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12/11/04

LEACHING OF ORGANIC CONTAMINANTS FROM STORAGE OF RECLAIMED ASPHALT PAVEMENT

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(Received 8 December 2003; Accepted 20 February 2004)

ABSTRACT

Recycling of asphalt has been promoted by rapid increases in both the use and price of petroleum-based bitumen. Semi-volatile organic compounds in leachates from reclaimed asphalt pavement, measured in field samples and in laboratory column test, were analysed through a GC/MS screen-test methodology. Sixteen PAH (polyaromatic hydrocarbons) were also analysed in leachates from the column study. The highest concentrations of semi-volatile compounds, ~ 400 µg l⁻¹, were measured in field samples from the scarified stockpile. Naphthalene, butylated hydroxytoluene (BHT) and dibutyl phthalate (DBP) were the most dominant of the identified semi-volatiles. The occurrence of these compounds in urban groundwater, also indicate high emission rates and persistent structures of the compounds, making them potentially hazardous. Car exhausts, rubber tires and the asphalt material itself are all probable emission sources, determined from the organic contaminants released from the stockpiles. The major leaching mechanism indicated was dissolution of organic contaminants from the surface of the asphalt gravels. In the laboratory column test, the release of high-molecular weight and more toxic PAH was higher in the leachates after two years than at the commencement of storage. The concentrations of semi-volatiles in leachates, were also several times lower than those from the field stockpile. These results demonstrate the need to follow up laboratory column test with real field measurements.

Keywords: Reclaimed asphalt pavement, recycling, storage, leaching mechanism, semi-volatile organic contaminant, PAH, naphthalene, BHT, DBP, GC/MS

INTRODUCTION

The construction and expansion of asphalt roadways results in large amounts of used and milled asphalt, while interest in recycling of used asphalt intensified during the 1970s, when the price of bitumen rose rapidly. Used and milled road asphalt, known as reclaimed asphalt pavement (RAP), is temporarily stored before recycling by incorporation into new asphalt mixtures. In 2000, the yearly production of asphalt in Sweden was 7.5 million tons [1]. An investigation made by the Swedish National Road Administration showed that the Swedish recycling goal was reached, when approximately 90% of the road asphalt was recycled in 2000. Accordingly, large amounts of asphalt are removed from road surfaces and used again as new pavement, generating a need for storage and knowledge of the environmental effects of leachates. For logistical reasons it is practical to use gravel pits and rock quarries for temporary RAP storage. Glacio-fluvial deposits represent the main type for public groundwater supplies in Sweden. Leaching RAP facilities may therefore contaminate present or future water supplies in this hydrogeological setting.

In this study polycyclic aromatic hydrocarbons (PAH)

and potentially hazardous semi-volatile organic contaminants, and their leaching mechanisms from temporary storages of asphalt, are investigated. Semi-volatile organic compounds are in this study defined as, the organic compounds possible to elute from a gas chromatograph in the temperature interval 45°C to 300°C. The occurrence of semi-volatile organic pollutants in the asphalt leaching water is also compared with the presence of organic contaminants in stormwater ponds and in shallow groundwater in the urban environment, exemplified by the conditions in Göteborg. Results from leaching in the field are also compared with results from a laboratory column test.

Asphalt is a mixture of mineral aggregates, stone materials, filler and bitumen (~ 5%). Bitumen is a hydrocarbon material, derived from petroleum crude oil by a vacuum distillation process, and contains thousands of components in various chemical forms [2]. The complexity of the composition makes chemical characterisation difficult; the precise composition varies greatly depending on the source of the crude oil used. Bitumen is characterised by classification into four groups of organic substances: asphaltenes, saturates, aromatics and resins. In bitumen, PAH are present at low concentrations, 1 – 86 mg kg⁻¹ [3]. In Sweden, tar was used as

a substitute, an additive or as an adhesive agent in asphalt until 1975; tar contains approximately 10^3 to 10^5 times more PAH than the bitumen used today. Organic compounds are also used as additives to modify the properties of the asphalt; these include adhesives, plastics and rubbers [4-6], and different types of small fraction fillers (< 0.074 mm) commonly of natural origin such as lime or other mineral compounds. To our knowledge no study specifically on leaching of additives from asphalt pavement has yet been made.

PAH have been identified in contaminated soil beneath asphalt roads [7], and in runoff from highways paved with impervious and pervious asphalt [8]. Asphalt material used in the field, without any inputs from vehicle exhausts and rubber tyres, has also been proven to leach PAH to the surrounding soil [9]. In a recently presented study, the occurrence of n-alkanes and the chemical and biodegradable stable compounds, pentacyclic triterpanes and steranes, in urban river sediments, was shown to originate from road asphalt particles [10]. Benzothiazoles derived from asphalt containing rubber material, have also been measured in urban runoff [11].

In column leaching tests, the analysis of organic contaminants has dealt so far mainly with PAH, volatile organic compounds, phenols and total semi-volatiles [12-14]. In these studies, the concentrations of the organic contaminants in the leachates were reported to be under the detection limit or in very low concentrations.

Much attention is given to PAH, which have documented environmental and health effects, such as bioaccumulation [15], high toxicity [16] and carcinogenicity [17]. It has even been suggested that PAH have estrogenic effects [15]. Source PAH profiles, in road dust and road

runoff, have been used to trace PAH from tyre particles, brake lining wear, exhausts, and fuel oil [18-20]. There are, however thousands of partially known substances in car exhausts, which are the major sources of hydrocarbons in the road environment [21]. Results from a field experiment showed that pollutants generated from road traffic were the major source of inorganic contamination in leachates from used asphalt [22].

Due to the complex origin of organic contaminants leaching from asphalt storage, it is difficult in advance to choose analytical methods that best reveal the chemical composition. The choice of analytical methods heavily influences the results and their interpretation. In the present study, a GC/MS screening method was used to assess the semi-volatile organic compounds in the asphalt leachates, as well as in stormwater and groundwater samples. The main reason for choosing the GC/MS screen-test methodology was to find semi-volatile compounds that have not yet been investigated as pollutants from RAP.

MATERIALS AND METHODS

Asphalt Stockpiles

An experimental site was constructed to evaluate the unsaturated leaching process of RAP, e.g. milled road asphalt, stored before recycling. The site, which lies in the rural district of H arryda, on the Swedish West Coast, was originally used as a gravel pit. The outdoor asphalt storage was two circular stockpiles, 12 m in diameter, each divided into four sections, see Figure 1. Each section was separated by kerbstones, which made it possible to separate the leachates. The geometric parameters of the stockpiles are presented in Table 1.

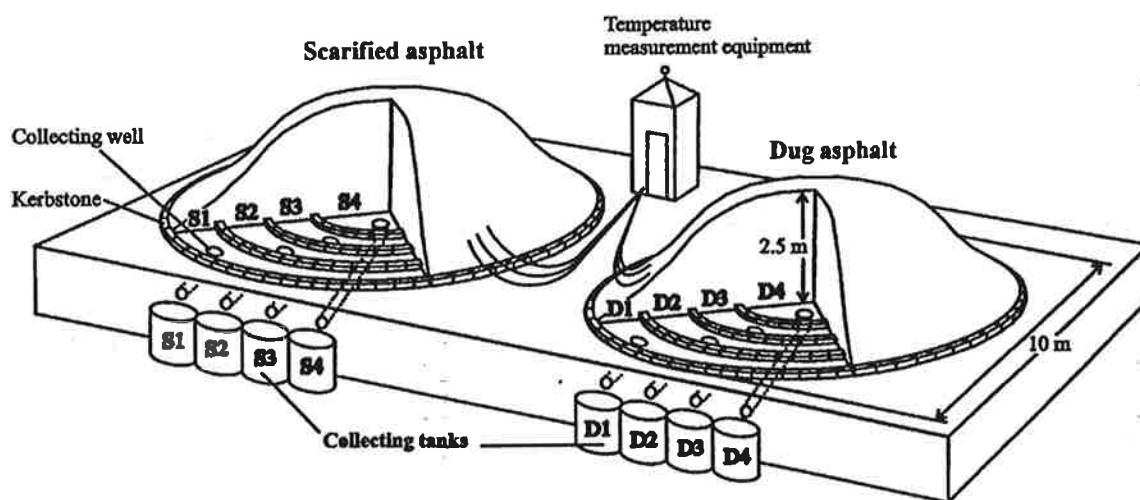


Figure 1. Experimental site with asphalt stockpiles of two material textures: scarified asphalt (S) and dug asphalt (D). Each storage is divided into four sections.

