

Emissions and evaluation of health effects of PAH's and aromatic mines from tyres

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Survey of Chemical Substances in Consumer
Products, No. 54 2005

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Content

CONTENT	3
PREFACE	5
SUMMARY AND CONCLUSIONS	7
1 INTRODUCTION	11
2 COLLECTION OF TYRES	15
2.1.1 <i>Content of PAHs in the collected tyres – knowledge available</i>	15
2.1.2 <i>Consumer’s pattern</i>	15
2.2 PURCHASED TYRES AND IMPACT ABSORBING PLAYGROUND SURFACING	16
3 CHEMICAL ANALYSIS	18
3.1 ANALYTICAL METHODS AND SAMPLE PREPARATION	18
3.1.1 <i>Introduction</i>	18
3.1.2 <i>Sample preparation and methods of analysis</i>	18
3.2 SCREENINGSANALYSIS	22
3.2.1 <i>GC/MS analysis. Results</i>	22
3.2.2 <i>TLC analysis, results</i>	23
3.3 QUANTITATIVE ANALYSIS	25
3.3.1 <i>Selection of tyres for quantitative analysis</i>	25
3.3.2 <i>Results</i>	25
3.4 MIGRATION TESTS	27
3.4.1 <i>Selection of tyres for the migration tests</i>	27
3.4.2 <i>Full scale experiment</i>	30
4 HEALTH ASSESSMENT	35
4.1 INTRODUCTION	35
4.1.1 <i>Scenarios</i>	35
4.1.2 <i>Identified substances</i>	36
4.2 SELECTED SUBSTANCES	37
4.2.1 <i>Fluoranthene</i>	37
4.2.2 <i>Pyrene</i>	40
4.2.3 <i>6PPD</i>	42
4.2.4 <i>IPPD</i>	45
4.2.5 <i>Benzo(a)pyrene</i>	48
4.3 OTHER IDENTIFIED SUBSTANCES	50
4.3.1 <i>Identification</i>	50
4.3.2 <i>Evaluation</i>	53
4.4 CONCLUSION	55
ABBREVIATION LIST	57
REFERENCES	59

Preface

The project "Migration and assessment of health effects of PAHs and aromatic amines from tyres" has been carried out in the period from 15 Th. April to 1 Th. November 2004. This report describes the results of the study.

The project was carried out by the Danish Technological Institute, Materials Division. MSc, PhD, Nils H. Nilsson was manager of this project and the liaison between the Institute and the National Agency of Environmental Protection.

Kim Munck Christensen has contributed to the project with regard to selection of tyres and playground adoption in connection with the selection of tyres.

M.Sc. Anders Feilberg, Chemistry and Water Technology has been responsible for the laboratory analysis and the migration studies.

B.Sc. Kirsten Pommer has been responsible for the screening and health impact (consumer exposure) and risks assessment in the project together with M.Sc. Ole Chr. Hansen.

The project manager has been responsible for the interviews carried out, the purchase of tyres and playground tiles to the project, information search and as expert in rubber materials and rubber technology.

The reference group consisted of Frank Jensen (chairman), the National Agency of Environmental protection, and Nils H. Nilsson, the Danish Technological Institute.

The purpose of the project was to focus on the problematic substances that occur in tyres in relation to their use as playing tools or as playing ground fall protection. Later a screening phase for problematic substances like PAHs and aromatic amines and migration/exposure experiments conducted under "worst case conditions" have been carried out. Finally, health screening based on the results from the migration tests. Finally, health screening based on the migration tests completed the project.

Summary and conclusions

On behalf of the National Agency of Environmental Protection, the Danish Technological Institute has gathered information regarding the consumption pattern of tyres and fall protection tiles based on rubber granulate from discarded tyres in relation to the use of the products at playgrounds.

The investigation has shown that tyres are used at playgrounds to various extends. Preferably discarded passenger car tyres are used for swings but also cheap new tyres from the Far East are used. Lorry tyres are also used for swings for more than one child at the same time, but interviews confirm that the use is limited. At some playgrounds fairly huge amounts of tyres are used for tight-rope walking. Both lorry and passenger car tyres are used for this purpose. One gets as a common rule the tyres free as the owner then save money for the state imposed taxes for dispose.

