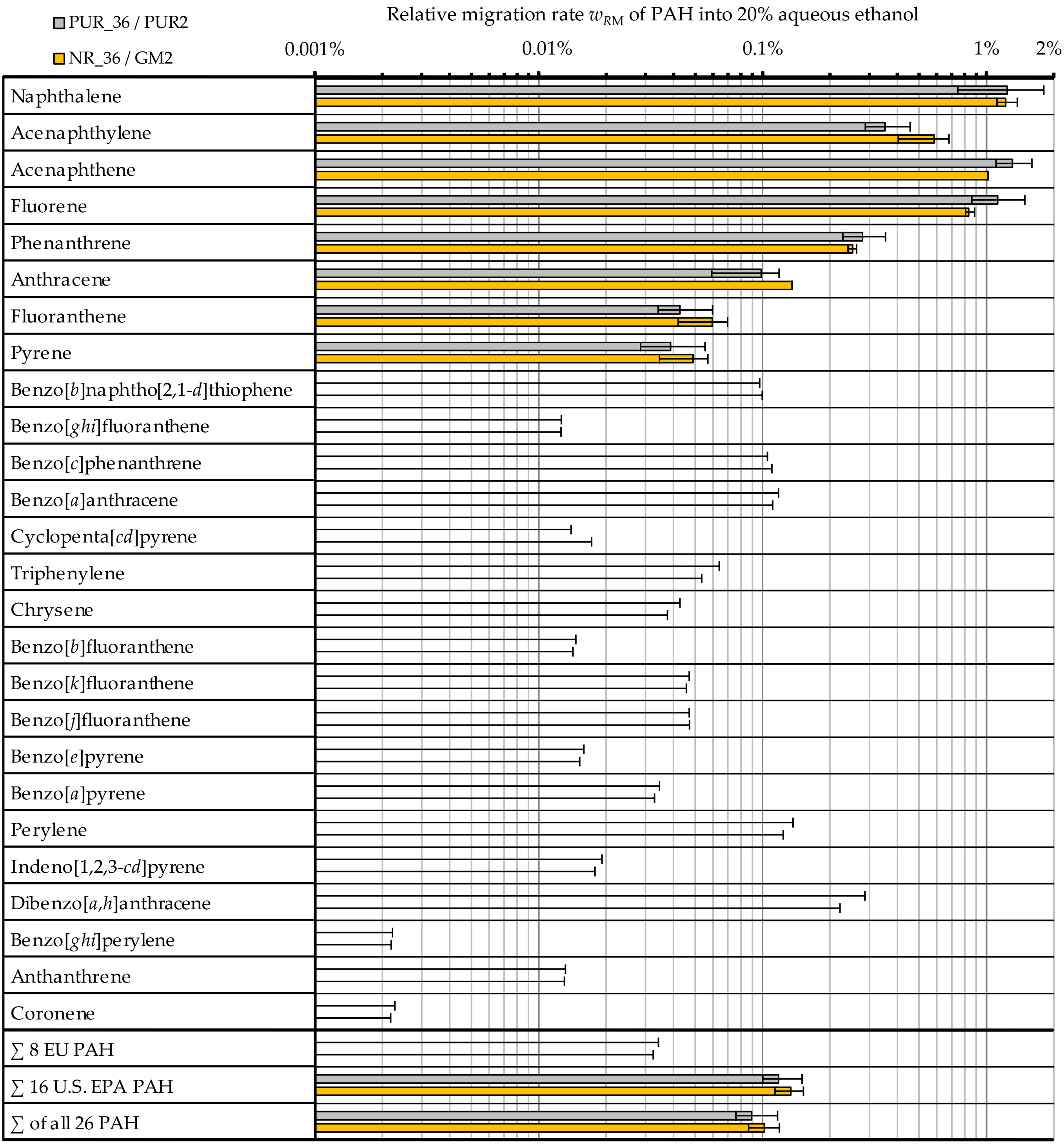

Figure 3. Results of relative migration rate w_{RM} for the blends whose PAH contents were determined by measurement. The bar graphs are the arithmetic mean of three measurements; the error bars are the minimum and maximum results.