Table 1. The geometric parameters of two asphalt stockpiles: scarified asphalt (S) and dug asphalt (D).

Section	Area (m ²)	Relative area ^a	Height ^b (m)		Volume (m ³)		Slope ^b		Mass ^c (tons)
			S	D	S	D	S	D	S
S1/D1	49.5	7	0.3	0.2	14	12	18	8	19
S2/D2	35.3	5	1.2	0.8	41	28	22	11	57
S3/D3	21.2	3	1.8	1.6	38	34	21	7	53
S4/D4	7.1	1	2.5	2.4	18	17	4	2	25
Total	113				111	91			154

^a Area of each section divided by the inner area S4/D4.

^b Mean values based upon measurements across and alongside each section.

^c A bulk density of 1400 kg m⁻³ was used for the calculations of the scarified asphalt.

The foundation of the storage was a gently sloping (< 2 %) plate of asphalt, 25 × 25 m. Two types of asphalt were used to fill the storages: scarified asphalt, S (gravel fraction), and asphalt dug from a road surface, D. The central sections of the stockpiles, S4 and D4, represent leachates that have percolated vertically. From the outer sections, S1 and D1, runoff samples were taken.

Leachates from the eight sections were collected in tanks, which were placed outside the storage. Sampling was done during the first year the asphalt was stored. Water samples were taken every month from the outlet tap, at the bottom of the collecting tanks (Figure 1). All materials in the tubing and collection tanks were carefully chosen to avoid organic contamination. Twenty-seven samples were selected for the analysis of semi-volatile organic compounds. The volume of leachate was also measured. Most of the samples were taken from the inner sections of both stockpiles, since a high content of organic compounds was expected in the leachate from these sections. Six samples were taken from inner section S4, seven from section D4, and two from each of the other sections. Sometimes, sample data is missing because the tanks were dry and no leachate was available for analysis. In parallel with the measurements of organic pollutants, inorganic parameters and metals were analysed [23].

Material Properties

The scarified and dug asphalt corresponds to 3 cm and 10 cm depth of road surface, respectively. The scarified asphalt was a highway road surface for 11 years, with a traffic load of approximately 7100 vehicles per day, of which 830 were lorries. Geologically, the scarified asphalt material is classified as gravel with an effective grain size (d_{10}) of 2 mm, porosity of 41 % volumetric, bulk density of 1370 kg m⁻³ and specific area of 1710 m² m⁻³. The physical properties calculated were based on the grain size distribution [23]. The binder content was 5.5 % of total weight. The dug asphalt pieces have

a diameter of 0.2 – 0.5 m. Both types of asphalt samples were taken directly from the road to the storage.

Meteorological data was obtained from the Swedish Meteorological and Hydrological Institute (SMHI) measurement stations nearby. The precipitation during the sampling period, October 1997 to October 1998, was 1190 mm, and evapotranspiration was 470 mm. The mean, maximum, and minimum air temperatures were 6°C, 19°C, and -12°C, respectively. In the storage, however, the temperature was higher during summer period (+5°C, 1 m below surface). Precipitation on the Swedish west coast has a pH value of around 4.5, sometimes even lower; it also has a high content of chloride, 4 – 20 mg l⁻¹ [22]. The composition of the rain contributes to a relatively aggressive leaching environment.

The Stormwater Pond and the Groundwater Sampling Area

Stormwater samples were taken at six occasions and analysed for their content of semi-volatile organic compounds. The samples were taken close to the inlet to the pond, a 400 mm concrete pipe. The pond, near the storage site and Lake Delsjön, 10 km east of Göteborg, receives drainage water from a major highway. Gross samples were collected at the stormwater pond by filling glass bottles with water.

Shallow groundwater samples were taken on two occasions, from three observation wells, 3 m deep, in the city of Göteborg: Chalmers, Järntorget and Magasinsgatan. The upper aquifers investigated all consist of filling material (1 – 7 m), overlying clay. The groundwater level varies between 1 – 2 m beneath ground level [24]. Gross samples were taken by pumping groundwater from the wells into glass bottles.

The Laboratory Column Test

In a laboratory column test, leaching of total organic carbon (TOC), PAH and semi-volatile organic compounds were investigated in samples of scarified asphalt from the

stockpile. The first asphalt sample, taken directly from a road when the road surface was being milled, was designated 'not stored' asphalt. The second sample, taken from the top of the stockpile after two years of storage, was termed 'stored asphalt'. The saturated column leaching of organic compounds was done with a modified method, use of glass columns and inert atmosphere, of NT ENVIR 002 [25], originally developed for inorganic leaching. Glass columns with an inside diameter of 0.12 m and a height of 1.00 m were used. The columns were filled with sieved scarified asphalt (< 2 mm), and acidic nanopure water (pH 4 with added H₂SO₄) was continuously pumped from a tank through a teflon tube into the bottom of the columns. The amounts of asphalt used were 10.3 kg 'not stored' asphalt and 6.6 kg 'stored asphalt'. Nitrogen was used in the tank to secure oxygen-free conditions, to avoid oxidative degradation of the organic contaminants. The columns were covered with aluminium foil and closed with teflon plugs, to minimise chemical degradation during the leaching process. Water samples were taken at two ratios for the amounts of liquid (L) and solid material (S): they were L/S ratio 0.05 (not stored), 0.07 (stored), and for both L/S ratio 1.0. The water samples were collected in dark glass bottles which were kept cold, 4 ± 2°C; they were analysed for organic compounds within six days.

Chemical Analysis

Leachates from the asphalt storages, water samples from the stormwater pond, urban groundwater samples, and leachates from the column test were analysed by an accredited geochemistry laboratory. All samples were analysed for semi-volatiles, and samples from the column test, with low L/S ratios, were also analysed for 16 specific PAH. The samples were extracted by separatory funnel liquid-liquid extraction, with hexane as extraction liquid, following the extraction procedure described in US EPA method 3510 [26]. The samples for semi-volatiles were identified and quantified through GC/MS, following the US EPA method 8270 [26], and the PAH were identified and quantified by GC/MS with a procedure based on US EPA method 8100 [26]. The limit for quantification of a specific semi-volatile compound was 10 µg l⁻¹, and for each PAH the detection limit was 0.01 µg l⁻¹.

The semi-volatiles in the samples were further identified through a GC/MS screen-test evaluation methodology developed by the authors, and based on information in chromatograms and mass spectra handed out from the geochemistry laboratory. For all samples evaluated, the compounds identified were systematically grouped according to their retention time and mass spectrum. These compounds were given a suggested structural formula and a chemical name, based on suggestions from the computer library search. The total number of organic compounds identified in each sample was used as an indication of high or low leaching. The total concentration of semi-volatiles in each sample was estimated by adding concentrations for compounds >10 µg l⁻¹.

For a few of the samples, the semi-volatile compounds identified from the geochemistry laboratory results, were further verified by running duplicates of the samples at Chalmers. These samples were extracted by solid-phase microextraction (SPME) and analysed through GC/MS by the authors. The SPME technique is based on the principle of adsorption and desorption of organic compounds on a polymeric phase, PDMS 7 µm, coated on a fused silica fibre [27]. With the screen-test method used at Chalmers, the samples were analyzed on a Varian 3800 gas chromatograph, equipped with a FSOT (Rtx 1701, 0.25 µm) column (30 m x 0.25 mm i.d.), and a Varian Saturn 2000 mass spectrometer as detector. The SPME fibre was injected with a syringe device, and desorbed for 5 minutes in the GC injector at a temperature of 280°C. The compounds were separated by increase of the column temperature, 10°C min⁻¹, from 45°C to 280°C. The electron-impact mass spectrometer analysed ions, 1 scan sec⁻¹, within the mass scan 45 – 450 m/z; giving a total ion chromatogram. The interface temperature was set to 280°C. The organic compounds were identified and verified by a comparison of the given mass spectrum with mass spectra from a computer library (Wiley and NIST).

