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Environmental impact of rejuvenators in asphalt mixtures containing high reclaimed asphalt content

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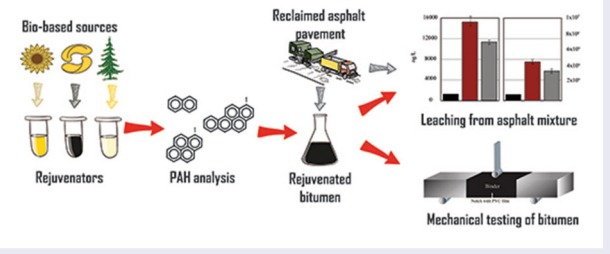
ABSTRACT

The use of reclaimed asphalt pavement (RAP) is of increasing importance due to fast-growing amounts of demolished road materials. However, reclaimed asphalt can contain relevant amounts of pollutants such as carcinogenic polycyclic aromatic hydrocarbons (PAHs) and toxic metals. In order to improve the mechanical properties of recycled asphalt, rejuvenators are used to reduce the stiffness of the aged binder. These rejuvenators in turn may potentially mobilise pollutants like PAHs and facilitate their leaching to surface and ground waters. The environmental impact of three rejuvenators with good mechanical performance was studied. The environmental impact was assessed by determining metal- and PAH contents in the RAP and in leachates. Chemical analyses showed that rejuvenators did not mobilise PAHs from RAP materials for 2–3 ring PAHs. However, some 4–6 ring PAHs that are relatively less toxic indeed leached more easily from unaged material. Ageing reduced the tendency for PAH leaching, without and with rejuvenator.



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Introduction

The use of reclaimed asphalt pavement (RAP) to substitute new construction materials has become an important research topic (Antunes et al., 2019; Kaseer et al., 2019) with the potential for various benefits including a reduction of asphalt costs (Zaumanis et al., 2016), an overall decrease of emissions over the entire life-cycle (Chiu et al., 2008), and the conservation of non-renewable natural resources (Mallick et al., 2014). Because of these reasons, the use of RAP has steadily increased over the last decades. In

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the USA, for example, average RAP content in asphalt mixtures has grown from 16% in 2009 (Hansen & Newcomb, 2011) to 21% in 2016 (Hansen & Copeland, 2017). RAP has become the most recycled and reused material in the USA (Bolden et al., 2013).

A reason against any further increase of RAP proportions is the fact that the reclaimed asphalt has experienced extended ageing during usage. As a result of aging, the binder in RAP is stiff and not elastic enough to resist cracking (Bressi et al., 2015; Cavalli et al., 2016). High RAP contents would thus compromise the performance of the pavement. Therefore, measures to compensate for the negative effects of aged binder are necessary.

When using high amounts of RAP, the use of rejuvenators to reduce the stiffness of the recycled binder has become a necessity (Baghaee Moghaddam & Baaj, 2016). Even at high RAP contents, rejuvenators can restore mechanical properties of the material, to achieve a performance similar to conventional mixtures (Arámbula-Mercado et al., 2018; Cavalli et al., 2018b; Zaumanis, Mallick, and Frank, 2014; Zaumanis, Mallick, Poulikakos, et al., 2014). Rejuvenators help to recover the mechanical properties of the aged binder (Karlsson & Isacsson, 2006). Various oils have been tested as rejuvenators, including flux oils, slurry oils, used lubrication oils, lube oil extracts, extender oils, bio-based oils, waste-engine oils, waste-vegetable oils, etc (Roberts et al., 1996; Zaumanis, Mallick, Poulikakos, et al., 2014). From a chemical point of view, these oils used as such or as binder additives are complex mixtures as they can contain various unknown constituents. Because of their variable origin and partly unknown compositions, it is not obvious that the proposed rejuvenators are safe to use for exposed workers, the environment and general public. The environmental sustainability of a specific rejuvenator should therefore be carefully assessed, before large-scale applications. This includes environmental impact of the rejuvenator and the modified RAP during production and paving, when exposed to elevated temperatures. In addition, relevant aspects during the service life of roads, when asphalt is exposed to traffic and weathering should also be evaluated.

The work presented in this paper is part of a large-scale national project where the mechanical performance of rejuvenated high RAP mixtures were studied from micro scale to full-scale plant production (Cavalli et al., 2018a, 2018b, 2019; Zaumanis, Arraigada, et al., 2019; Zaumanis, Boesiger, et al., 2019; Zaumanis et al., 2018, 2019).

The focus of the work presented in this paper is to study the environmental aspects of rejuvenator compositions, simulating aging processes at production temperature and determining the potential for leaching and mobilisation of toxic material from the RAP to surface and ground water.

The European Standard EN 13108-8 for reclaimed asphalt requires, among other aspects, the determination of contaminants present in it. Some of the pollutants found in reclaimed asphalt pavement are of concern; for example the presence and release of carcinogenic polycyclic aromatic hydrocarbons (PAHs) and toxic metals (Brantley & Towsend, 1999). PAHs are organic compounds mainly formed during incomplete combustion processes. Some PAHs are carcinogenic to humans according to the International Agency for Research on Cancer (IARC) (IARC Working Group on the Evaluation of Carcinogenic Risks to Humans, 2010).

In the past, coal derived tar was widely used as a binder for asphalt mixtures instead of crude oil-based bitumen. PAH contents in coal tar-based materials are up to three orders of magnitude higher than those in bituminous asphalt mixtures (Birgisdóttir et al., 2007). Tar-containing asphalt with more than 0.1% coal tar is classified as hazardous waste in Europe (Turk et al., 2014). Therefore, the risk of high PAH contents from tar-containing material arises and must be assessed whenever RAP material is reused. Although the use of coal tar is banned in Switzerland, still some older roads and the reclaimed material contain tar. Current regulations according to Swiss guidelines (BAFU, 2006) specify that RAP can only be reused if the content of the 16 priority PAHs is below 250 mg/kg in asphalt, which is about equivalent to < 5000 mg/kg in binder, otherwise, its use is prohibited. It is expected that these regulations will be tightened in the near future. Figure 1 displays chemical structures of those 16 PAHs considered as priority pollutants by the US EPA (2009). Eight of them are genotoxic according to the IARC (International Agency for Research on Cancer).