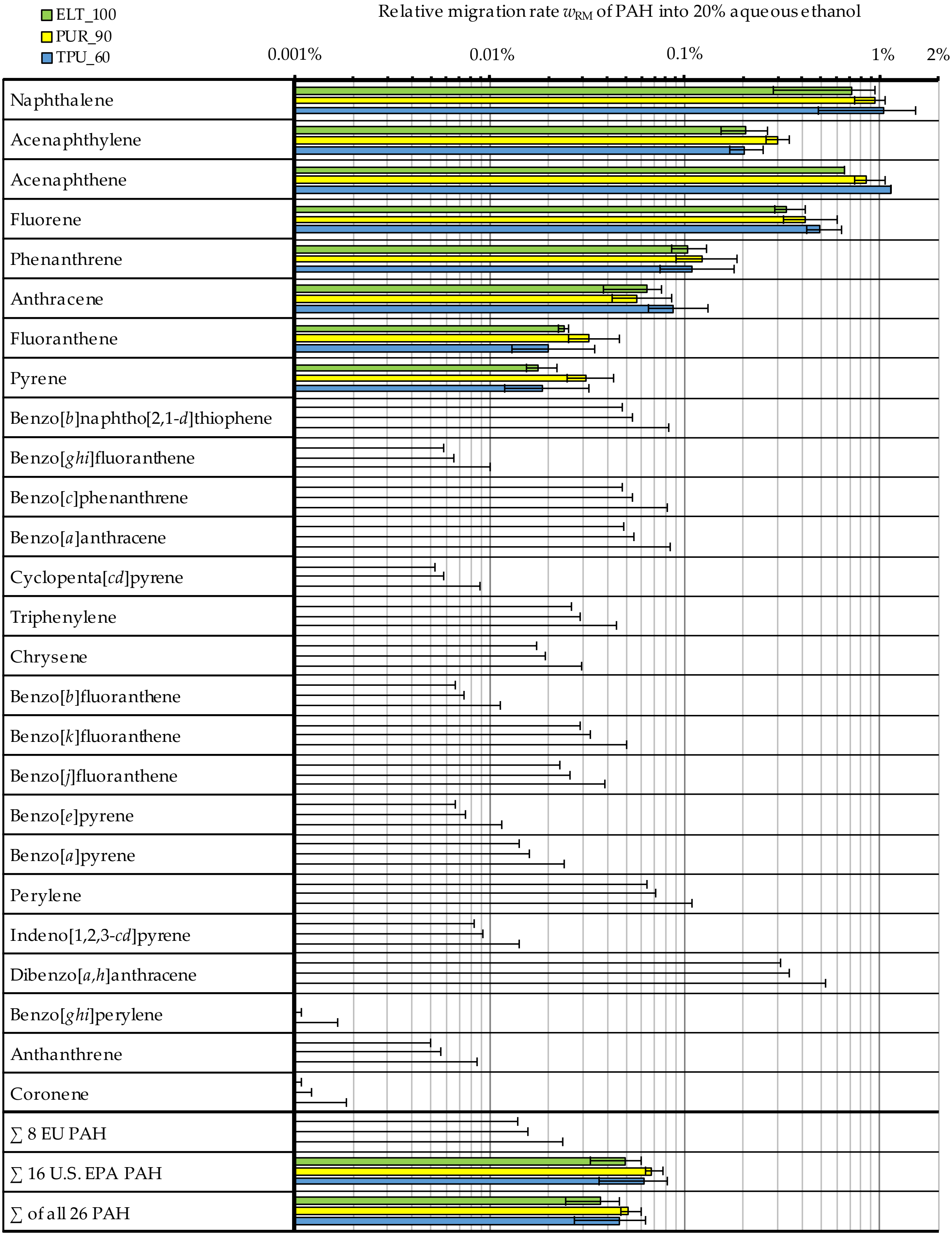

Figure 4. Results for relative migration rate w_{RM} for the blends whose PAH contents were estimated by the PAH content minimum of truck tires in [6] and the ELT content of the materials. The bar graphs are the arithmetic mean of three measurements; the error bars are minimum and maximum.

3. Discussion

Blended materials were produced from ELT recyclates and various matrix materials. For two selected blends the PAH content was determined using the Grimmer method. At the same time, an expected value range for the PAH content of these blends was calculated (see Section 2.1). This was derived based on the ELT content of the blends and the known PAH content of the applied ELT granulates from the same origin and period as already reported in [6], which were determined using the same analytical method. The range of these calculated expected values and the analytically determined PAH content are compared in Figure 1. The results are in excellent agreement for the majority of PAH compounds investigated, with exception of cyclopenta[*cd*]pyrene and anthanthrene, for which the measured values are considerably lower. The reasons for this discrepancy are currently unknown, but further scrutiny is required.

The PAH content of the two blends NR_36 and PUR_36 exhibits only minor differences. NR_36, with exception of anthracene and cyclopenta[*cd*]pyrene, has slightly higher content. This was to be expected considering the additional PAH introduced by the carbon black of the matrix material. For the eight EU PAH and the sum of the 16 U.S. EPA PAH (only these are specified by the supplier), these higher values are in the range of PAH potentially introduced by the carbon black (see Section 4.2). With a few exceptions for some PAH compounds, none of the two matrix materials thus appears to be a significant obstacle to extraction or to influence the content measurements to any appreciable extent. However, the few deviations found between measured and expected values and between the different matrix materials might be of interest for further investigations.

For the remaining three blends, the PAH content was not measured, but estimated in the same way as the expected value ranges, whereby the minimum of the measurement series in [6] was considered. Since, as mentioned above, measured and expected values agree well, the calculated PAH content seems to be a reasonable approximation. Consequently, by choosing the minimum values as a basis for calculation, the relative migration rate w_{RM} will be slightly overestimated.

Migration measurements were performed by linear shaking of samples ($30 \times 30 \times 2$ mm) in 20% aqueous ethanol at 40 °C for 24 h (analogous to the JRC report [11]). The results of a triple measurement are presented in Figure 2 (left). Since the materials varied widely in ELT content, the results were also normalized to the ELT content w_{ELT} of the blends and presented together with the confidence interval ($\alpha = 0.05$) in Figure 2 (right). These tests reveal that migration is only measurable for the eight PAH compounds with the shortest retention time. These are naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, and pyrene. No migration was measurable for the eight EU priority PAH. This is in agreement with the results of the JRC report [11] for the rubber samples that contained treated aromatic distillate extract (TDAE) as process oil. According to European Tyre & Rubber Manufacturers' Association ETRMA, distillate aromatic extract oils (DAE) have been replaced by alternatives, such as TDAE or similar low PAH process oils used in tire production since 2010 [14,15]. Thus, the TDAE-based rubber formulations of the STANPAH project are closer to today's tire compounds than those with DAE, which were also considered in their project.

The highest migration would be expected for the two materials ELT_100 and PUR_90. They either consist entirely of ELT and have a rough surface (ELT_100) or have the highest ELT content of all blends, the surface of which is in direct contact with the migration medium over a large area (PUR_90). However, Figure 2 (right) reveals that it is the two blends with the lowest ELT content, PUR_36 and NR_36, that exhibit the highest ELT-content-related migration rate. The absolute amounts of migrated PAH are even comparable to those of ELT_100 and PUR_90. This is unexpected since these materials are only one-third ELT and these are fully embedded in the matrix and thus have no direct contact with the migration solution. According to the JRC report [11], a barrier effect would be expected here, where the release of PAH might be up to three times lower compared to uncoated ELT. Comparing TPU_60 with ELT_100 on the other hand, migration scales relatively well with ELT content, but this still does not indicate a barrier effect of the matrix. Figures 3 and 4 present the relative migration rate w_{RM}, where the amount of migrated PAH m_{E} was set in relation to the amount of PAH m_{C} contained in the test specimens (see Table A3). In cases where a migration of individual PAH compounds was not detectable, the LOQ (see Table A2) was taken to calculate the maximum (error bar) for them and the sum parameters. This provides an estimation for the uncertainty resulting from the limit of quantification.

As a result, a theoretical upper limit for the migration rate w_{RM} of 0.034% (PUR_36) is found for the sum of the eight EU PAH. For the sum of the 16 U.S. EPA PAH as well as the sum of all 26 PAH investigated, the maximum migration rate is 0.15% and 0.12%, respectively (in both cases for NR_36). For the low molecular weight compounds, the individual migration rates are in the 1% range. The highest actually measured relative migration rate w_{RM} is found for naphthalene, acenaphthene, and fluorene, followed by acenaphthylene.

In 2010, the German Federal Institute for Risk Assessment (BfR) estimated the dermal exposure of humans in contact with PAH-contaminated consumer goods [16]. For B[*a*]P, migration rates of 10% per hour were assumed as the worst case and 1.5% per hour as the geometric mean. As a result of a risk assessment conducted on these assumptions, it was recommended to the European Commission to limit the PAH content in consumer products to a maximum of 0.2 mg/kg (ppm) [17]. As already described in the JRC Report for TDAE-based rubber and confirmed by the measurements here, migration of B[*a*]P into 20% aqueous ethanol is not detectable. Even taking into account the limit of quantification, a maximum migration rate of 0.035% (PUR_36) is to be assumed under the selected experimental conditions. As a consequence, it therefore seems likely that the assumptions made by the BfR in 2010 [16] greatly overestimated the migration of B[*a*]P from products in contact with the skin.