Organic compounds with environmental effects, i.e. organic pollutants, often occur in extremely low concentrations and are not detected with the low sensitivity screening methodology. However, screen-test methods are useful, to analyse large quantities of samples of unknown composition or, as in this study, to find new compounds not studied before.

The samples from the column study were also analysed for TOC on a Total Organic Carbon analyser, Model 700 TOC, with a technique based on combustion and infra-red analyser detection, following the procedure in US EPA method 415 [28]. In this standardized method, the total inorganic carbon is purged from the samples and not included in the final TOC value.

RESULTS AND DISCUSSION

Leaching of PAH, Total Semi-Volatiles and TOC in the Column Study

Concentrations and total amounts of PAH, total semi-volatiles and TOC, leached from scarified asphalt in the column study, are presented in Table 2. Results are given for leachates, both before and after two years of stockpile storing of scarified RAP. The highest concentrations and amounts of TOC 33 mg kg⁻¹, at L/S ratio 1.0, were found in the leachate from the RAP at the start of the field storage. The amounts released were as expected, ten times higher in the sample with the highest L/S ratio. After two years of storage, the amounts of TOC released decreased by more than 50%, but concentrations in the leachates and the released amounts are still high. The total concentrations of PAH follow the same leaching trend as the TOC values, however the total PAH amounts released, 1.8 and 0.9 µg kg⁻¹, constitute only

Table 2. Concentrations and total amounts of polycyclic aromatic hydrocarbons (PAH), total semi-volatiles and total organic carbon (TOC), released from leachates in the column study of scarified asphalt, before and after 2 years of stockpile storing.

PAH compound	Asphalt not stored L/S 0.05		Asphalt stored L/S 0.07		Total amounts leached L/S 100 $\mu\text{g kg}^{-1}$ [14]	Percent of total available amounts (%) ^a
	$\mu\text{g kg}^{-1}$	$\mu\text{g l}^{-1}$	$\mu\text{g kg}^{-1}$	$\mu\text{g l}^{-1}$		
Naphthalene	1.414	28	0.645	9.2	392	3.6
Acenaphthylene	0.023	0.5	0.025	0.4	33.8	0.06
Acenaphthene	0.150	3.0	0.051	0.7	5.70	2.6
Fluorene	0.107	2.1	0.038	0.5	12.3	0.9
Phenanthrene	0.090	1.8	0.048	0.7	16.9	0.5
Anthracene	0.027	0.5	0.008	0.1	<1.78	-
Fluoranthene	0.007	0.1	0.010	0.1	<3.56	-
Pyrene	0.005	0.1	0.009	0.1	6.23	0.08
Benzo(a)anthracene*	<0.0005	<0.01	<0.0007	<0.01		
Chrysene*	<0.0005	<0.01	<0.0007	<0.01	24.9 ^b	<0.002
Benzo(b)fluoranthene*	<0.0005	<0.01	<0.0007	<0.01	<5.34	-
Benzo(k)fluoranthene*	<0.0005	<0.01	<0.0007	<0.01	<3.56	-
Benzo(a)pyrene*	<0.0005	<0.01	<0.0007	<0.01	<7.12	-
Indeno(123cd)pyrene*	0.001	0.02	0.003	0.04	<5.34	-
Benzo(ghi)perylene	<0.0005	<0.01	<0.0007	<0.01	<3.56	-
Dibenz(ah)- anthracene*	0.002	0.04	0.013	0.2	<3.56	-
Σ PAH	1.8	36	0.85	12	530	- 0.4
Total semi-volatiles	1.9	37	2.5	50		
TOC	3 400	68 000	2 000	28 000		
TOC (L/S 1.0)	33 000	33 000	17 000	17 000		

* Classified as cancerogenic PAH.

^a Total amount of polycyclic aromatic hydrocarbons in leachates from asphalt not stored divided with the total amounts leached.

^b The sum of benzo(a)anthracene and chrysene.

approximately 0.005% of the TOC. Consequently, the values for TOC show clearly that the major part of the organic compounds leachate from used asphalt is still unidentified organic compounds of unknown origin. For total semi-volatiles, the concentration and total amounts released (Table 2) were higher for the stored sample, $2.5 \mu\text{g kg}^{-1}$, than for the unstored sample, $1.9 \mu\text{g kg}^{-1}$; this indicates a trend opposite to that of the release of TOC and PAH. An explanation could be the low concentrations and the few compounds identified in the leachates from the column study, depending on the dilution of the compounds at the L/S ratios used.

In Table 2, the total amounts of leached PAH are also compared, with the total available amounts of PAH, leached from asphalt taken before storage and finely ground (< 125 μm), in a batch test, at a L/S ratio of 100 [14]. The total available test was carried out by a modification of a standardised method for inorganic compounds. The purpose was to obtain a value for the total amounts of PAH, which theoretically and in a long-term perspective could be leached

from the RAP. This 'total available' sample was taken on asphalt from the same location as the asphalt used in this study. The amounts of total PAH leached, in the present column test, were < 0.4% of the total amounts available for leaching.

The total amounts of PAH leached from scarified asphalt in the column study are presented, both before and after 2 years of stockpile storing, in Figure 2. The results show clearly that naphthalene, the two-ring and most volatile PAH, dominates in the leachates. Hence, naphthalene is an important 'marker substance' for RAP. The total leaching of PAH is more than twice as high at the start of the storage, and the most volatile and most water soluble of the PAH, those with 2 - 4 aromatic hydrocarbon rings, clearly dominate. After two years of stockpile storage, the amounts of the most volatile PAH released decrease considerably, due to leaching processes, volatilisation, and chemical and microbial degradation [29]. In contrast, the PAH of highest molecular weight, with five rings, clearly increased in concentration, in

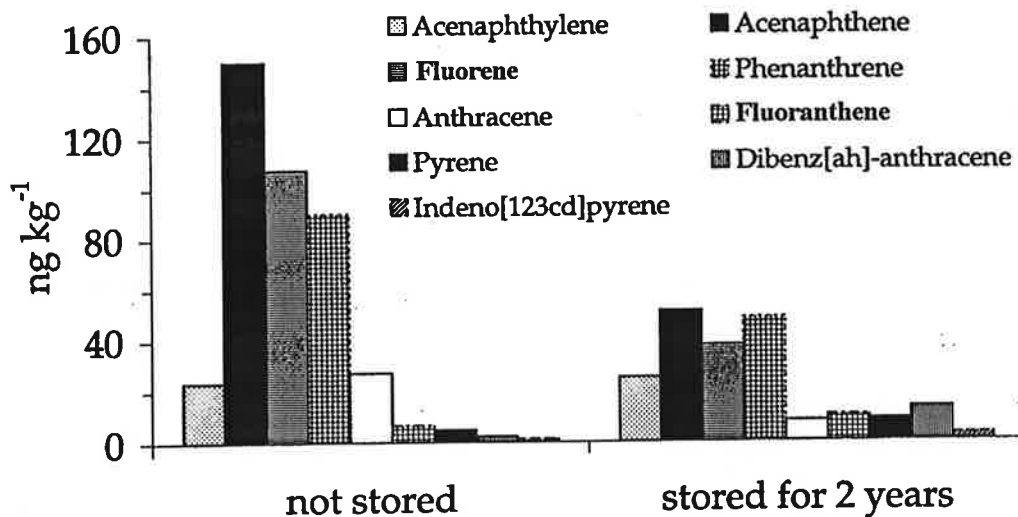
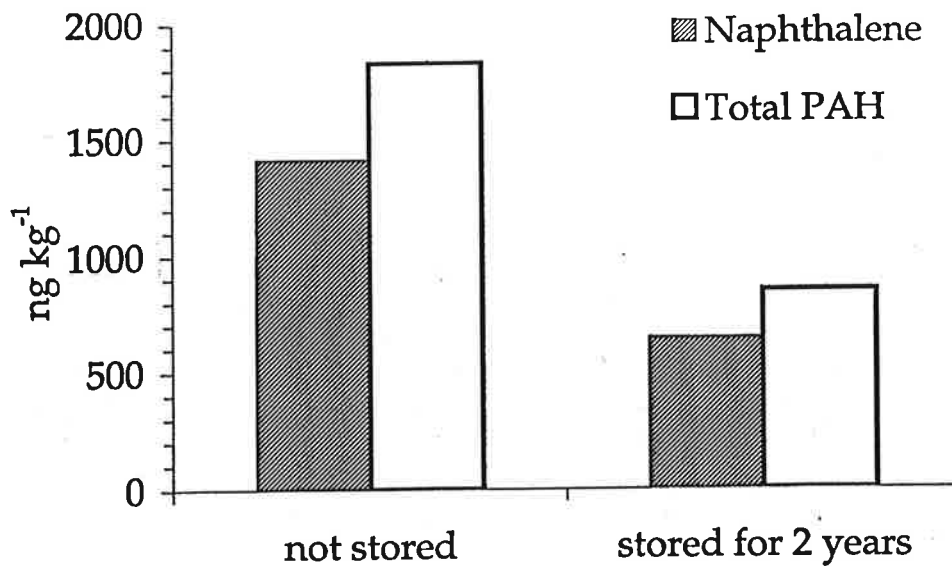