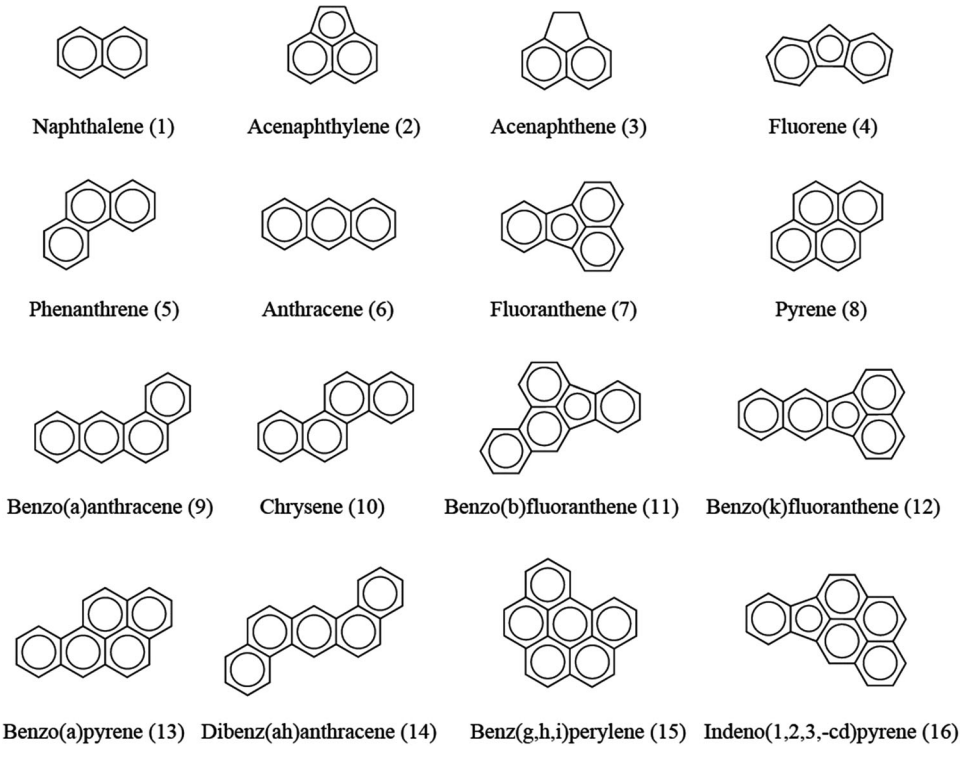

Figure 1. Chemical structures of 16 priority PAHs. According to Swiss regulations, their sum may not exceed 5000 mg/kg in binder. Eight PAHs (1, 9–14, 16) are genotoxic, with benzo(a)pyrene (13) being a group 1 carcinogen (IARC Working Group on the Evaluation of Carcinogenic Risks to Humans, 2010).

Even when RAP materials are within legal limit values, and therefore can be reused, as is the case presented here, it is imperative to assess the potential of rejuvenators to alter leaching properties. When RAP is reused or deposited in stockpiles, metals and PAHs of it can be released by runoff waters, which may end up in surface water- and fresh water systems, ground water and soils. Limit values for PAHs and metals are much lower in these instances. PAH levels in contaminated soils range from 0.05 to 0.3 mg/kg and ambient background levels range from 0.001 to 0.01 mg/kg (Maliszewska-Kordybach, 2003). Concentrations of individual PAHs in surface and coastal waters are typically 1–50 ng/L and 10–200 ng/L in rain (IARC Working Group on the Evaluation of Carcinogenic Risks to Humans, 2010). Several European directives regulating waste and water quality (The Council of the European Union, 1991, 1999; The European Parliament and the Council, 2008b) refer to pollutants that might eventually end up in ground water (The European Parliament and the Council, 2006) or surface water systems (The European Parliament and the Council, 2000). These directives regulate water quality and protect ecosystems. Further directives regulate the water quality for human consumption (The Council of the European Union, 1998) including limits for PAHs and metals. In Switzerland, laws for water protection (Bundesrat, 2017) and for drinking and recreational use of water regulate the contents of toxic substances including PAHs and metals (Eidgenossenschaft, 2018). In this study, pollutant levels found in leachates were compared with limit values in order to assess if they pose a risk to humans and aquatic life.

Pollutants may also be released from abraded road particles, deposited on road surfaces and mixed with particles from traffic, brake wear and tire wear. For the materials reported in this paper, this aspect was studied as reported by Zaumanis et al (Zaumanis, Arraigada, et al., 2019). Other potential

sources include vehicle exhausts, accidental fuel spills, and lubricating oils, among others (Mangani et al., 2005).

Objective

The objective of the work reported in this paper is to determine if rejuvenators mobilise PAHs and metals present in RAP in the form of leachates. Furthermore, the effects of rejuvenator ageing on PAH and metal release are evaluated.

Three rejuvenators have been mechanically tested in the scope of a research project titled 'Sustainable Fully Recycled Asphalt Concrete'. From the three tall oil provided the best overall performance, and therefore, it is used for an in-depth study of environmental impact for the work presented in this paper.

Methodology

RAP was obtained from an asphalt producer in Switzerland. The binder was extracted from the RAP material according to EN 12697-1 and recovered according to EN 12697-3.