Two inconsistencies were observed with respect to the results of the JRC report [11]. Firstly, no indication for a barrier effect as a result of the incorporation of the ELT material into a matrix material was found. Secondly, migration seems not to scale with the ELT content and thus ultimately with the PAH content for some blends investigated. However, the experimental design of this work focused on quantifying the migration of a broad range of PAH compounds from ELT based blends following the methodology outlined in the JRC report. Objective explanations for the observed inconsistencies can therefore hardly be derived from the experimental setup, especially since the ELT material itself varies considerably in its composition. In particular, tires consist of about nine different rubber components such as tread or sidewall [18], which in turn have manufacturer- and product-specific material formulations that are unknown in detail. Consequently, the material composition of each sample of ELT varies to some extent, which can hardly be analyzed in detail (e.g., the type of carbon black with its specific surface area). However, the inconsistencies found here suggest that further fundamental investigations into this method are necessary. In view of the high relevance of such measurements for the safe recycling of the large quantities of ELT that are accumulated annually, it would certainly be useful to carry out such tests specifically on ELT-like materials with a known composition. For this purpose, ELT-like rubber compounds should be purposefully prepared, varying, for example, the type and amount of plasticizer oil and carbon black.

Further issues that should be addressed in the context of a more in-depth analysis and further development of this method are the real size of the test specimen surface and its pre-cleaning. In the JRC report, it is assumed that the total surface area is the sum of the six individual macroscopic faces of the test specimen. In this work, the same approach is applied, but at the same time the qualitative differences in the microscopic surface structure are pointed out (Figure 6). In order to obtain comparable characteristic values for the specific—surface related—migration w_{M} of different blends, the real surface size should be determined accurately. Unfortunately, measurement by nitrogen adsorption (BET method, Brunauer–Emmett–Teller) proved unsuitable for rubber powder in experiments conducted by Hoyer [19]. Since the nitrogen adsorption was insufficient, the adsorption-desorption isotherm could not be determined [19]. Holland et al. reported measurements by gas adsorption with mixtures of krypton and helium gas [20]. A technical specification recently published by the German Institute for Standardization (DIN) also proposes measurement with krypton gas [21]. However, Sing [22] makes a restrictive statement about the BET method, stating that "derived values of surface area should not be considered 'absolute' areas". A further consideration would be to what extent even an accurate surface measurement will be relevant with regard to the wettability of the test liquid, and thus the real migration-effective area. This raises the question of whether such measurements are reasonable in terms of the effort involved and the usefulness of the results. Conversely, the experimental effort could be reduced by maintaining consideration of only the macroscale surface. In this case, the results would not be material-specific, but product-specific. However, this would require the surface structure of the test specimen to be corresponding to that of the real product. This seems particularly difficult since this would have to apply to all surfaces in contact with the migrating medium. The JRC report also states that the test specimens should not be washed with water or any other solvent prior to the migration tests. The same procedure was followed in this work. However, this severely limits the conclusions that can be drawn about the inconsistencies with the results of the JRC report, since PAH could have migrated to the surface already during the manufacture of the test specimens. This procedure should therefore be reconsidered, as PAH migrated to the surface during processing would thus be incorrectly recorded as having migrated from the material during testing. It therefore seems reasonable to investigate whether pre-cleaning the test specimens with 20% aqueous ethanol can contribute to better accuracy of the measurement.

4. Materials and Methods

4.1. Methods

In this study, the migration of PAH from blended materials, which contain ELT material in significant amounts, into 20% aqueous ethanol (Brenntag, Essen, Germany) is characterized. The experimental setup is shown schematically in Figure 5.

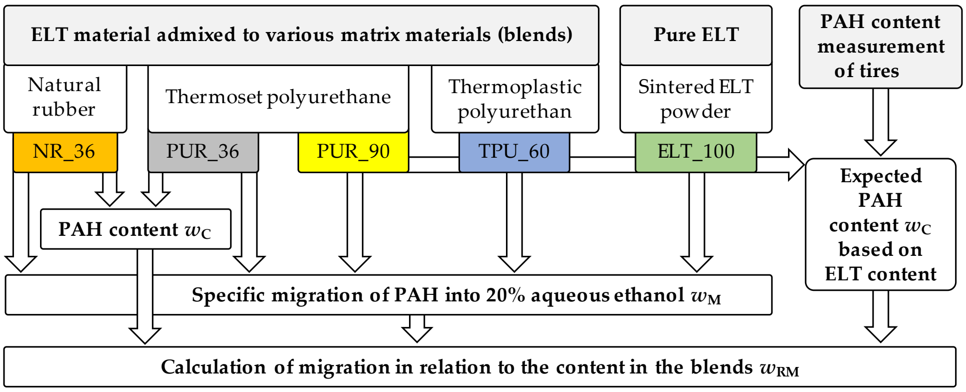

Figure 5. Experimental setup.(PAH content measurement of tires [6]).

Based on the results of the JRC report [11], indicating that the relative migration of PAH is strongly dependent on the matrix, migration tests were performed for a number of potentially relevant matrix materials. Therefore, molded parts were made from blended materials of ELT and rubber (natural rubber, NR_36), thermoset (polyurethane, PUR_36 and 90), and thermoplastic (polyurethane, TPU_60) as well as pure sintered ELT recyclate (ELT_100). For two samples (NR_36 and PUR_36), the PAH content was then determined analytically by hot extraction in toluene (Grimmer method). For the remaining blends, the PAH content was estimated based on the ELT content of the blends. Subsequently, the specific migration of PAH from samples of the same geometry as in the JRC report into 20% aqueous ethanol was determined. Finally, the absolute amount of PAH migrated from the samples was related to the amount of PAH contained in the samples to derive the relative amount of PAH migrated.

4.2. Materials

Various material formulations were prepared for the tests, which are summarized in Table 2. The samples differ primarily in the matrix material used and the content of ELT recyclates. The matrix materials selected were those typically found in the manufacture of secondary products from ELT material. These include a thermoset polyurethane, in this case a two component (2C) system consisting of polyol and aromatic isocyanate, a typical rubber compound based on natural rubber, with a special low-PAH carbon black used as a filler, as well as a thermoplastic polyurethane. Lastly, a sample of pure ELT powder was also prepared by high-pressure high-temperature sintering.