A limited use of tyres for sandpit takes place. Only discarded and worn-out tractor tyres are used. They are offered free of charge.

It is possible for the consumers to buy passenger car tyres in DIY centres. They are equipped with mounting and robes for easy installation in the stands by the consumers.

In total 20 tyres and two different types of falling protection tiles base don granulated rubber from tyres were purchased. The aim was to screen the falling protection tiles and the tyres for content of PAHs and aromatic amines. The tyres purchased comprised as well worn- out tyres as new tyres intended for use for passenger cars, lorries and tractors.

For the initial semi quantitative screening analysis for PAHs and aromatic amines in total 18 tyres and two impact absorbing playground surfacing have been investigated. Based on the results from the screening analysis six tyres have been selected for quantitative analysis of the content of PAHs and aromatic amines. Further migration studies have been carried out with six selected samples. Also a full scale experiment with a worn-out tractor tyre used for sandpit. In this experiment migration of PAHs and aromatic amines to sand has been studied.

The results of the investigations are summarised below:

- The rubber from all the investigated tyres contains a row of PAHs, among these the carcinogenic chemical substance benz(a) pyrene. The amount varies.
- Benz(a)pyrene can be used as a PAH-indicator.
- The rubber from all the investigated tyres contains high concentrations of aromatic amines belonging to the chemical substance group para-phenylene-diamines. The para-phenylene-diamines are added to the rubber to prevent degradation due to ozone attack.
- Migration studies with artificial sweat have revealed that only the most water soluble PAHs migrate from the tyre rubber to the sweat.

- The aromatic amines in a similar way migrate from the tyre rubber to sweat.
- Full scale migration study with a worn-out tractor tyre used as out door sandpit has revealed that the added aromatic amines migrate to the sand. By a comparison between the PAH profile in the tyre and the composition /profile of PAH in the sand it must preliminarily be concluded that migration from the tyre is not a significant source for the PAH contamination of the sand. The results indicate that the PAH content in the sand origin from atmospheric deposition.

Health Assessment

The PAHs and aromatic amines, detected in the migration tests in contact with artificial skin and full scale tests of sandbox sand and for certain identified in the chemical analysis, were estimated in greater detail to assess the health risks proportional to the exposure of the user (child).

The following substances had migrated in the laboratory tests.

Table 0.1. Detected mean values for migration of components (ng cm⁻²)

Test type	Vans, used, tread	Impact absorbing playground surfacing, new	Car, used, side rubber	Car, used, tread	Car, new, tread	Car, used, tread
Test no	2	5	10	11	13	19
Fluoranthene	0.03	0.03	0.05	0.03	0.3	0.05
Pyrene	0.04	0.03	0.8	0.06	0.5	0.07
6PPD *)	0.95	5.1	19	44	50	0.7
IPPD **)	5.8	0.5	0.4	IP	0.1	10

"IP" means "not detected"

*) 6PPD = 1,4-benzenediamine N-(1,3-dibutyl)-N'-phenyl

**) IPPD = N-isopropyl-N'-phenyl-4-phenyldiamine

Worst case is that a skin area of 200 cm² on the thighs of a child is exposed for an hour five times a week during one year.

The following substances were detected in the full scale test with the sandpit of tractor tyre in the mentioned concentrations.

Table 0.2. Detected values for content of components in sand (µg kg⁻¹ (wet weight))

	Ref. initial	Ref. 15/8	Test 15/8
Fluoranthene	1.67	2.89	10.12
Pyrene	1.12	3.64	12.57
Benz(a)anthracene	0.25	0.50	1.02
Chrysene	1.42	1.96	2.27
Benz(b+j+k)fluoranthene	0.10	0.22	0.25
Benz(e)pyrene	0.06	0.14	0.18
Benz(a)pyrene	0.03	0.07	0.09
Dibenz(ah)anthracene	IP	0.01	IP
Indeno(1,2,3-cd)pyrene	0.02	0.05	0.08
Benz(ghi)perylene	0.03	0.11	0.15
6PPD	IP	IP	109.84
IPPD	IP	IP	4.56

"IP" means "not detected"

By way of comparison the results from the sand before migration test are included (ref. initial) and the result from plastic covered side of the tractor tyre with plastic film (ref. 15/8). The migration test has been carried out during July, 4 and August, 15 2004. During the period the test samples have been exposed to some rather unusually heavy pour downs. The total rainfall for the period was 84 mm (DMI, Viby J. station).