Three rejuvenators A, B and C were added to the extracted binder. Rejuvenator A is sunflower seed oil, rejuvenator B is a commercial product based on cashew nut shell oil and rejuvenator C is a commercial product based on distilled tall oil, a byproduct of the Kraft manufacturing process. All rejuvenators were added to the binder at 5% (m/m) as previously reported (Cavalli et al., 2018b).

Aged samples were obtained after a two-stage laboratory aging procedures. Samples were aged using the rolling thin film oven test according to the standard EN 12607-1:2014. Subsequently, the samples were treated in a pressure ageing vessel according to the standard EN 14769:2012. The two stage aging procedure simulates short term aging during the production process and long term aging after multiple years in service.

A wearing course asphalt mixture with maximum aggregate size of 8 mm (AC8) was selected for leaching tests since it fulfils the test requirement of maximum particle size (Agency, 1992). The reference mixture is a plant-produced AC8 with 6.2% binder content. Conventional 50/70 penetration grade bitumen containing no tar was used in this mixture. The recycled mixture contained RAP only and a binder content of 5.6%. After addition of 5% rejuvenator C (from the binder mass), the total binder content of the recycled mixture increased to 5.9%. The RAP mixture gradation nearly fits the requirements for the AC8 mixture type, but its' mix design or binder content were not optimised since that was not important for reaching the objectives of this study.

Test results on physical and chemical properties and performance of the materials reported in the present paper are reported elsewhere as summarised in Table 1.

The characterisation of environmental impacts of the tested materials consisted of the analysis of PAHs and metals in raw samples and in leachates as illustrated in Figure 2. Only rejuvenator C, which performed best in the physical tests, was used for leaching tests both in unaged and aged conditions.

Table 1. References to results of physical and chemical characterisation of the rejuvenators and RAP used in this paper

Characterisation	References
Micro/nano-scale binder properties and chemical characterisation	Cavalli et al. (2019, 2018b, 2018a)
Meso-scale mixture properties and mix design validation	Zaumanis et al. (2020), Zaumanis, Arraigada et al. (2019), Zaumanis, Boesiger et al. (2019)
Full-scale production and emissions	Zaumanis et al. (2018), Zaumanis, Boesiger et al. (2019b)
Environmental impact	The present paper

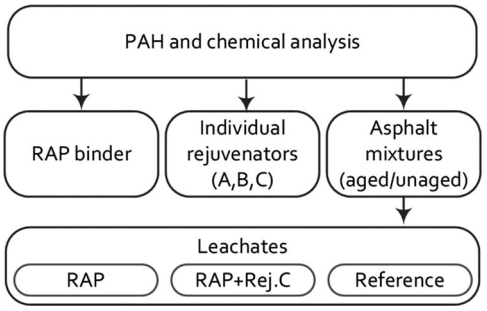

Figure 2. Flow chart with methodology.

Determination of PAH and metal contents

A preliminary analysis was performed in order to determine whether the PAH content in the binder was below the Swiss recommendation limit of 5000 mg/kg. An aliquot of the extracted binder and the extraction solvent (toluene) were analyzed as reference and background samples. PAH analyses were performed following a multistep cleanup procedure described before (Muñoz et al., 2016; Muñoz, Haag, Honegger, et al., 2018). Aliquots of binder extracts and solvent were spiked with internal standard (16 deuterated PAHs). These solutions were concentrated to a minimum volumne, adsorbed on silica and fractionated with n-hexane and a n-hexane/dichloromethane (9/1) mixture. The later fraction contained PAHs. The final extract is analyzed by means of gas chromatography (Fisons Instruments HRGC Mega 2, Rodano, Italy) on a 30 m $\times$ 0.25 μm $\times$ 0.10 μm capillary column (Restek, Bellefonte, USA). Detection and identification of compounds were achieved by high resolution mass spectrometry (Thermo Finnigan MAT 95, Bremen, Germany) in electron-impact ionisation mode (GC/EI-HRMS).

An in-house method, which is briefly described, was used for PAH quantification. Prior to analysis, all samples were spiked with known amounts of 16 deuterated PAHs (Figure 1). Five concentrations containing deuterated and native PAHs (Supelco, Bellefonte, USA) were analyzed in parallel to determine calibration curves and response factors for individual PAHs which were used to correct for response deviations of native and isotopically-labelled PAHs. A similar approach was used for determination of PAH contents of the rejuvenators.

Before performing the leaching tests, binder from each sample was extracted with dichloromethane in a Soxhlet apparatus, followed by a cleanup procedure described elsewhere (Muñoz, Haag, Zeyer, et al., 2018). These extracts were analyzed by GC-Ultra-HRMS (Orbitrap QExactive, Thermo-Fisher Scientific, Germany). The samples studied were: Reference material, RAP and RAP with rejuvenator C (RAP + Rej C) in both, unaged and aged conditions (Figure 2). Rejuvenator C was singled out for environmental experiments as this rejuvenator resulted in the best mechanical performance in Table 1.

Metals were qualitatively measured in the reference asphalt, RAP, RAP + Rej C and in rejuvenator C. Metal contents were determined following a standardised Empa procedure (SOP 6000) by means of semi-quantitative wavelength dispersive-X-ray fluorescence spectroscopy (WD-XRF) in powdered samples with the standardless calibration mode (Rigaku Primus IV, Japan).

Leaching tests

Leaching tests were performed in triplicates (except for reference material, which was analyzed twice). Different procedures are used to evaluate leachates (Brantley & Towsend, 1999; Legret et al., 2005) among them, the batch toxicity characteristic leaching procedure (TCLP) is widely used (Agency, 1992). This methodology was adapted taking into account the equipment and materials available. The leaching test is applied to a size-reduced sample (particle size $<$ 9.5 mm) in an acidic solution for 18 h at a liquid-to-solid ratio of 20 to 1.