Table 2. Material composition of the blends.

Material	Composition and Properties
ELT_100	ELT content w_{ELT}: 100% (powder, K0204), produced by HPHT sintering Density: 1.15 g/cm^3
PUR_90	Thermoset matrix (polyurethane, aromatic polyether, 2C system) ELT content w_{ELT}: 90% (granulates, W1035); 10% polyurethane Density: 1.14 g/cm^3
PUR_36	Thermoset matrix (polyurethane, aromatic polyether, 2C system) ELT content w_{ELT}: 36% (powder, K0204); 32% kaolin, 30% polyurethane, 2% Zeolite Density: 1.38 g/cm^3
TPU_60	Thermoplastic matrix, thermoplastic polyurethane (TPU, polyether) ELT content w_{ELT}: 60% (powder, K0204); 40% TPU (Elastollan 1170 A) Density: 1.12 g/cm^3
NR_36	Elastomer matrix (natural rubber) 37% aluminum hydroxide (Apyral 40), 36% ELT (powder, K0204), 16% natural rubber (SVR CV 60), 5.5% carbon black (SPHERON® SO-LP) Density: 1.37 g/cm^3

In all cases, ELT material from whole truck tires was used (TW), which was provided by Mülsener Rohstoff- und Handelsgesellschaft mbH MRH (Mülsen, Germany). On average, truck tires consist of around 30% natural rubber, 15% synthetic rubber, 25% steel, 20% carbon black, and 10% other additives, e.g., curing systems, extender oil, and textiles [23]. The W1035 material was produced by granulating whole truck tires and has a mesh size of 1.0–3.5 mm. The material K0204 has the same origin, was produced by cryogenic grinding, and has a mesh size of 200 to 400 µm. Both materials are largely free of steel and textile components.

The ELT content of the blends is different, pursuing different objectives: Sample ELT_100 consists entirely of ELT powder and is intended to generate a reference value for the migration of PAH without the interfering barrier of a matrix material.

The samples NR_36 as well as PUR_36 contain an ELT portion (36%) which ensures that the limit values according to Regulation (EU) 1272/2013 are safely complied with. Specifically, this means that the content of each of the eight EU PAH is below 1 mg/kg.

In sample NR_36 additional PAH are introduced into the rubber compound by the carbon black. This is a special low-PAH carbon black (SPHERON® SO-LP, Cabot Corporation) for which, however, only the upper limits of its PAH content are specified, and the input of additional PAH can therefore not be calculated exactly. The maximum of additional PAH are 0.014 mg/kg for B[*a*]P, 0.055 mg/kg for each of the other seven EU PAH and 1.1 mg/kg for the sum of the 16 U.S. EPA PAH (the carbon black itself is specified with a maximum of 0.25 ppm B[*a*]P, 1 ppm for each of the eight EU PAH and 20 ppm for the sum of the 16 U.S. EPA PAH).

The sample PUR_90 corresponds to a typical ELT product as used e.g., as impact protection or anti-slip mat and is containing relatively coarse ELT granulates.

The sample TPU_60 was manufactured by extrusion and calendaring as described in [24]. It has an ELT content which represents the technically upper limit of manufacturability with this technology.

Morphologically, the prepared test specimens differ in particular in the surface structure and thus ultimately in the real surface area. The surface structures are compared qualitatively in Figure 6. ELT_100 has a rough and porous surface. TPU_60 shows a number of small pores. All other specimens have relatively smooth and largely non-porous surfaces. At this point, no estimation can be made about the exact surface sizes. In this study, the area of all migration test specimens is assumed to be 0.204 dm^2.