Figure 2. Cumulative amounts of polycyclic aromatic hydrocarbons (PAH) released into leachates in the column study of scarified asphalt, before and after 2 years of stockpile storing.

the leachates with time. These PAH of higher molecular weight also have the most negative environmental effects and the most serious health risks. TOC decreases with time, while PAH with a higher molecular weight and more toxic composition increase with time. These results clearly show the importance that measures of sum parameters, such as TOC and total semi-volatiles, should always be accompanied by measurements of specific organic pollutants, otherwise ecotoxicological risk assessments of the release of organic compounds from the stockpiles are impossible.

Source identification of the polycyclic aromatic hydrocarbons (PAH)

In a recently presented study, the increases of PAH in urban aquatic systems are explained by the increase in vehicle traffic [30]. The relative composition of PAH in the asphalt leachates from the column study is presented in Table 3 and compared with the PAH composition in bitumen [31,32], rubber tyres [31], light-duty diesel and petrol vehicle exhausts [33]. These results indicate the sources of the PAH leached from the RAP, by given characteristic chemical PAH indicators for each potential source. The comparison is

Table 3. The relative composition (%) of polycyclic aromatic hydrocarbons (PAH) released from stored asphalt pavement, compared with the relative composition in light-duty diesel exhausts, bitumen and vehicle tyre rubber.

PAH compound	Stored asphalt L/S 0.07	Light-duty diesel exhaust [33]	Bitumen B 180 [31]	Bitumen B 80 [32]	Tyre rubber [31]
Naphthalene	76	61	19	1.5	n.d.
Acenaphthylene	2.9	1.6	n.d.	0.20	n.d.
Acenaphthene	6.0		0.8	0.52	n.d.
Fluorene	4.5	2.5	1.4	2.3	n.d.
Phenanthrene	5.6	19	7.4	3.7	12
Anthracene	0.94	2.0	2.9	0.33	2.5
Fluoranthene	1.2	2.7	n.d.	1.4	17
Pyrene	1.1	7.1	9.5	4.1	58
Benzo(a)anthracene*	<0.08	0.28	n.d.	13	n.d.
Chrysene*	<0.08	0.40	19	16	n.d.
Benzo(b)fluoranthene*	<0.08	0.50	9.3	19	3.8
Benzo(k)fluoranthene*	<0.08	0.20	1.8	n.d.	0.9
Benzo(a)pyrene*	<0.08	0.60	12	9.2	4.3
Indeno(123cd)pyrene*	0.35	0.80	1.8	3.6	1.8
Benzo(ghi)perylene	<0.08	1.4	15	15	n.d.
Dibenz(ah)anthracene*	1.5	0.09	n.d.	9.9	n.d.

* Classified as cancerogenic PAH.

possible because the transport process of PAH from asphalt surface is a diffusion process, controlled by the PAH water solubility, but also by the concentration of the PAH on the surface of the asphalt gravels. As an example, chrysene is a PAH with low water solubility, but in the total available test leached from the RAP in high amounts (Table 2), depending on high amounts in bitumen materials [32,34,35].

The dominant polycyclic aromatic compound leached from the asphalt is naphthalene with an occurrence of ~80% of the total PAH. The percentages of naphthalene found in literature studies vary widely, which is probably explained by errors in the measurement techniques used. A study of the PAH composition in exhausts, from light-duty diesel and petrol vehicles, showed that naphthalene was the most prominent of the PAH [33]. For diesel exhausts, naphthalene constituted ~60% of the total PAH, and for petrol exhausts as much ~80%. These results demonstrate that car exhausts could be the main contributor to the naphthalene in the leachates of RAP. Heavy-duty diesel vehicles are otherwise known to emit much larger amounts of PAH, but depending on the number of vehicles the total amounts of PAH released in Sweden are much higher from the light-duty vehicles and petrol cars. The asphalt material itself is also a possible but minor source of PAH, because naphthalene is a PAH component in bitumen [32-35]. Naphthalene could also be leached from rubber tyres on the asphalt surface, since it is a component in coal tar or petroleum based process oils used as additives in tyres [36]. In composition studies of tyre rubber, naphthalene has received little attention [19,31,37].

Semi-volatile PAH, with three and four aromatic rings,

as acenaphthylene, acenaphthene, fluorene, phenanthrene and anthracene, are leached in relative amounts higher than 1% from the asphalt samples. Of these compounds, acenaphthene is the highest, 3%; it may originate from petrol car exhausts that contain large amounts of acenaphthylene and acenaphthene [33]. Earlier studies have indicated benzo[g,h,i]perylene and coronene as a petrol marker in car exhaust, and pyrene, fluoranthene and phenanthrene as diesel exhaust markers [20, 38]. All of these compounds are identified in the leachates from the RAP.

The PAH concentrations in rubber tyres are high, 30 – 100 mg kg⁻¹ [31]. Pyrene, the polycyclic aromatic hydrocarbon that occurs in the highest concentrations (~60%), together with fluoranthene and phenanthrene, are chosen as 'markers' for the release of tyre rubber. Here, in the RAP leachate, pyrene is found in small amounts, and it can be concluded that rubber tyres are not the main source of PAH. However, the occurrence of pyrene, fluoranthene and phenanthrene in the leachates indicates that smaller amounts could originate from rubber.

The main sources of the PAH released in our study have so far been indicated as car exhausts. On the other hand, leaching of PAH from the asphalt material itself is possible and high concentrations of PAH and other hydrocarbons have been recorded in soil, beneath an asphalt cover [9]. The composition of the PAH in bitumen is quite variable; it depends on the tar content and the origin of the crude petroleum oil used, see Table 3. Benzo[a]pyrene, benzo[g,h,i]perylene, chrysene, benzo[b+k]fluoranthene and indeno[1,2,3-c,d]pyrene could all be chemical indicators of

PAH leaching from bitumen [32, 34, 35]. The concentration of chrysene and benzo[a]anthracene is high in the 'total available' asphalt sample (Table 2); if bitumen was the major source of PAH in the RAP leachates, chrysene and benzo[a]anthracene should be in higher concentration than reported in this study.

Semi-Volatiles Identified by the GC/MS Screen-Test

Number of semi-volatile compounds.

The number of compounds identified by their characteristic mass spectrum and retention time in the samples is of importance because it is often correlated to the total concentration of compounds released: more compounds identified, indicates a higher total leach of semi-volatiles. Thirty different semi-volatile compounds were identified in the samples analysed by the GC/MS screen-test, and the number of compounds and the total concentration of semi-volatiles were highest in the leachates from the scarified stockpile. In leachates from both stockpiles, the number of compounds identified and their concentrations were highest in the inner sections, S4 and D4. This points to heavy leaching of organic compounds from the inner sections, which is explained by the longer vertical transport process, and an asphalt layer thicker than in the outer sections. The longer contact between the percolating water and the asphalt makes different leaching mechanisms of organic compounds from the asphalt possible.