During the test, the initial alkalinity of the material is measured to determine the extraction fluid to be used. If the pH is lower than 5, an acidic extraction fluid is needed. In our case, an acetic acid solution in ultrapure water with pH 4.93 was used. 100 g of the material was placed in glass bottles and 2 L of the acidic solution was added. After 18 h of rotation, the extraction fluid was removed and filtrated through a 0.6–0.8 μm borosilicate filter.

Extraction of the PAHs was performed with solid-phase extraction disks (ENVI^{TM}-18 DSK SPE disks, Supelco) according to the US EPA Method 525.1. Identification of PAHs was performed by GC-Ultra-HRMS (Orbitrap QExactive).

All PAH concentrations were above detection limits except for dibenzo(a,h)anthracene (Figure 1, 14), benzo(g,h,i)perylene (15) and indeno(1,2,3,c,d)pyrene (16) in the unaged reference material and in all aged samples. Limits of detection (LOD) were determined to be 0.3 ng/L. These are low detection limits, compared to previous studies with reported LODs ranging from 500 to 5000 ng/L (Brantley & Towsend, 1999).

Determination of metals in leachates

Aliquots from filtered solutions were used for the metal analyses and performing quantitative mercury analysis in leachates. Determination of Al, As, Cd, Cr, Cu, Ni, Pb, V and Zn was performed by means of inductively coupled plasma-mass spectrometry (ICP-MS, Agilent 8800 QQQ). Determination of Hg was done with an atomic absorption flow injection mercury systems FIMS, (FIMS-400, Perkin-Elmer) after stabilisation with $KMnO_4$ solution (5%) and reduction of Hg^{2+} to Hg^0 with a solution of $SnCl_2$ (1.1%), NaCl (6%) and hydroxyl ammonium chloride (6%). For the determination of Fe and Mn, inductively coupled plasma-optical emission spectroscopy (ICP-OES, Agilent 5110, Australia) was used. Certified standard materials were analysed in parallel for quality assurance.

Results and discussion

PAH contents in initial binder and rejuvenators

The total concentration of the 16 priority PAHs (Figure 1) in the extracted binder from RAP was 4800 mg/kg, which is just below the Swiss limit of 5000 mg/kg. Very low PAH concentrations were found in all tested rejuvenators. These values agree with the literature, e.g.: pyrene concentrations in sunflower oils were reported to be 0.001–0.0027 mg/kg (Ciecierska & Obiedziński, 2013; Mafra et al., 2010). In other words, the three rejuvenators will not increase PAH contents of the modified RAP materials. PAH limit values differ between countries. Germany, for example, has established a value of 25 mg/kg in RAP for the 16 priority PAHs (Umwelt Bundesamt, 2016). Considering 5% binder content in the RAP, this corresponds to around 400 kg/kg in the binder. The Swiss requirements, however, are currently being re-evaluated and new, stricter norms with be put in place in 2026.

PAH contents in RAP mixtures without and with rejuvenators

Before performing leaching tests, binder material from each RAP sample was extracted with dichloromethane. Sum concentrations of the 16 priority PAHs in these RAP samples, which were later used for leaching tests, are shown in Figure 3. It was found that PAH contents (sum of 16 PAHs) were below the Swiss legislation limit of 250 mg/kg indicating that these asphalt samples can be reused in Switzerland.

Even though PAH concentrations were below the limit in both, the RAP and the RAP with rejuvenator C, leaching tests were performed to evaluate the risk that pollutants such as PAHs present in the asphalt may leach from the material due to a better mobilisation with the rejuvenator. Figure 3 also illustrates that RAP with rejuvenator contains less PAHs (sum of 16 PAHs) than RAP without rejuvenators. Levels were 8% and 33% lower in the unaged and aged samples, respectively. It may happen that PAHs are partially retained in the matrix and not fully extracted with the organic solvent

(dichloromethane) under the given conditions. On average, PAH contents in these RAP samples varied from 120 to 180 mg/kg. They were seven-fold higher than in the reference material.

Aging has small effects on PAH concentrations of the RAP material itself, whereas concentrations in aged RAP with rejuvenator C were 27% lower than in the unaged material (Figure 3). However, these are results from few samples only, thus some uncertainties should be expected.

Threshold values or tolerable concentrations of PAHs in groundwater, soil and other types of water are in the order of few µg/L, much lower than those values reported in Figure 3. Even small amounts of PAHs, leaching from roads to groundwater or to soil have the potential to damage ecosystems and biota and contaminate drinking water as will be addressed later.

Metal contents in binder extracts and rejuvenators

Most toxic metals (Cd, Cr, Cu, Ni, Pb and Zn) were not detected or found only in low concentrations in the extracted binder samples (Table 2). However, even these low concentrations could pose a risk if these metals leach from RAP and finally end up in surface and ground water systems, e.g. in drinking water catchment areas.

PAH and metal contents in leachates

Concentrations (ng/L) of the sum of 16 priority PAHs in leachates are shown in Figure 4 (upper left).