Worst case scenario is that a child weighing 10 kg ingests 10 g of sand five times a week for half a year and that 100 % of the substances in the sand are absorbed in the body of the child.

Some PAH compounds and amine compounds have been detected in sand exposed to discarded tyre and in migration tests, where artificial sweat has been in contact with discarded tyres. The substances have been identified and quantified.

The following substances have been identified and quantified:

Table 0.3. Identified chemical components in the contact exposure experiments

Migration test, artificial sweat	Exposed to sand	
Fluoranthene	Fluoranthene	Benzo(b+j+k)fluoranthene
Pyrene	Pyrene	Benzo(e)pyrene
6PPD	6PPD	Benzo(a)pyrene
IPPD	IPPD	Dibenz(ah)anthracene
	Benzo(a)anthracene	Indeno(1,2,3-cd)pyrene
	Chrysene	Benzo(ghi)perylene

It was expected to find more PAHs in the migration test. This expectation was based on the results from studies on PAH migration to soil from rubber particles due to wear of tyres from traffic. On the other hand, there has former not been focus on the amino-compounds, 6PPD and IPPD, with respect to migration from used tyres before.

The four substances found in the migration test and benzo(a)pyrene was assessed. A screening including the other substances was performed.

The assessment showed:

- Fluoranthene causes no acute health effects. Related to long term exposure damages to liver and kidneys have been seen in animal studies. A child may be exposed to 10 ng per day per kg b.w. and with a NOAEL of 125 mg/kg this results in a MOS of more than a million.
- Pyrene may be toxic by ingestion and causes mild irritation to skin. Pyrene is not classified as a carcinogen. No data on reproduction or mutagenicity was available. A child may be exposed to 13 ng per day per kg b.w. and with a NOAEL of 75 mg/kg it results in a MOS of more than a million.
- 6PPD may be irritating to skin and a potential sensitizer. Long term effects such as haematological changes and ongonenic effects as well as effects on reproduction have been observed. A child may be exposed to 100 ng per day per kg b.w. and with a NOEAL of 4 mg/kg, it results in a MOS of 10.000.
- IPPD may be toxic if swallowed in large quantities. Skin contact may cause sensitization. Data on long term effects, except for developmental toxicity, has not been found. A child may be exposed to 200 ng per day per kg b.w. and with a NOAEL of 62.5 mg/kg it results in a MOS of 100.000.

- Benzo(a)pyrene is a substance that may cause cancer as well as genetic and developmental effects. A child may be exposed to 0.1 ng/kg b.w. per day. Compared with a NOAEL of 3 mg/kg it results in a MOS of more than one million.
- The other identified PAHs causes the same type of health effects as benzo(a)pyrene but with a lower risk level. A child may be exposed to in total 4 ng/kg b.w. per day of these PAHs. Comparing this with a NOAEL of 3 mg/kg it results in a MOS of 750.000.

From these results it can be concluded that the potential health risk related to use discarded tyres on playgrounds is insignificant.

Although the MOS is high for all the identified components it is notable that the lowest MOS are found for the two identified amino-compounds.

1 Introduction

Tyres are used both of private consumers and by childcare institutions as playing tools, among these as sandpits. A risk exists that children can be exposed for chemical substances liberated from the tyres. Exposure can take place by contact with the skin, e.g. when the tyres are used as seats for swings or for sandpits. In the last application exposure to potential liberated chemical substances can also take place orally in case the playing smaller children put sand in the mouth or eat it.