The number of semi-volatile compounds identified and the concentrations were also higher in the leachates from the field storage compared with the leachates from the column study. The main reason is that the L/S ratio in the field was much lower than in the standardised methodology for column leaching. During the first year, the L/S ratio in the inner section of the scarified stockpile varied from 0.0003 to 0.2. The results also indicate that the composition of the semi-volatile compounds leached from the laboratory column test differs from that of the leachates from the field stockpile. The time perspective is another key factor that could affect the result: at a lower leaching rate, the molecular diffusion is reduced [39]. The leaching in columns continued for a few days, while the study in the field extended to a whole year; this demonstrates the concern to follow up laboratory testing for leached organic compounds with real field measurements. It is crucial to make further studies and measurements of field leachates, because the column study results for PAH and other semi-volatiles are under or close to the limit of detection [12, 14]. Previous conclusions from column studies were that there is no ongoing leaching of PAH and other semi-volatiles and, therefore, no environmental problems correlated with leaching from temporary storages of asphalt.

Time-dependent leaching

The time dependence of the total concentrations of semi-volatiles is presented in Figure 3 for the inner sections of

the asphalt storages, the stormwater and groundwater. The curves clearly indicate differences in leaching behaviour between the two structural types of asphalt stored in the stockpiles; in the dug asphalt stockpile, the flow rate is faster and the concentrations are always lower, which is likely to be related to the smaller contact area between the leachate and the asphalt. For both stockpiles, the number and concentration of compounds increases during Spring and Summer, which could be explained by the rise in temperature during the summer season [40], thereafter the concentration decreases. The concentration of total semi-volatiles was in the same level at the end of the measurements in the autumn, as at the start of the project one year earlier.

The concentrations of total semi-volatiles found for all samples are lower than the true values, because only the areas of the peaks with a concentration $>10 \mu\text{g l}^{-1}$ are included. In the chromatograms with the highest concentrations of organic compounds, the scarified asphalt in Figure 4, there was also a high background, which disturbed the resolution of the peaks, resulting in smaller areas and hence lower concentrations. This background, common in chromatograms with old and higher molecular weight petroleum products, is an indication of incomplete biological degradation [41]. These compounds are relatively persistent, strongly isomeric hydrocarbons, or highly polar degradation products. In the chromatograms from the column study, the humps have more or less disappeared after two years of storage of the asphalt.

The content of total semi-volatile organic compounds in the stormwater, and groundwater, is several orders of magnitude less than the content of the leachate from the asphalt storage. In the groundwater the concentration was within the same range as in the stormwater on the first sampling occasion, however on the second occasion it was at least twice as high. This can be related to the higher mean temperature on the second sampling occasion, and indicates that solubility increases with temperature while percolation decreases during summer. The concentration of semi-volatile organics in the stormwater is more uniform.

Identification of semi-volatiles

Six of the thirty compounds identified that occur most frequently in the leachates and water samples are presented in Table 4. For all of these compounds, the retention time (t_R) from the chromatograms, characteristic mass values (m/z) from the mass spectra, frequency of occurrence in the samples, and the highest given probability of conformity are provided.

Naphthalene, identified in eight of the 27 leachate stockpile samples, was indicated with a high probability, however a concentration of $>10 \mu\text{g l}^{-1}$ was found in only two of the samples. Naphthalene was also identified and quantified in high concentrations in the PAH analysis. Butylated hydroxytoluene (BHT) had a high probability as well; the presence of BHT was also verified in a few of the samples, by analysis with an SPME extraction and GC/MS

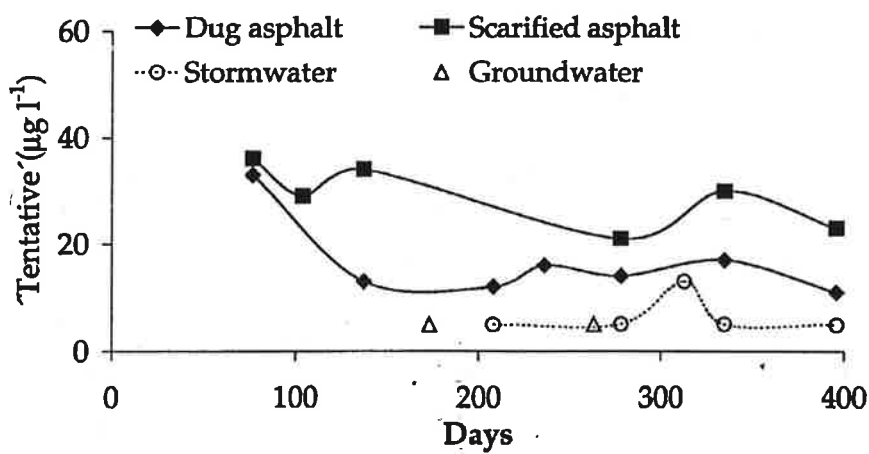
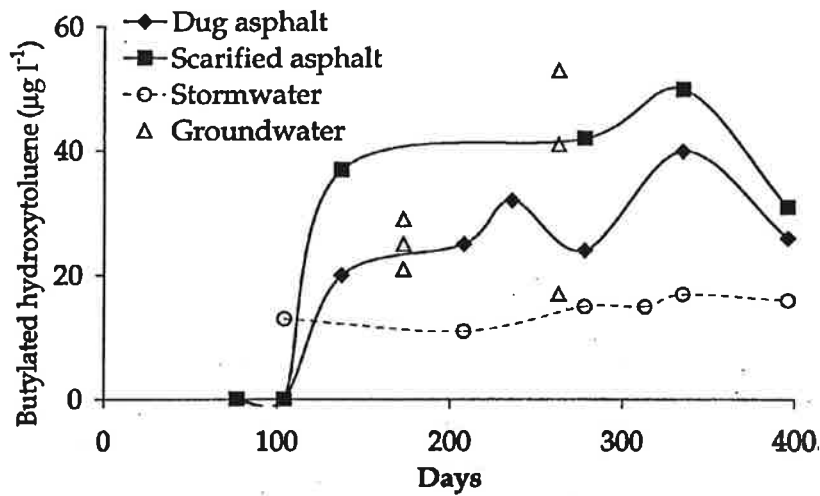
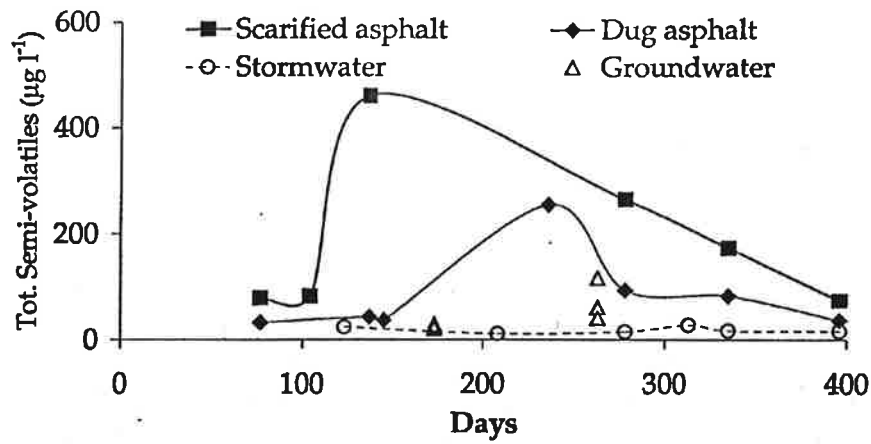


Figure 3. Time-dependent leaching behaviour of total semi-volatiles, the suggested *m*-phenethyl-benzonitrile compound and butylated hydroxytoluene (BHT), in leachates from the inner sections of the stockpiles with scarified asphalt, S4 and dug asphalt, D4, compared with concentrations in stormwater and groundwater samples (■ Scarified asphalt; ◆ Dug asphalt; ○ Stormwater; △ Groundwater).