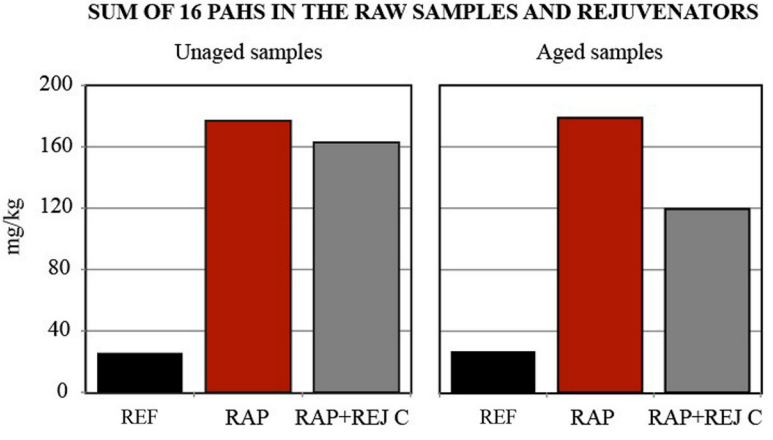

Figure 3. PAH contents (sum of 16 priority PAHs) of binder materials extracted from unaged and aged RAP materials without and with rejuvenator C. These six materials were later used for leaching tests.

Table 2. Element contents in extracted binders and rejuvenators (XRF method).

Sample	Result and concentration range
RAP	High concentration (%): S Medium concentration (< 1000 ppm): Si, Cl, K, Ca, V, Fe Very low concentration (traces, few ppm): Ni, Cu, Zn
RAP + 5% rejuvenator C	High concentration (%): S Medium concentration (< 1000 ppm) Si, Al, Mg, Cl, K, V, Fe Very low concentration (traces, few ppm): Ni, Cu, Zn
Reference	High concentration (%): S Medium concentration (< 1000 ppm): Al, V Very low concentration (traces, few ppm): Ca, Fe, Ni, Zn
Rejuvenator C	High concentration (%): none Medium concentration (< 1000 ppm): Si Very low concentration (traces, few ppm): Ca, P, S, Zn

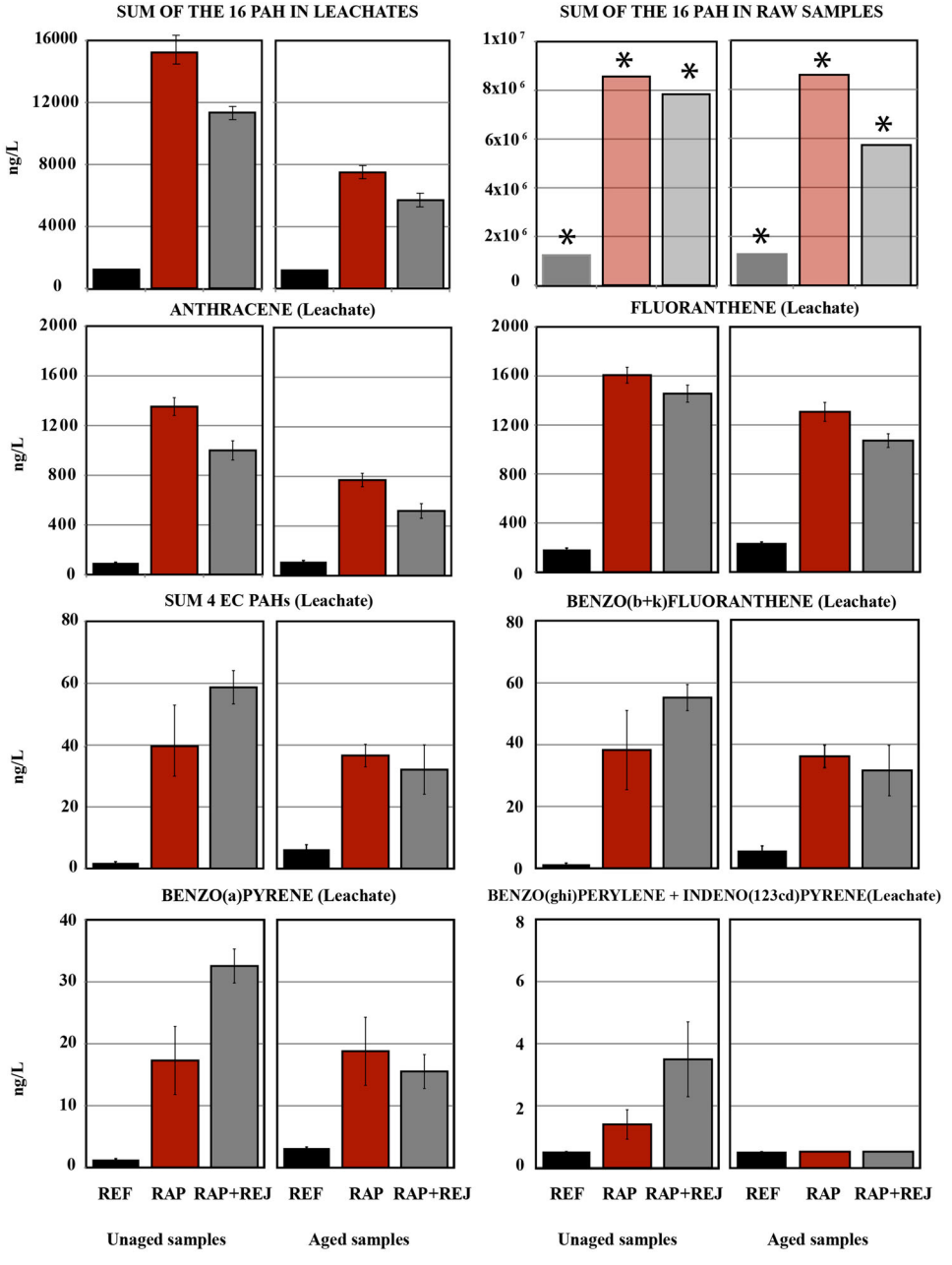

Figure 4. Concentrations (ng/L) of individual PAHs and sums of certain PAHs in leachates. Samples of 100 g were exposed to 2 L acetate buffer (pH 4.93, solid-to-liquid ratio 1/20). Estimated maximal leachate concentrations (marked with ∗) are reported in the upper right diagram (semi-transparent) assuming that all PAHs contained in 100 g of the material would be dissolved in the extract (2 L). Concentrations of some individual PAHs like anthracene (6), fluoranthene (7) and benzo(a)pyrene (13) are also shown together with sum values of other carcinogenic PAHs. Relative standard deviations were below 10% in most cases.