In many of the formularies used for tyres mineral oils are used as plasticizers. The basic structures of the hydrocarbons which occur in mineral oils are n-paraffines, iso-paraffines, naphthenes (aliphatic cyclic hydrocarbons) and aromatics (cyclic unsaturated hydrocarbons). The mineral oil based plasticizers are classified based on their viscosity / density constant. Based on this constant the oils are classified as highly aromatic, relative aromatic, naphthenics, relative naphthenics and paraffinics. In particular the highly aromatic oils can contain a considerable amount of polycyclic hydrocarbons (PAHs). Some of the PAHs are classified as carcinogenic. One should mention that at least in Western Europe the trend is to replace the highly aromatic oils with naphthenics in the tyre formularies. The latter types are mainly composed of cyclo aliphatic hydrocarbons, but contain also PAHs but in reduced amounts.

Problems regarding PAHs in relation to the use of aromatic mineral oil based plasticizers for tyre formularies have among other scientific sources been considered in an article by L. von Meyerinck *et al.* and by R. Wommelsdorff, 1999. Baumann (1997) has investigated the PAH-content in a number of high aromatic oils in different tyres as well as the liberation of PAHs due to wear particles from the tyres in relation to the traffic. The same issue, but in a broader scope, has been discussed by the scientific committee for toxicity, ecotoxicity and the environment (CSTEE, 2004). The complete title of the document from CSTEE, 2004 is to be found in the reference list.

The latter two references have some open questions left in relation to the health and environmental impact due to tyres and caused by the wear particles from the tyres as a result of the traffic on the roads. Both references focus primarily on the potential risk due to the adverse influence from PAHs, due to known carcinogenicity or suspected carcinogenicity.

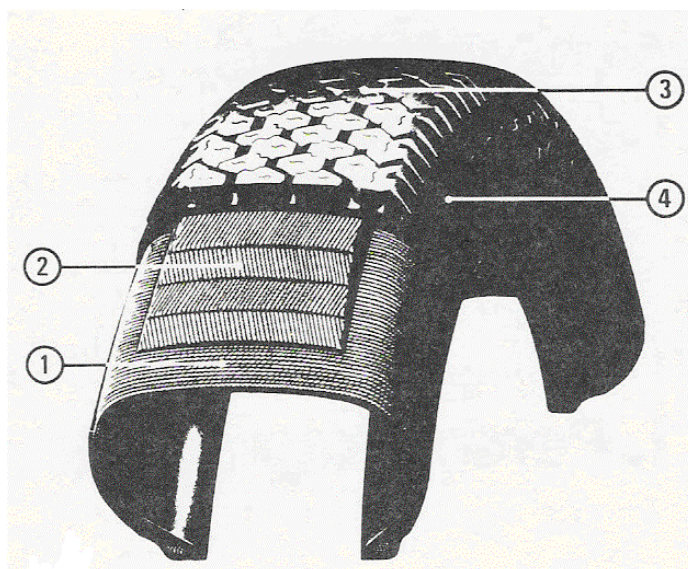
However considerable amounts of protective agents are added to rubber formularies for tyres besides the plasticizing oils. The protective agents are added because the types of rubber used for the manufacturing of tyres are easily degraded by exposure to different weather conditions as mainly rubber raw materials with unsaturation in the polymer chains. This unsaturation means that degradation easily takes place due to breakage of the chains by exposure to light, high temperature, oxygen and ozone. In particular the sidewall rubber has to be well protected due to high heat build up due to mechanical stress due to flex movements. Ozone is a very strong oxidation agent. Ozone primarily attacks rubber under mechanical stress. The degradation due to ozone attack already takes place at the very low ozone

concentration in outdoor air (normal level 10-50 ppb). Aromatic amines are added to the rubber formularies to prevent this attack. This is different from plastic where phenolic antioxidants are sufficient for protection (phenolic based antioxidants are also used in rubber). P-phenylene derivatives are very common used in rubber formularies for tyres, but also other aromatic amines are used. During the vulcanisation process aniline might be formed from the antiozonants. Aniline is an aromatic amine which is classified as carcinogenic.

The amounts of p-phenylenediamines and aromatic amines will be present in the rubber formularies in significant higher amounts than is the case for the PAHs. This can be calculated from information about rubber formularies for tyres found in the open literature. It is further foreseen that the p-phenylenediamines will be present in much higher concentrations on the surface of the rubber as they are tailor-made to have a reduced solubility in the rubber. Due to the low solubility they will migrate to the surface of the tyres. Their presence at the surface will protect the tyre from ozone degradation.