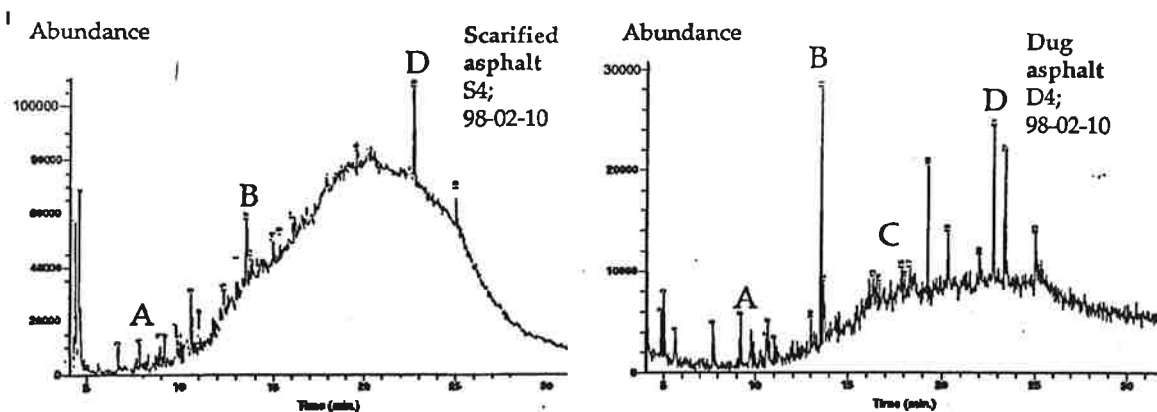


Figure 4. Chromatograms with the occurrence of organic contaminants in leachates from asphalt storages (A = naphthalene; B = BHT; C = DBP; D = tentative 'm-phenethyl-benzonitrile').

Table 4. Number of samples^a with the suggested semi-volatile organic compound^b in asphalt leachates from the column study and field storages, stormwater and groundwater, together with identification data from the GC/MS screen-test.

Chemical name	Column study asphalt	Asphalt stock-piles	Storm-water	Ground-water	t _R ^c (min)	Mass values ^d (m/z)	Probability ^e (%)
Naphthalene	1 (1)	2 (8)	- (2)	- (5)	9.2	128 102	87
Butylated hydroxytoluene, BHT	- (-)	10 (12)	6 (6)	6 (6)	13.5	205 220	88
Dibutyl phthalate, DBP	- (-)	6 (13)	- (-)	- (-)	18.5	223 149	20
N-butyl-benzenesulfonamide	2 (-)	- (-)	- (-)	- (-)	17.2	213 141	91
m-phenethyl-benzonitrile or Dibenzylhydroxylamine	- (-)	22 (22)	1 (6)	- (6)	22.7	312 207	5 or 53
Di(2-ethylhexyl)phthalate, DEHP	- (2)	- (-)	- (-)	- (-)	23.4	279 149	78

^a Based on 27 asphalt stockpile leaching samples, 4 column leachates, 6 stormwater and 6 groundwater samples.

^b Bold figures = number of samples with the suggested compound in a concentration >10 µg l⁻¹. (Figures in parenthesis) = number of samples with the concentration of the compound below the limit of quantification included. - = not detected.

^c t_R = retention time from the chromatograms.

^d Characteristic ions from the mass spectra. Left column gives the base peak, ~ molecular weight. Right column shows one of the characteristic, most abundant, ion identified.

^e Highest probability for the suggested chemical formula given by the computer library.

screen test made at Chalmers. In 12 of the stockpile leachate samples, BHT occurs at the highest concentrations, 20 – 50 µg l⁻¹. Dibutyl phthalate (DBP) is also indicated: it occurs in 13 of the samples of stockpile leachate water, although in low concentrations. The N-butyl-benzenesulfonamid and Di(2-ethylhexyl)phthalate DEHP are both indicated with a high probability, but identified only in the leachates from the column study. N-butyl-benzenesulfonamid was present in relatively high concentrations ~ 40 µg l⁻¹ in the column. For one compound, two structures and chemical names are given: m-phenethyl-benzonitrile or dibenzylhydroxylamine,

however both structures proposed have a low probability. The long retention time and high mass values on the base peak in the mass spectrums for this compound, indicates a higher molecular weight compound than the suggested structural formulae. This compound is important to follow up by further identification, since it occurs in high concentrations in nearly all of the leachate samples. Most of the compounds in Table 4 were also present in the stormwater, as well as in all of the groundwater samples.

For two of the compounds, the tentative 'm-phenethyl-benzonitrile' and butylated hydroxytoluene, the

concentrations were high enough, in the inner sections of both of the stockpiles, to make it possible to follow the leaching behaviour throughout the year. The time-dependent leaching for both compounds is presented in Figure 3.

The tentative compound 'm-phenethyl-benzonitrile' was also identified in all groundwater and stormwater samples, but in concentrations < 10 µg l⁻¹, with the exception of a single stormwater sample in which it was 13 µg l⁻¹. In all of the stormwater and groundwater samples, BHT is detected in concentrations >10 µg l⁻¹. However, the content in the stormwater was always lower than in the leaching water. The BHT content in the urban groundwater is, on the other hand, surprisingly high (17 - 52 µg l⁻¹); in one sample it is even higher than that in the leachate from the asphalt stockpile (Figure 3). Although this indicates a persistent chemical structure of BHT, and a likelihood of accumulation in groundwater, it also means that other sources are possible. Hence, BHT is indicated as a potential contaminant for groundwater and stormwater. The results in this investigation contrast somewhat with earlier ones, in that relatively high concentrations of new semi-volatile organic substances have been identified. The reasons for finding more compounds are the analytical methodology used (repeated GC/MS-screening) and experimental design (field experiment), which results in a low L/S ratio.

Source identification of butylated hydroxytoluene (BHT) and dibutylphthalates (DBP)

Butylated hydroxytoluene, commonly used as an antioxidant, is added to petroleum products, jet fuels, plastics and rubber, and has also been used in food products [42]. In bitumen, it is used as an antioxidant stabilizer and in asphalt as a binder in the form of petroleum resins. In addition, BHT is added (~ 1%) to asphalt to decrease hardening when mixing with rock aggregates and to retard skin formation during hot storage [43]. Vehicles are also a possible emitter of BHT, since it is emitted from polymer materials used as the interior trim in automobiles [44]. Plastics from road vehicles, car exhausts, and fuel spills could also be possible sources.

Phthalates are essentially used as plasticisers in the production of polymeric materials [45]; DBP is used as a plasticiser, as a binding agent, in rubbers, plastics and surface coatings and as a high boiling solvent. It is also readily used as an additive to bitumen [46].

Calculations of Cumulative Leaching

The cumulative leached amount $A_{t,j}$ (µg kg⁻¹) for all of the semi-volatile organics, BHT and the tentative compound 'm-phenethyl-benzonitrile', was calculated for the first year of storage, for the inner section of the scarified stockpile (equation i).

$$A_{t,j} = \frac{1}{m} \sum_{i=0}^t c_i V_i \quad (i)$$

The calculations are based on: the mass of scarified asphalt, m_i (kg), in section S4 (Table 1), the concentration of each component, c_i (µg l⁻¹), each time samples were taken (Figure 3) and the total volume of leachate, V_i (l), between the sampling occasions.

The volume of leachate, measured during the first 140 days of storage, needed 50 days before the first precipitation percolated through the 2.5 m depth of the scarified asphalt (the inner section (S4) of the stockpile). The measured volume for the first four months showed that the outflow corresponds to approximately 10% of the net precipitation (precipitation minus evapotranspiration). Thereafter, the volume of leachate was estimated to be 10% respectively 50% of net precipitation, assuming that the water content in the storage continues to build up; allowing only a limited precipitation to seep through the stockpile. The results from the field storage correspond to a period where the asphalt is slowly getting wet, and a complete annual cycle with respect to moisture content is therefore not obtained.