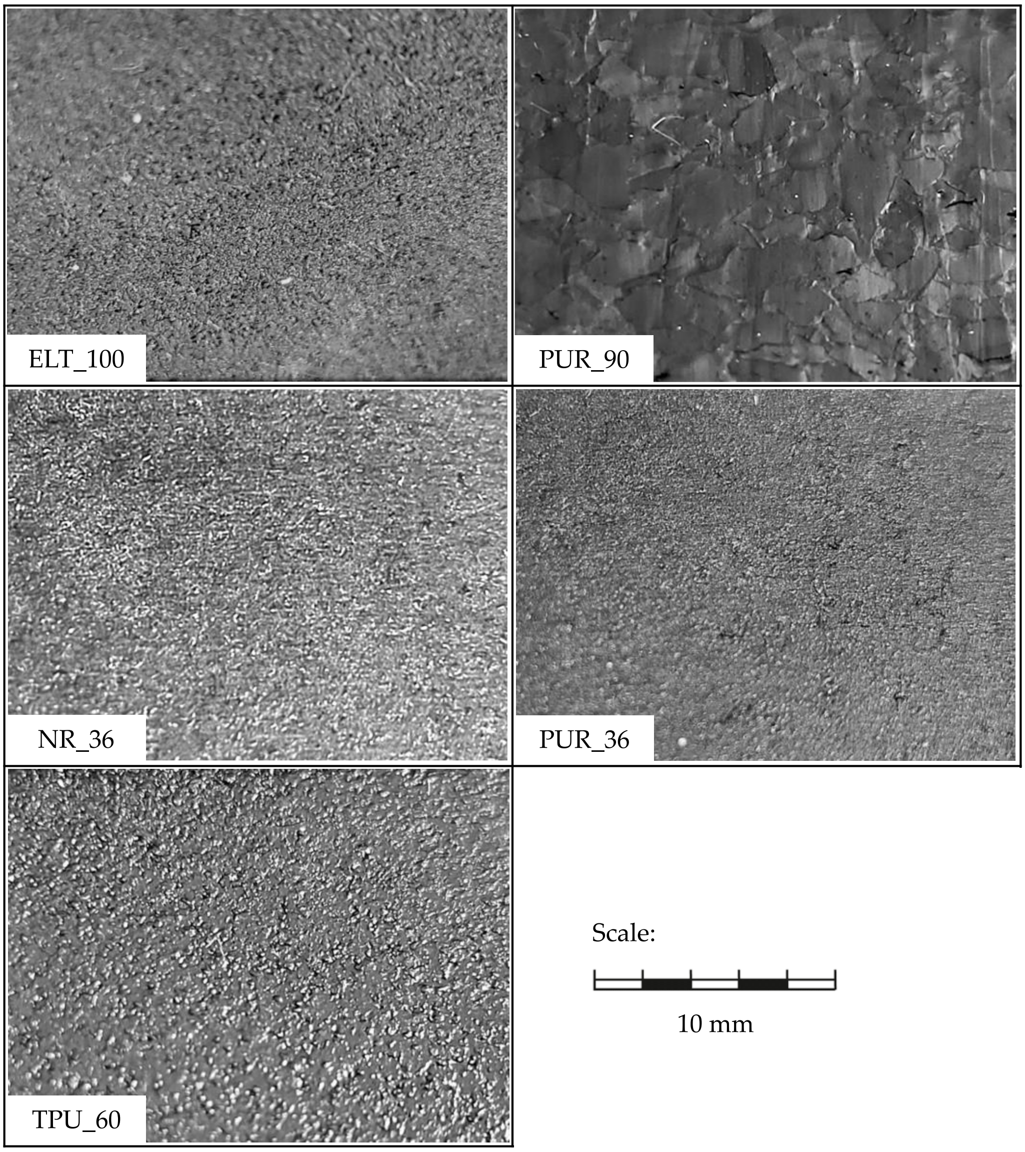

Figure 6. Comparison of the surface structures of the test specimens.

4.3. Preparation of Materials and Test Specimens

To produce the test specimens for the migration measurements, 2 mm thick plates were manufactured. Depending on the material, the pre-products were either molded directly into a 2 mm thick plate or peeled from a thicker plate (PUR_90). Finally, the test specimens with a dimension of 30 × 30 × 2 mm (surface area of 0.204 dm^2) were produced from these plates by cutting.

To prepare the granulates for PAH content analysis (NR_36 and PUR_36), the 2 mm thick plates were crushed by granulation and sieved. The particle size distribution resulted in the range of mesh size 0.5–2.0 mm.

The materials and test specimens were produced using different processes. In particular, the thermal and mechanical stress during processing is very different. Since it cannot be ruled out that these parameters have an influence on the experimental results, a brief description of the manufacturing processes is given below.

The samples for ELT_100 were prepared by high-pressure high-temperature sintering (HPHTS). For this purpose, the powder was put in a mold and pressed at 150 °C using a specific pressure of 145 bar for 20 min to form plates of 2 mm thickness.

To prepare the PUR samples, the two polyurethane components were premixed first and then incorporated into the other components. This was followed by compression molding at a temperature of 90 °C and a specific pressure of about 70 bar for 10 min. The samples for PUR_90 were produced by peeling 2 mm thick sheets from a molded body. For the PUR_36 sample, 2 mm thick plates were produced directly. The rubber powder for sample PUR_36 was pre-dried by adding a powdery molecular sieve (zeolite A) approximately 15 min before processing. The proportion of the molecular sieve was about 5% of the rubber powder.

The TPU_60 samples were prepared using a single-step direct processing technology, which is described in detail in [24]. Rubber powder and TPU were mixed in a co-rotating twin screw extruder (E2.30, screw diameter: 31 mm, length: 1.24 m/40D; ERMAFA, Chemnitz, Germany), and then directly formed into continuous 2 mm thick sheets using a wide slit nozzle attached to a gear pump (Etrex GP 36; Maag, Grossostheim, Germany). The processing temperature was between 184 and 194 °C. The rubber powder was pre-dried before processing at 100 °C and a pressure of 100 mbar (vacuum) for 100 min.

For NR_36, the ELT powder was mixed with a rubber compound at about 80 °C for one minute in a laboratory internal mixer (Plasticorder, rotor N50, mixing chamber temperature: 50 °C; Brabender, Duisburg, Germany). This was followed by compression molding to 2 mm thick sheets at 150 °C and a pressure of about 30 bar for 10 min.

PUR_90 differentiates in a notable way from the other specimens. Since the ELT particles are relatively large and the test specimens are produced by peeling, relatively large areas of the ELT granulates are exposed and are thus in direct contact with the migration liquid. For all the other samples, with the exception of ELT_100, the fine particles tend to be encapsulated by the matrix material.

4.4. PAH Content Measurement

For the two materials PUR_36 and NR_36 a dedicated analysis of their PAH content was carried out. For this purpose, a sample was determined in triplicate in each case.

The PAH profile analyses were performed at the Biochemical Institute of Environmental Carcinogens (BIU) Prof. Dr. Gernot Grimmer-Foundation (Grosshansdorf, Germany) applying the Grimmer method. This analytical method is based on the stable isotope dilution principle using GC-MS with selected ion monitoring (SIM mode) and allows the quantification of the PAH content in the sub-ppb range. The Grimmer method has been validated for various matrices during the work of BIU for the Environmental Specimen Bank of the German Federal Environment Agency (UBA) and is published [13].

In brief, an aliquot of the rubber granulates (3 g) is subjected to a continuous hot extraction in a Twisselmann apparatus with toluene for 8 h. For the instrumental PAH analysis an Agilent 6890N gas chromatography mass spectrometry (GC-MS) instrument is used connected to a 5973N MSD operated in the selected ion monitoring (SIM) mode. Separation of the PAH profile is performed on an Agilent DB-35MS capillary (30 m × 0.25 mm × 0.25 mm) using helium as carrier gas. A 3-point calibration is performed for each PAH compound with linear curve fitting in a working range of 0.03–10 ng. Identification of PAH is performed based on relative retention times and molecular ions compared to reference materials. Quantification is achieved via the PAH applied as internal standards (stable isotope dilution method).

A more comprehensive description of the applied analytical method as well as detailed results of a two-year measurement campaign of the PAH content of car and truck tires as well as truck tire treads has recently been published [6].

4.5. PAH Release from Rubber into the Ethanolic Test Liquid

4.5.1. General

The dynamic migration measurement of PAH from ELT test specimens was performed according to a recently published solvent-based method of the German Federal Institute for Risk Assessment BfR (in accordance to JRC [11], 20% ethanol for 24 h in a shaking water bath at 40 °C instead of 37 °C as originally reported [9]) and based on the experience gained by BIU during the attendance of a limited inter-laboratory comparison study hosted by the JRC of the EU in Ispra [11] as part of the STANPAH project to specifically evaluate this method.

4.5.2. Preparation of the Migration Extract

The test specimens (30 × 30 × 2 mm, surface area of 0.204 dm^2) were weighed with an analytical balance and placed in a robust 100 mL screw-top glass (previously rinsed with ethanol) together with 20 mL of freshly prepared 20% (aq.) ethanol (v/v).

To achieve controlled dynamic PAH migration, the screw tube is agitated in a shaking water bath at 40 °C and 120 rpm for 24 h. After cooling to room temperature, the rubber test item is removed and subsequently rinsed with 5 mL of 20% (aq.) ethanol. Pilot experiments showed that individual particles could occasionally detach from the surface of the rubber specimen. In this case, the particles were separated by filtration.