Reported are mean values with one standard deviation indicated. Relative standard deviations were in all cases below 10% indicating a good repeatability of the methodology. Concentrations of individual PAHs and observed relative standard deviations are given in Table S1 (Supporting information, SI). Concentrations of 1310, 15,230 and 11,360 ng/L were obtained in the unaged reference material, in

RAP and RAP with rejuvenator C, respectively, whereas 1170, 7490 and 5700 ng/L were obtained in aged samples (Table S1). According to these results, PAH sum concentrations of leachates from the RAP sample with rejuvenator C, were found to be 25% and 24% lower in the unaged and aged samples, respectively. Thus, a mobilisation of PAHs (sum of 16) was not observed.

Aging is having a substantial effect on PAH concentrations of leachates. Concentrations were two times lower in leachates of aged materials of RAP and RAP and rejuvenator C.

Assuming that all PAHs found in the extracted binder, which accounted for 27–180 mg/kg were leached in one batch of water (2 L), concentrations of 1.3–9.0 mg/L would have to be expected (Figure 4, upper right). These values are up to three orders of magnitude higher than those found in the actual leachates. In other words, less than 1% of the PAHs present in the extracted binder material did leach under the given stringent conditions (i.e. the mixture is in loose form and not compacted). Thus, the remaining materials still represent large reservoirs for PAHs. Lower PAH concentrations (sum of 16) were found in leachates of the RAP with rejuvenator C than the RAP material. Thus, the trend observed before for raw materials, was also found for leachates.

Looking at individual PAHs (Table S1), different trends can be observed. Leachate concentrations of selected PAHs and group of PAHs are also shown in Figure 4. Given are values for anthracene (Fig. 1, 6), fluoranthene (7), benzo(a)pyrene (13), the sum of the so-called 4 EC PAHs (The Council of the European Union, 1998), which includes the carcinogens benzo(b)fluoranthene (11), benzo(k)fluoranthene (12), benzo(g,h,i)perylene (15) and indeno(1,2,3,c,d)pyrene (16), as well as the sum of benzo(b)fluoranthene (11) and benzo(k)fluoranthene (12) and the sum of benzo(g,h,i)perylene (15) and indeno(1,2,3,c,d)pyrene (16). Target or limit values for these individual PAHs or groups of PAHs are given in some water quality regulations.

Slightly increasing levels are observed for certain PAHs in leachates of the rejuvenated RAP. The benzo(a)pyrene concentration is about two-fold higher with rejuvenator than without it. In other words, more benzo(a)pyrene leached from the unaged sample in presence of rejuvenator C. About 2.5 times more benzo(g,h,i)perylene and indeno(1,2,3,c,d)pyrene were released from the unaged rejuvenator sample than from RAP without rejuvenator. These trends are reversed after aging.

Concentrations of selected PAHs and sums of some PAHs are compared with limit values in two different regulations (Table 3). Leachate concentrations of certain PAHs exceed limit values for drinking water, groundwater and surface waters. It may be questioned if data from RAP leachates should be compared with limit values from water quality directives as the EU and Swiss drinking water regulations 98/83/EC (Eidgenossenschaft, 2018; The Council of the European Union, 1998) and the EU inland/surface water regulation 2008/105/EC (The European Parliament and the Council, 2008a). However, these regulations set limits for certain PAHs present in RAP. Assuming that leachates from such materials may end up in, for example, a drinking water system, would mean that benzo(a)pyrene concentrations are 1–3 times above the limit value of 10 ng/L (Table 3). In other words, PAHs contained in run-off water from roads or leachates have to be diluted before mixing with ground water. A dilution-attenuation factor (DAF) is used to describe this process (Holleran et al., 2016). DAF values from 2 up to 20 are used. According to these DAFs, PAH concentrations given in Table 3 would be acceptable.

Regarding the metal contents in leachates of three independent experiments ($n = 3$), concentrations in most samples were found to be below detection limits (Table S2, SI). For comparison, concentration limits of the EU drinking water standard (EC Directive) are 5 μg/L for Cd, 50 μg/L for Cr, 2000 μg/L for Cu, 10 μg/L for Pb, 1 μg/L for Hg, 20 μg/L for Ni and 10 μg/L for As. Metal concentrations found in RAP leachates are in agreement with literature (Legret et al., 2005). Iron levels were found to be slightly higher than values given in the regulation. A list of all metals tested is shown in Table S2 (SI).

Comparison of PAH patterns in leachates and binder materials

Patterns of the 16 priority PAHs given in Figure 1 are displayed in Figure 5. Patterns of leachates are similar in unaged and aged samples. But proportions of high-molecular weight PAHs increase to some

Table 3. Concentrations (ng/L) of selected PAHs in leachates and limit values in different regulations.