The total cumulative semi-volatiles leached from the inner section of the scarified asphalt, during the first year of storage, was 4 - 10 µg kg⁻¹ of asphalt, see Figure 5. The corresponding values for BHT and 'm-phenethyl-benzonitrile' are 0.5 - 2.1 µg kg⁻¹ and 0.6 - 1.5 µg kg⁻¹, respectively. Recalculation of the total semi-volatiles leached from the column gives a much lower concentration, 1.9 - 2.5 µg kg⁻¹, i.e. approximately 25% of the total cumulative semi-volatiles leached from S4, which is explained by the much more diluted leachates from the column test.

Leaching mechanism

The behaviour of the leaching mechanisms deserves close attention in studies on leaching of pollutants from materials such as asphalt. Existing theories and mathematical models of different mechanisms controlling the leaching of inorganic compounds are applied in the present study [39, 47-51]. In these studies, the different leaching mechanisms are described by the time-dependence of the accumulative amounts released. This involves some uncertainty however, since these theories were developed for laboratory experiments. In Figure 5, the accumulative amounts of semi-volatiles released are presented versus the square root of time. If pure diffusion were the sole leaching mechanism, then the curves would, according to Fick's second law, have a linear proportionality to the square root of time. The results in Figure 5 show first a period of low amounts leached followed by a faster dissolution process, for the semi-volatiles and BHT. For the tentative 'm-phenethyl-benzonitrile' the curve is more linear and indicates a diffusion-controlled process. The low accumulative amount released under the first period of three months depends on the time needed for the precipitation to percolate through the asphalt layer. Thereafter, the accumulative amounts increase with time; especially for BHT and total-semi volatiles when the larger volume of leachate (50%) is used; an effect of increasing water content in the storage.

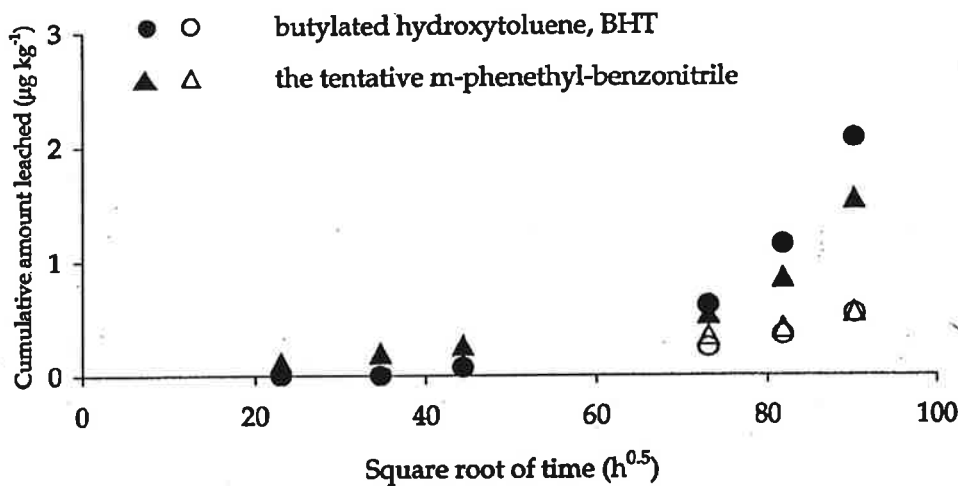
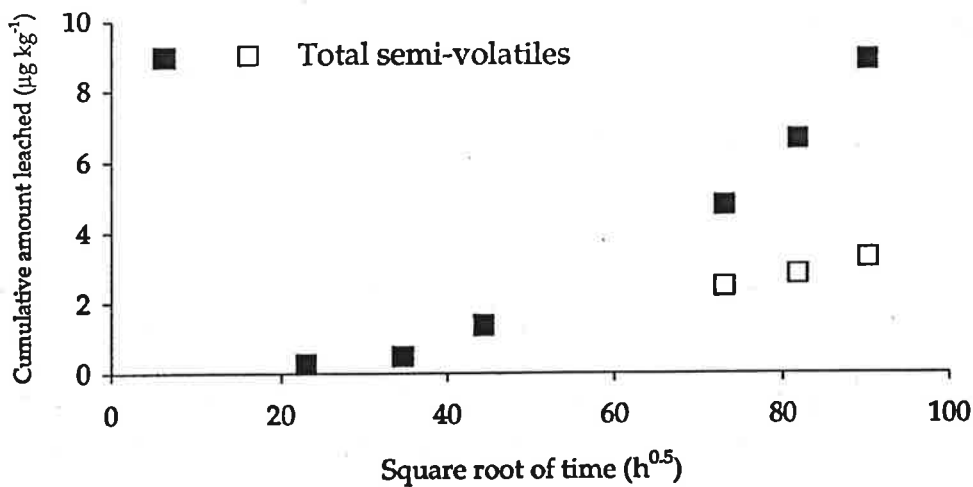


Figure 5. Cumulative leaching of total semi-volatiles(■, □), the tentative *m*-phenethyl-benzonitrile(▲, △) compound and butylated hydroxytoluene, BHT (●, ○) in leachates from the stockpile of scarified asphalt, section S4. The closed and the open figures correspond to an outflow of 10% and 50% respectively of the net precipitation.

The leaching mechanism can also be identified from calculation of the slope of the curve logarithm accumulative amounts released versus the logarithm of time [49]. The results calculated here, indicate that dissolution is the dominant leaching process for total semi-volatile organics as well as for BHT (slopes > 0.65), while diffusion could be the dominant process for the tentative '*m*-phenethyl-benzonitrile' (slope 0.54), provided the outflow corresponds to 10% of net precipitation. Dissolution is the dominant process when the solubility of the product matrix is such that dissolution of material from the surface proceeds faster than diffusion through the pores of the matrix [49]. It has been shown that dissolution is a common leaching mechanism in granular material [39].

The concentration of '*m*-phenethyl-benzonitrile' in the leachates decreases slowly with time (Figure 3). This together with the indicated diffusion leaching process, suggests the compound is emitted from the asphalt material itself or from traffic related sources, such as oils and rubber impressed into the surface layer of the material. For BHT and the total semi-volatiles, the pattern is the opposite. The concentrations increase initially and with time until the end of the summer, after which they decrease. This makes it more likely that these compounds are washed out or dissolved from the surface of the asphalt. This suggests that the compounds are emitted from the surface of the asphalt, i.e. traffic related, with unburnt fuels or vehicle exhaust residues and rubber from tyres, as probable sources.

Polycyclic aromatic hydrocarbons (PAH).

PAH are of environmental concern because these compounds are known to have both acute toxic effects [16] and long terms effects such as carcinogenicity [17], high bioaccumulation ability and esterogenic effects on living

organisms [15]. The chemical data, bioconcentration characteristics and toxicity data for the PAH in this study are presented in Table 5. The concentrations of total PAH in the leachates, for both the unstored and the stored asphalt, exceed the threshold of the Swedish recommended value of $10 \mu\text{g l}^{-1}$ for groundwater in polluted soils at petrol stations [51]. The serious ecotoxicological effects of the leaching of PAH into the

Table 5. Chemical and ecotoxicological data for polycyclic aromatic hydrocarbons, PAH:s ^a.