4.5.3. PAH Analysis of the Migration Extract

The Grimmer method was used to determine the PAH content in the migration extracts (see Section 4.4) with some modifications. In brief, the separated ethanolic migration solution was extracted in a separatory funnel 2 times with cyclohexane (50 mL each) (Brenntag, Essen, Germany). A mixture of 10 deuterated PAH was added to the combined cyclohexane phase as isotopically labeled internal standards (1 mL PAH-STD-1118 (dilution 1:250) in toluene) and subsequently washed with water (100 mL).

Further sample preparation included liquid-liquid partitioning with mixtures of DMF/H_2O/cyclohexane followed by a silica gel SPE step using cyclohexane. Since the PAH content to be determined is very low, the processed sample must be concentrated to a very small volume (<10 µL). Finally, an aliquot of the resulting concentrated PAH solution is used for GC-MS(SIM mode) analysis (Agilent Tech. with Chem Station software; Agilent 6890 N instrument equipped with a 5973 MSD and a 7683 series autosampler injector) (Agilent Technologies Inc., Santa Clara, CA, USA), applying a GC capillary suitable for PAH determination with attention to the separation of triphenylene and chrysene as well as the 3 isomeric benzofluoranthenes. For quality assurance, regular calibrations of the analytical instruments with reference materials and blank analyses of the laboratories were carried out. The migration results for the individual PAH were related to the surface area and reported in $\mu g/dm^2$ after conversion.

4.5.4. Calculation of the Relative Migration Rate w_{RM}

To calculate the relative migration of PAH from the samples into the ethanol–water mixture w_{RM}, the ratio of the absolute amount m_E of migrated PAH to the absolute content m_C of PAH in the test specimens is calculated as follows:

$$w_{RM} = m_E/m_C \tag{1}$$

The absolute PAH content m_C of the samples is calculated by the following equation

$$m_C = \text{vs.} \times \rho_S \times w_C \tag{2}$$

with sample volume vs. (1.8 cm^3), density of the sample ρ_S (see Table 2), and specific PAH content of the material w_C (see Table 2).

For PUR_36 and NR_36, the mean values of the PAH content measurements is taken for w_C (see Section 2.1. and Table A1). For the other three samples, an estimation is made based on the results already reported [6]. For this purpose, the minimum of the PAH content of whole truck tires (TW) is multiplied by the ELT content w_{ELT} of the blends (results see Table A1). Using the minimum of the PAH content for this calculation leads to a conservative estimate of the relative migration rates w_{RM}, as this tends to slightly overestimate them.

The absolute amount of migrated PAH m_E is calculated according to the equation,

$$m_E = w_M \times A_S \tag{3}$$

with the specific migration w_M (Table 1) and the sample surface A_S (0.204 dm^2).

In the five cases (see Table 1, footnotes 1–3) where some of the readings for the migration of specific PAH w_M were below the limit of quantification (LOQ, see Table A2), the LOQ itself was taken as the measured value. This means that in these cases the specific migration of PAH w_M will be somewhat overestimated for these PAH compounds.

For the arithmetic mean and the minimum in the diagrams in Figures 3 and 4, the exact measured values of the migration tests were taken into account in each case. For the maximum, the limit of quantification (LOQ) was assumed in these cases where the values of the PAH compounds were generally below the LOQ. Therefore, there are also maximum values for all PAH that did not show any measurable migration, and this was considered in the same way for the maxima of the respective sum parameters. This serves for estimating the uncertainty resulting from the limit of quantification.

5. Conclusions

This study provides for the first time data on the migration of the 16 U.S. EPA priority PAH and the eight EU priority PAH (REACH) from ELT blend samples manufactured with different matrix materials and various proportions of ELT using a migration simulant reflecting realistically the conditions on human skin. The results obtained are expected to strengthen the available data pool for authorities in order to conduct an improved risk assessment and review of maximum permitted levels of PAH in consumer products in the future. The migration of PAH from cured rubber material is a complicated physico-chemical process, as discussed by Geiss et al. ([10], and references therein) and is determined by the complex compounding, including process oils and carbon black as dominant carriers of PAH. The reported data result from an arbitrary selection of test samples and warrant confirmation by more systematically conducted studies in the future to better understand the complex process of PAH migration from rubber and to further optimize the measurement procedure and test specimens.

Author Contributions: Conceptualization, S.H. and A.S.; methodology: S.H., A.S. and B.F.; validation, S.H. and A.S.; formal analysis, S.H. and A.S.; investigation, resources: A.S., B.F. and K.P.; data curation: S.H. and A.S.; writing—original draft preparation, visualization, S.H.; writing—review and editing, A.S., B.F. and K.P.; supervision, project administration: S.H. and L.K.; funding acquisition: S.H. and L.K. All authors have read and agreed to the published version of the manuscript.

Funding: The research was performed within the Federal Cluster of Excellence MERGE (EXC 1075) as part of the research project "RubberTyRec". This work was financially supported by the German Federal Ministry of Education and Research (BMBF) within the framework of the funding initiative "Clusters–Networks–International" [grant number 03INT510BA].

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: The authors would like to thank the funding bodies, the Project Management Jülich (PtJ) and all project participants for the support of this project. Special thanks are due to the companies MRH Mülsener Rohstoff- und Handelsgesellschaft mbH (Mülsen, Germany) for the generous provision of the ELT materials.

Conflicts of Interest: The authors declare no conflict of interest.

Appendix A

Table A1 presents the results of the PAH content analysis according to Sections 2.1 and 4.4. The margin of error e corresponds to half the width of the two-sided confidence interval of the arithmetic mean value at the confidence level of 95% ($\alpha = 0.05$).

Table A1. PAH content of the materials w_C in mg/kg.