	Concentration in leachates (ng/L)						Limit values in the regulation (ng/L)		
	Unaged			Aged			Drinking water	EQS – Inland/Surface waters	
Chemical	Ref	RAP	RAP+REJ C	Ref	RAP	RAP+REJ C	98/83/EC Swiss leg.	2008/105/EC	x-Fold (max)
Naphthalene (1)	202	680	380	54	162	240		2400	
Anthracene (6)	95	1350	1000	113	772	522		100	13.5
Fluoranthene (7)	180	1610	1460	238	1310	1070		100	16.1
Benzo(a)pyrene (9)	1.3	17	33	3.2	19	16	10	50	3.3
Sum Bghi + Ipyr (15, 16)	0.5	1.4	3.5	0.5	0.5	0.5		2	
Sum BbF + BkF (11, 12)	1.3	38	55	5.7	36	32		30	1.8
Sum 4 EC (11, 12, 15,16)	1.8	40	60	6.3	37	32	100		
Sum 16 PAHs	1310	15230	11360	1170	7490	5700			

Limit values set in the Swiss and European drinking water quality regulation 98/83/EC (Eidgenossenschaft, 2018; The Council of the European Union, 1998) and the European inland/surface water regulation 2008/105/EC (The European Parliament and the Council, 2008a) were included. Concentrations at the detection limit are indicated in italics. Values in bold indicate that levels in leachates are x-fold higher than respective limit values. The sum of benzo(g,h,i)perylene (15, Bghi) and indeno(1,2,3,c,d)pyrene (16, Ipyr) and the sum of benzo(b)fluoranthene (11, BbF) and benzo(k)fluoranthene (12, BkF) are given. In addition, the sum of the so-called 4 EC PAHs (The Council of the European Union, 1998) are reported. They include benzo(b)fluoranthene (11), benzo(k)fluoranthene (12), benzo(g,h,i)perylene (15) and indeno(1,2,3,c,d)pyrene (16).

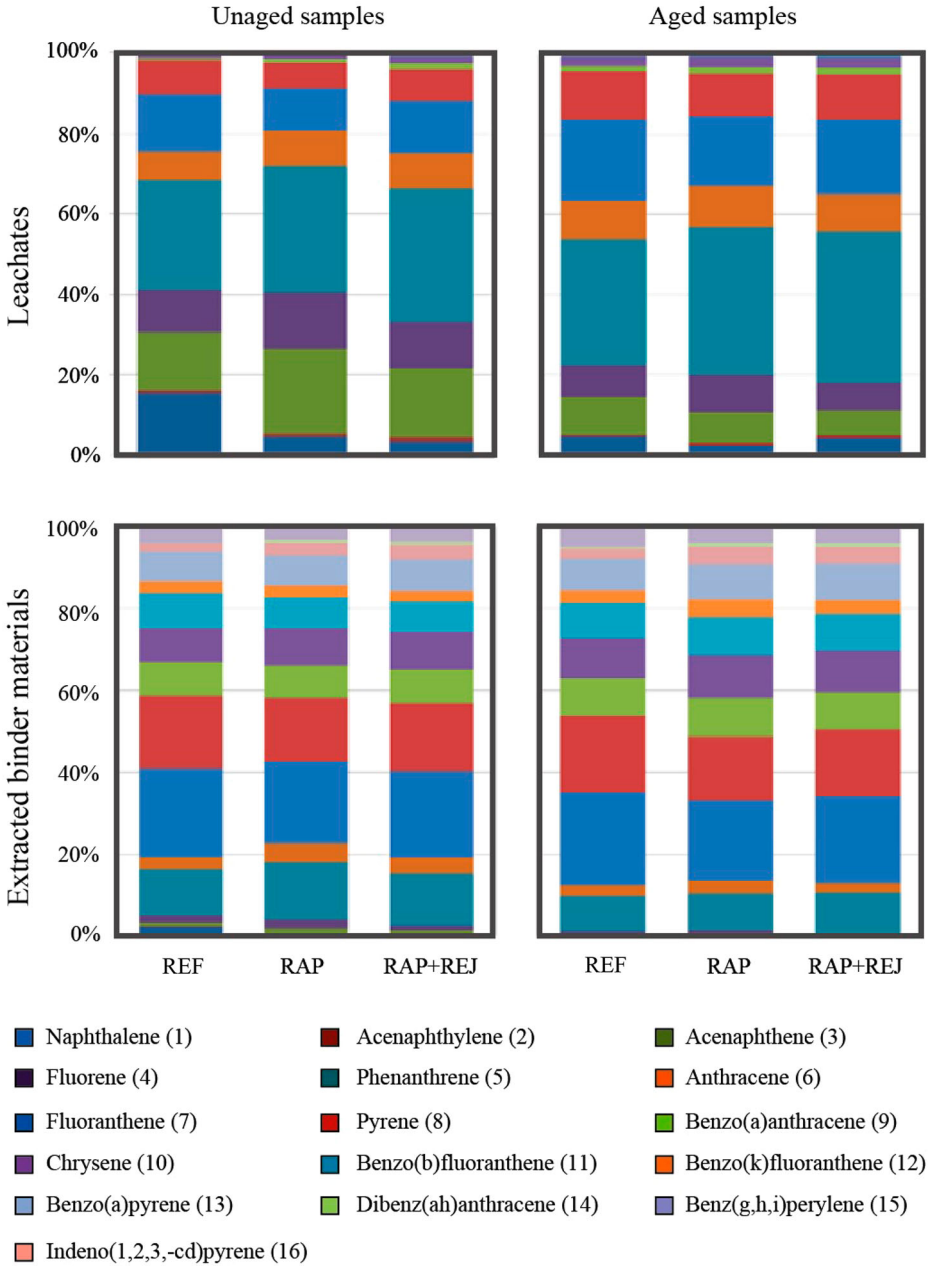

Figure 5. Patterns of 16 priority PAHs both, in leachates (top) and extracted binder materials (bottom). Different colours have been assigned to the 16 priority PAHs.

degree upon aging. Accordingly, proportions of low-molecular weight PAHs (2- and 3-ring PAHs) like naphthalene (1, blue) and acenaphthene (3, green) were higher in unaged materials (Figure 5). Similar effects have been described for other leaching processes. Norin and Strömvaix (Norin & Strömvaix, 2004) reported that the amounts of low-molecular weight PAHs decrease considerably in leachates from a stockpile of asphalt.