Chemical name	Structural formulas	Boiling point (°C)	Vapour pressure(Pa)	Solubility in water (mg l ⁻¹)	Log K _{ow} ^b	LC ₅₀ ^c (mg l ⁻¹)	BCF ^d (fish)
Acenaphthylene		279	$9 \cdot 10^{-1}$	3.9	4.0	0.2 – 3.7	387 – 631
Acenaphthene		279	$3 \cdot 10^{-1}$	3.5	3.9	25 – 1270	400
Fluorene		295	$8 \cdot 10^{-2}$	>0.19	4.2	219 – 830	501
Phenanthrene		340	$2 \cdot 10^{-2}$	1.18	4.5	0.4 – 1.4	2512
Anthracene		340	$1 \cdot 10^{-3}$	>0.004	4.5	0.06 – 0.3	501 – 794
Fluoranthene		375	$1 \cdot 10^{-3}$	0.26	5.2	0.005 – 0.6	1 584
Pyrene		404	$6 \cdot 10^{-4}$	0.013	5.2	0.001– 0.2	2 511
Benzo(a)-anthracene		437	$3 \cdot 10^{-5}$	0.014	5.9	0.01	10 000
Chrysene		448	$6 \cdot 10^{-3}$	0.002	5.8	1.0 – 1.4	6 309
Benzo(b)-fluoranthene		-	$2 \cdot 10^{-5}$	0.0012	5.8	0.03 – 0.8	10 000
Benzo(k)-fluoranthene		480	$2 \cdot 10^{-5}$	0.00055	6.8	-	12 589
Benzo(a)pyrene		495	$3 \cdot 10^{-7}$	>0.0038	6.5	0.001– 0.3	50 – 5 012
Indeno(1,2,3,cd)-pyrene		536	$1 \cdot 10^{-8}$	0.062	7.7	-	18 100
Benzo(ghi)-perylene		>500	$1 \cdot 10^{-9}$	0.0003	6.9	0.8	26 100
Dibenz(ah)-anthracene		524	$4 \cdot 10^{-10}$	0.0006	6.7	0.001– 0.2	10 000

^a [16, 42].^b K_{ow} = partition coefficient octanol-water.^c LC₅₀ = lethal concentration for 50% of the population exposed.^d BCF = bioconcentration factor.

environment is well documented and the environmental effects will not be discussed further [15-17].

Naphthalene, butylated hydroxytoluene (BHT) and dibutylphthalates (DBP).

The identification of naphthalene, BHT and DBP permits an assessment of ecotoxicological risks, because these compounds have not been studied as much as the more high-molecular weight PAH. Data on persistence, solubility in water, vapour pressure, partition, toxicity and bioavailability are given in Table 6.

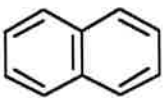
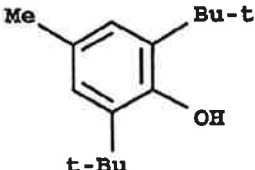
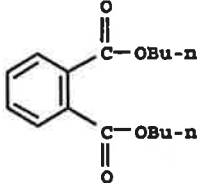
Naphthalene is the most volatile of the PAH. In natural water and soils, volatilisation and biodegradation [27] are the major removal processes for naphthalene, and the removal time (persistence) is short (Table 6). The toxicity of naphthalene has been studied for many different species of aquatic organisms [52]. The LC₅₀ data and the ability to bioaccumulate, given as the bioconcentration factor (BCF), are presented for fish in Table 6; the BCF varies greatly among different aquatic organisms and species. Naphthalene released from RAP may cause long-term adverse effects in urban aquatic environments because of the bioaccumulating ability.

Knowledge about the persistence of BHT in the environment is incomplete [53-55]. However, BHT and BHT-derivatives have been found in soil and groundwater [56],

which can indicate that the substance is not easily degraded. BHT has also been identified in drinking water from a pipe coated with petroleum-asphalt [57]. Decomposition products from BHT have also been identified in aquatic systems [58]. Surfactants, such as alkylphenol polyethoxylates, decompose into alkylphenols, such as nonylphenols and octylphenols, compounds with suspected estrogenic effects [59]; BHT, with a structural formula similar to the alkylphenols, has also been reported to have some potential endocrine-mediated activity [60]. Ecotoxicological effects of BHT have received little attention. Although the BCF of BHT is rather low (Table 6), it has high toxicity to aquatic organisms. In tests on animals, BHT has been shown to have genotoxic effects, but there is no evidence of carcinogenicity to humans. Leaching of BHT from asphalt can be an environmental problem because of suspected hormone-like effects, the relatively high amounts leached, and the suspected persistent chemical structure.

Since phthalates are easily released into the environment, they are ubiquitous environmental pollutants [61]. When the BCF factor for DBP is high (Table 6), phthalates are readily taken up *via* all exposure routes and quickly distributed throughout the organism. Due to their persistence in the environment, phthalates are also common in groundwater, rivers and drinking water [45]. Although DBP is readily degradable under aerobic conditions, degradation

Table 6. Chemical^a and ecotoxicological data^b for organic contaminants identified in leachates from asphalt storage, stormwater and urban groundwater.

Chemical name	Naphthalene	Butylated hydroxytoluene (BHT)	Dibutyl phthalate (DBP)
Structural Formulas			
CAS-nr	91-20-3	128-37-0	84-74-2
Boiling point (°C)	218	265	340
Vapour pressure (kPa)	0.0072	1.333	20
Solubility, water (mg l ⁻¹)	31	0.4	20
Log K _{ow} ^c	3.6	5.1	4.9
Persistence t _{1/2} (days)	20 - 258	540	1 - 23
LC ₅₀ ^d (mg l ⁻¹)	1.2 - 6.4 (fish)	2.5 - 13.5 (aquatic org.)	0.3 - 30 (fish)
BCF ^e (fish)	79 - 426	25	12 - 5000

^a [42].

^b [16, 42, 62-66].

^c K_{ow} = partition coefficient octanol-water.

^d LC₅₀ = lethal concentration for 50% of the population exposed.

^e BCF = bioconcentration factor.

apparently stops at concentrations in the range of 20–100 ng l⁻¹. The transport of DBP into groundwater is facilitated by complex formation, e.g. with humic acids. In particular, DBP has estrogenic activity [44].

CONCLUSIONS

The results in this study show that the concentrations and the cumulative amounts of semi-volatile organic contaminants are high in the leachates from temporary storage of RAP, especially from the stockpile with scarified asphalt. For the scarified asphalt the concentrations of total PAH in the leachates, for both unstored and stored asphalt, exceeded the threshold of the Swedish recommended value for groundwater in polluted soils at petrol stations. These findings clearly show that the release of organic pollutants from asphalt storages could cause environmental problems.

Naphthalene, butylated hydroxytoluene (BHT) and dibutyl phthalate (DBP) were the most dominant of the organic contaminants identified. The occurrence of these compounds in urban groundwater, also indicates high emission rates and persistent structures of the compounds, making them potentially hazardous. The major part of the organic contaminant leachate from used asphalt is, however, still unidentified organic compounds of unknown origin, and strengthens the serious need to make more extensive investigations that focus on a characterisation and identification of organic compounds in the leachates.

Naphthalene, the most volatile PAH, dominates in all leachates, and is here suggested to be an important 'marker substance' for RAP. The PAH of highest molecular weight, clearly increases in concentration in the leachates of stored scarified asphalt; these more high molecular weight PAH have also the most negative environmental effects and are classified as carcinogenic.

In the laboratory column test, the concentrations of semi-volatiles in the leachates, were much lower than in the

leachates from the field stockpiles. The main reason is that the L/S ratio in the field was much lower than in the standardised methodology for column testing. The leaching in the columns only continued for a few days, while the study in the field was ongoing for a whole year. Consequently, the quantification and identification of semi-volatile organic contaminants from the column study was less reliable. The results for PAH and other semi-volatiles in previous column studies have been below or close to the limit of detection, leading to the conclusions that there is no ongoing leaching of PAH and other semi-volatiles and, therefore, no environmental problems correlated with leaching from asphalt materials. The reasons for finding more compounds in this project are the analytical methodology used (repeated GC/MS-screening), and the experimental design (field experiment), which resulted in a low L/S ratio. The results demonstrate the concern to follow up laboratory column test for leached organic compounds with real field measurements.

The dominant leaching process indicated for the total semi-volatile contaminants was dissolution, which is the dominant process when the solubility of the product matrix is such that dissolution of material from the surface proceeds faster than diffusion through the pores of the matrix. This suggests that the semi-volatile organic contaminants are emitted from the surface of the asphalt, i.e. traffic, with residues of rubber from tyres, unburned fuels or vehicle exhaust, are suggested as the most probable sources. The results in this study highlight the need for further research to better understand the leaching mechanism of organic contaminants, both from storages of RAP and the asphalt material in use within a road body.

ACKNOWLEDGMENT

Financial support for this study was provided by the SNRA (Swedish National Road Administration) and the Department of Geology, Chalmers University of Technology.

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