	NR_36 (n = 3)				**PUR_36 (n = 3)**				**ELT_100**	**PUR_90**	**TPU_60**
	Arithmetic Mean $\bar{x}$	**Margin of Error e**	**Standard Deviation s**	**Maximum Value**	**Arithmetic Mean $\bar{x}$**	**Margin of Error e**	**Standard Deviation s**	**Maximum Value**	**Mathematically Estimated Content**	**Mathematically Estimated Content**	**Mathematically Estimated Content**
Naphthalene	0.994	0.280	0.113	1.124	0.839	0.101	0.041	0.867	1.805	1.625	1.083
Acenaphthylene	0.718	0.105	0.042	0.753	0.685	0.033	0.013	0.700	1.480	1.332	0.888
Acenaphthene	0.065	0.032	0.013	0.073	0.067	0.012	0.005	0.072	0.104	0.094	0.062
Fluorene	0.103	0.012	0.005	0.106	0.105	0.035	0.014	0.116	0.239	0.215	0.143
Phenanthrene	1.823	0.122	0.049	1.868	1.762	0.051	0.020	1.777	4.042	3.638	2.425
Anthracene	0.123	0.013	0.005	0.128	0.139	0.025	0.010	0.145	0.258	0.232	0.155
Fluoranthene	2.962	0.121	0.049	3.000	2.887	0.047	0.019	2.909	7.821	7.039	4.693
Pyrene	10.027	0.568	0.229	10.244	9.792	0.428	0.172	9.921	25.443	22.899	15.266
Benzo[*b*]naphtho [2,1-*d*]thiophene	0.066	0.001	0.001	0.067	0.068	0.006	0.003	0.070	0.164	0.148	0.098
Benzo[*ghi*]fluoranthene	1.052	0.029	0.012	1.065	1.041	0.053	0.021	1.056	2.694	2.425	1.616
Benzo[*c*]phenanthrene	0.053	0.015	0.006	0.058	0.055	0.004	0.002	0.056	0.144	0.130	0.086
Benzo[*a*]anthracene	0.104	0.006	0.003	0.107	0.098	0.005	0.002	0.100	0.281	0.253	0.169
Cyclopenta[*cd*]pyrene	0.769	0.162	0.065	0.837	0.941	0.051	0.020	0.959	3.025	2.723	1.815
Triphenylene	0.124	0.016	0.006	0.131	0.103	0.006	0.002	0.104	0.301	0.271	0.181
Chrysene	0.176	0.022	0.009	0.183	0.154	0.005	0.002	0.156	0.455	0.410	0.273
Benzo[*b*]fluoranthene	0.175	0.005	0.002	0.177	0.168	0.017	0.007	0.176	0.446	0.401	0.268
Benzo[*k*]fluoranthene	0.054	0.005	0.002	0.056	0.052	0.010	0.004	0.057	0.101	0.091	0.061
Benzo[*j*]fluoranthene	0.053	0.020	0.008	0.061	0.052	0.015	0.006	0.058	0.129	0.116	0.077
Benzo[*e*]pyrene	0.651	0.021	0.009	0.660	0.620	0.039	0.016	0.637	1.763	1.587	1.058
Benzo[*a*]pyrene	0.528	0.024	0.010	0.535	0.498	0.014	0.006	0.504	1.457	1.311	0.874
Perylene	0.080	0.011	0.005	0.085	0.072	0.011	0.004	0.077	0.186	0.167	0.112
Indeno [1,2,3-*cd*]pyrene	0.603	0.048	0.019	0.618	0.557	0.026	0.010	0.569	1.546	1.391	0.928
Dibenzo[*a*,*h*]anthracene	0.019	0.001	0.001	0.019	0.014	0.015	0.006	0.021	0.016	0.014	0.010
Benzo[*ghi*]perylene	3.399	0.205	0.083	3.461	3.327	0.162	0.065	3.402	9.176	8.258	5.506
Anthanthrene	0.572	0.121	0.049	0.611	0.561	0.050	0.020	0.578	1.772	1.595	1.063
Coronene	3.419	0.330	0.133	3.513	3.248	0.312	0.126	3.383	8.181	7.363	4.909
∑ 8 EU PAH	1.760	0.090	0.036	1.794	1.656	0.091	0.037	1.698	4.889	4.400	2.933
∑ 16 U.S. EPA PAH	21.873	0.901	0.363	22.189	21.143	0.353	0.142	21.295	57.225	51.503	34.335
∑ of all 26 PAH	28.711	1.504	0.605	29.242	27.903	0.513	0.206	28.135	76.129	68.516	45.677

Appendix B

Table A2 lists the limit of quantification for the migration measurements according to Sections 2.2.1 and 4.5.3.

In migration analysis, the absolute amount of migrated PAH per test specimen surface (here 30 × 30 × 2 mm = 20.4 cm^2, volume = 1.8 cm^3) is determined. Based on the standard limits of quantitation (DIN 32645, calibration line method), the limit of quantitation (LOQ) for a standard sample (concentration specification) is converted to the absolute amount of PAH.

Example: the LOQ for benzo[*a*]pyrene, based on a sample weight of 10 g, is 42 ng/kg. This corresponds to 0.420 ng absolute of B[*a*]P in the sample. Accordingly, a LOQ for benzo[*a*]pyrene of 0.42 ng/sample (=0.420 ng/0.204 dm^2) is applied to the migration samples. The results are given in the dimension ng/dm^2, so that the limit of quantification of 0.42 ng/0.204 dm^2 (0.204 dm^2 is the sample size here) is converted to the value for the reference size of 1 dm^2 by using the factor 1/0.204 = 4.902. The LOQ for benzo[*a*]pyrene in the measurement performed is thus 2.059 ng/dm^2.

This procedure is applied to all other analytes, resulting in the following limits of quantification:

Table A2. Limits of quantification (LOQ) for the specific PAH migration rates w_M.

PAH	Limit of Quanti-Fication in ng/dm^2
Naphthalene	52.4
Acenaphthylene	13.7
Acenaphthene	6.7
Fluorene	1.4
Phenanthrene	0.8
Anthracene	0.2
Fluoranthene	0.4
Pyrene	1.3
Benzo[*b*]naphtho [2,1-*d*]thiophene	0.8
Benzo[*ghi*]fluoranthene	1.6
Benzo[*c*]phenanthrene	0.7
Benzo[*a*]anthracene	1.4
Cyclopenta[*cd*]pyrene	1.6
Triphenylene	0.8
Chrysene	0.8
Benzo[*b*]fluoranthene	0.3
Benzo[*k*]fluoranthene	0.3
Benzo[*j*]fluoranthene	0.3
Benzo[*e*]pyrene	1.2
Benzo[*a*]pyrene	2.1
Perylene	1.2
Indeno [1,2,3-*cd*]pyrene	1.3
Dibenzo[*a*,*h*]anthracene	0.5
Benzo[*ghi*]perylene	0.9
Anthanthrene	0.9
Coronene	0.9

Appendix C

Table A3 shows statistical parameters for the results of the calculation of relative migration according to Sections 2.2.2 and 4.5.4.

Table A3. Results for the relative migration rates *wRM* in percent [%].