PAH patterns of extracted binders of reference material, RAP and RAP with rejuvenator C are also similar (Figure 5, bottom). Effects of aging on these patterns are moderate as well. Proportions of 2- and

Table 4. Solubility (mg/L) and octanol/water partition coefficients of PAHs.

Chemical name (number)	Number of rings	Solubility in water (mg/L)	Octanol/water partition coefficient (log K_{ow})
Naphthalene (1)	2	31.6	3.45
Acenaphthylene (2)	3	3.9	4.08
Acenaphthene (3)	3	3.5	3.92
Fluorene (4)	3	> 0.19	4.18
Phenanthrene (5)	3	1.18	4.50
Anthracene (6)	3	> 0.004	4.63
Fluoranthene (7)	4	0.26	5.22
Pyrene (8)	4	0.013	5.18
Benzo(a)anthracene (9)	4	0.014	5.91
Chrysene (10)	4	0.002	5.70
Benzo(b)fluoranthene (11)	5	0.0012	6.20
Benzo(k)fluoranthene (12)	5	0.00055	6.20
Benzo(a)pyrene (13)	5	> 0.0038	6.04
Dibenzo(a,h)anthracene (14)	5	0.0006	6.20
Benzo(g,h,i)perylene (15)	6	0.0003	7.10
Indeno(1,2,3,c,d)pyrene (16)	6	0.062	7.10

Solubility data of PAHs is obtained from Norin and Strömvaix (2004), octanol/water partition data from Mackay, Shiu, and Ma (1992).

3-ring PAHs including naphthalene (1), acenaphthylene (2), acenaphthene (3), fluorene (4), phenanthrene (5) and anthracene (6) accounted for only 20% and 15% in unaged and aged binder extracts, respectively (Figure 5, bottom). But in leachates these 2- and 3-ring PAHs represent about 80% and 65% (Figure 5, top).

Low-molecular weight PAHs such as 2- and 3-ring PAHs have highest volatilities and solubilities in water as shown in Table 4. Indeed the concentrations of these PAHs are the highest in leachates of our samples. Similar trends were observed by Brandt and De Groot, 2001. Transport processes of PAHs from the binder without and with rejuvenator to the asphalt surface are not well understood and may be a task for future investigations. It has been claimed that such diffusion processes are controlled by the PAH water solubility, but also by the concentration of the PAH on the surface of the asphalt gravels (Norin & Strömvaix, 2004). Other parameters like the octanol-water partition coefficients, which vary over 3 orders of magnitude for those PAHs tested (log K_{ow} = 3.5–7.1), might also affect PAH transport in rejuvenated RAP materials (Table 4).

Aging has small effects on PAH patterns of leachates and binders. PAH concentrations in leachates from aged samples were about 2 times lower than in unaged samples. These findings are significant because relative standard deviations were below 10% in most cases. However, the relation between aging and leaching needs more investigations (Guo et al., 2018).

Conclusions

In this study, the release of toxic metals and genotoxic PAHs from rejuvenated binders were tested and physical properties of respective RAP mixtures were investigated. The goal was to investigate if rejuvenators can restore the properties of binders and if they can mobilise certain pollutants like PAHs from RAP materials. Respective leachates could contain toxic compounds and affect drinking water, surface and ground water quality.

Transport of PAHs from the asphalt surface possibly is a diffusion-controlled process influenced by the PAH water solubility (Table 4), but also by the concentration of a PAH on the surface of asphalt material. We tested the initial hypothesis that rejuvenators may mobilise certain PAHs bound in the RAP and therefore may induce an accelerated release of PAHs. No such accelerated release was observed if the sum of the 16 priority PAHs is considered. On the contrary, sum concentrations of the 16 PAHs in leachates from RAP with tall oil-based rejuvenator were 25% and 24% lower than in the RAP without rejuvenator for non-aged and aged materials.

However, a more detailed analysis of individual PAHs shows increased concentrations of certain carcinogenic PAHs like benzo(a)pyrene (13), in leachates of unaged materials with rejuvenator C. This 5-ring PAH has a low water solubility and a high log K_{ow} value of 6.0 (Table 4). Other PAHs, especially 2- to 3-ring PAHs with lower log K_{ow} values of 3.5–4.6, are retained better in the material with rejuvenator.

We conclude that the leachability of individual PAHs is structure-dependent. It is influenced by size, water solubility and partitioning coefficient (log K_{ow}).

Comparing concentrations of carcinogenic PAHs in leachates with respective limit values from drinking and inland/surface water regulations, one can observe exceedances in some cases (Table 3). We conclude that the applied rejuvenator did not mobilise extra loads of PAHs present in RAP. However, certain PAH concentrations in leachates are at of above limit values of certain water regulations.

The rejuvenator did not mobilise relevant amounts of metals and metal concentrations found in leachates ($n = 3$) were within the legal limits. Respective limit values are reported in Tables S3 and S4 (SI).

As an outlook, it may be discussed if the leaching experiments performed are realistic as they tested the loose mixture not the compacted one. In this worst-case scenario, we were able to investigate whether or not rejuvenators mobilise critical compounds from RAP when exposed to water. As mentioned, less than 1% of the available PAHs in the RAP were released during batch leaching. Even if PAH leachate concentrations were low, there is a potential for a steady release of PAHs during continuous exposure to rain. It is, therefore, recommended to develop guidelines as to which values of leachates should be compared to regulation limits.

More work is also needed to establish a mechanism describing how rejuvenators could affect the chemical structure of the asphalt. Do rejuvenators dissolve in the binder, changing its polarity which would allow a better or worse up-take of certain compounds? Do rejuvenators change the adsorption characteristics of the binder on the matrix surfaces? These questions should be addressed if more RAP materials, which now accumulate in stockpiles worldwide, will be reused with the help of rejuvenators.

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