Compound	**ELT_100**			**PUR_90**			**TPU_60**			**NR_36**			**PUR_36**			**All**
	$\bar{x}$	**min**	**max** [1]	$\bar{x}$	**min**	**max** [1]	$\bar{x}$	**min**	**max** [1]	$\bar{x}$	**min**	**max** [1]	$\bar{x}$	**min**	**max** [1]	$\bar{x}_{max}$ [2]
Naphthalene	0.723	0.284	0.945	0.940	0.747	1.059	1.043	0.486	1.523	1.217	1.115	1.373	1.237	0.744	1.802	1.340
Acenaphthylene	0.206	0.153	0.266	0.301	0.261	0.343	0.201	0.171	0.251	0.584	0.403	0.680	0.352	0.288	0.456	0.399
Acenaphthene	0.663	0.663	0.663	0.850	0.743	1.062	1.135	1.135	1.135	1.018	1.018	1.018	1.307	1.103	1.593	1.094
Fluorene	0.330	0.289	0.412	0.416	0.324	0.601	0.494	0.423	0.635	0.833	0.806	0.886	1.121	0.860	1.486	0.804
Phenanthrene	0.103	0.085	0.129	0.124	0.090	0.186	0.110	0.075	0.179	0.253	0.240	0.263	0.280	0.228	0.354	0.222
Anthracene	0.064	0.038	0.076	0.057	0.043	0.086	0.087	0.065	0.131	0.135	0.135	0.135	0.099	0.059	0.118	0.109
Fluoranthene	0.024	0.023	0.025	0.032	0.025	0.047	0.020	0.013	0.035	0.060	0.042	0.070	0.043	0.034	0.060	0.047
Pyrene	0.018	0.015	0.022	0.031	0.025	0.043	0.019	0.012	0.032	0.049	0.035	0.057	0.039	0.029	0.055	0.042
Benzo[*b*]naphtho [2,1-*d*]thiophene	n.d.	n.d.	0.048	n.d.	n.d.	0.054	n.d.	n.d.	0.082	n.d.	n.d.	0.100	n.d.	n.d.	0.097	0.076
Benzo[*ghi*]fluoranthene	n.d.	n.d.	0.006	n.d.	n.d.	0.007	n.d.	n.d.	0.010	n.d.	n.d.	0.013	n.d.	n.d.	0.013	0.010
Benzo[*c*]phenanthrene	n.d.	n.d.	0.048	n.d.	n.d.	0.054	n.d.	n.d.	0.082	n.d.	n.d.	0.110	n.d.	n.d.	0.105	0.080
Benzo[*a*]anthracene	n.d.	n.d.	0.049	n.d.	n.d.	0.055	n.d.	n.d.	0.084	n.d.	n.d.	0.111	n.d.	n.d.	0.118	0.083
Cyclopenta[*cd*]pyrene	n.d.	n.d.	0.005	n.d.	n.d.	0.006	n.d.	n.d.	0.009	n.d.	n.d.	0.017	n.d.	n.d.	0.014	0.010
Triphenylene	n.d.	n.d.	0.026	n.d.	n.d.	0.029	n.d.	n.d.	0.045	n.d.	n.d.	0.053	n.d.	n.d.	0.064	0.044
Chrysene	n.d.	n.d.	0.017	n.d.	n.d.	0.019	n.d.	n.d.	0.030	n.d.	n.d.	0.038	n.d.	n.d.	0.043	0.029
Benzo[*b*]fluoranthene	n.d.	n.d.	0.007	n.d.	n.d.	0.007	n.d.	n.d.	0.011	n.d.	n.d.	0.014	n.d.	n.d.	0.015	0.011
Benzo[*k*]fluoranthene	n.d.	n.d.	0.029	n.d.	n.d.	0.033	n.d.	n.d.	0.050	n.d.	n.d.	0.046	n.d.	n.d.	0.047	0.041
Benzo[*j*]fluoranthene	n.d.	n.d.	0.023	n.d.	n.d.	0.026	n.d.	n.d.	0.039	n.d.	n.d.	0.047	n.d.	n.d.	0.047	0.036
Benzo[*e*]pyrene	n.d.	n.d.	0.007	n.d.	n.d.	0.008	n.d.	n.d.	0.011	n.d.	n.d.	0.015	n.d.	n.d.	0.016	0.011
Benzo[*a*]pyrene	n.d.	n.d.	0.014	n.d.	n.d.	0.016	n.d.	n.d.	0.024	n.d.	n.d.	0.033	n.d.	n.d.	0.035	0.024
Perylene	n.d.	n.d.	0.064	n.d.	n.d.	0.071	n.d.	n.d.	0.109	n.d.	n.d.	0.124	n.d.	n.d.	0.137	0.101
Indeno [1,2,3-*cd*]pyrene	n.d.	n.d.	0.008	n.d.	n.d.	0.009	n.d.	n.d.	0.014	n.d.	n.d.	0.018	n.d.	n.d.	0.019	0.014
Dibenzo[*a,h*]anthracene	n.d.	n.d.	0.308	n.d.	n.d.	0.345	n.d.	n.d.	0.527	n.d.	n.d.	0.222	n.d.	n.d.	0.286	0.338
Benzo[*ghi*]perylene	n.d.	n.d.	0.001	n.d.	n.d.	0.001	n.d.	n.d.	0.002	n.d.	n.d.	0.002	n.d.	n.d.	0.002	0.002
Anthanthrene	n.d.	n.d.	0.005	n.d.	n.d.	0.006	n.d.	n.d.	0.009	n.d.	n.d.	0.013	n.d.	n.d.	0.013	0.009
Coronene	n.d.	n.d.	0.001	n.d.	n.d.	0.001	n.d.	n.d.	0.002	n.d.	n.d.	0.002	n.d.	n.d.	0.002	0.002
∑ 8 EU PAH	n.d.	n.d.	0.014	n.d.	n.d.	0.016	n.d.	n.d.	0.024	n.d.	n.d.	0.032	n.d.	n.d.	0.034	0.024
∑ 16 U.S. EPA PAH	0.049	0.033	0.059	0.068	0.063	0.077	0.061	0.036	0.081	0.134	0.113	0.152	0.118	0.100	0.150	0.104
∑ of all 26 PAH	0.037	0.024	0.046	0.051	0.047	0.060	0.046	0.027	0.063	0.102	0.086	0.119	0.089	0.076	0.117	0.081

[1] The maximum values for the PAH compounds from benzo[*b*]naphtho [2,1-*d*]thiophene to coronene are based on the LOQ as a notional measurement result, which is also the basis for calculating the maxima of the sum values; [2] Arithmetic mean of the maximum values (max) of the different blends; n.d.: not detectable.

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