The formulation of the problem is however complex. This is due to the fact that many different types of tyres and with different rubber formularies are produced. And there are several different producers as well. The formularies are not open to the public as far as one deals with commercial rubber compounds for tyres. It is however possible to find examples of standard formularies in the open literature for tyres (Ciullo, 1999). It is expected that these formularies are rather close to the formularies used in commercial formularies for tyres.

A tyre typically consists of rubber based on seven rubber formularies. The most important formularies are the compounds used for the tread, the sidewall and the inner liner. The tread is frequently produced from SBR rubber with a small amount of butadiene rubber added. For the tread used for lorries and trucks natural rubber is added to the rubber compound due to the excellent elasticity and wearing qualities. The sidewall rubber typically is composed of natural rubber and butadiene rubber. However EPDM is also used in the side wall formularies. The inner liner is typically produced from butyl rubber due to the high tightness against air. In total the manufacture of tyres comprise approximately 35 separate processes and in total 50-100 different raw materials (different rubber types and rubber chemicals). During vulcanisation chemical reactions take place and new chemical compounds are formed. The rubber chemistry of the tyre is as one can imagine very complex.



Radial tyre

1. Carcass layer
2. Stabilizing belt
3. Tread
4. Side wall rubber

It is foreseen that exposure and contact with chemical compounds in the rubber during use of tyres as playground equipment mainly will happen from the tread and the sidewall rubber.

In Table 1.1 formularies for the tread for a passenger car and for a lorry are listed.

Table 1.1. Examples of tread rubber formularies with a content of high aromatic mineral oils as plasticizers.

	Passenger car tyre formulary for summer tyres pphr	Passenger car tyre formulary for winter tyres pphr	Tyre for lorries Formulary 1 pphr	Tyre for lorries Formulary 2 Phr
Natural rubber		50		80
SBR-rubber	80	40	75	
Butadiene rubber	20	10	25	20
Carbon Black A		25	55	45
Carbon Black B	75	45		
High aromatic mineral oil	35	45	10	20
Zinc oxide	3	4	5	5
Stearic acid	1.5	2	2	3
Antioxidants/ Antiozonants	1	1	1.5	1.5
Wax	1	1		
Accelerators	1.5	1.5	1	1
Sulphur	2	2	1.5	2
Parts in total	220	226.5	176	177.5

It has to be mentioned that the Amount of rubber polymer always is quoted to 100 parts in a formulary (pphr = parts per hundred). The amount of an ingredient can be calculated from the total amount of parts. The amount of high aromatic mineral oil based plasticizer added to a passenger car tyre is par example according to the listed formulary above $35/220 \%w/w = 15.9\% w/w$.

Tractor- and caterpillar tyres have tread formularies close to the ones listed for tyres for lorries.

Higher amounts of antioxidants/antiozonants are foreseen added to the sidewall rubber in comparison with the tread. As mentioned before the reason for higher protection is the heat build up and the high mechanical wear due to flex movements. To prevent ageing of the rubber by weathering (UV light, oxygen, ozone and temperature) such a higher level of protection is needed.

According to a survey made by Baumann (1997) the concentration in plasticizers based on high aromatic mineral oil plasticizers the amount of PAHs in the plasticizers varies between 98 mg/kg and 1,350 mg/kg. A permit limit set to 50 ppm for benz(a)pyrene at the time for the survey made was not exceeded for any of the plasticizers analysed.

The content of PAHs in the tyres investigated varied between 11.4 mg/kg and 147.2 mg/kg. As expected the amount of lower molecular weight chemical compounds in worn tyres is lower than for new tyres.

In the survey migration of some of the other rubber chemicals or added to the rubber in tyres (or their degradation products) was measured. This part of the investigation dealt with the migration of p-phenylenediamine, aniline and some benzothiazoles. The latter are typically used as accelerators for cross linking of rubber used for tyres. The investigation did not include a migration study like the one dealt with in this project.

Empirically the amount of p-phenylenediamines added to rubber formulations for tyres is approximately 1% w/w. This adds up to 10 g/kg tyre. The amount of PAHs in tyres is according to calculations made on standard rubber formulations for tyres in the order of 10-100 lower under presumption that the PAH content in the plasticizers is in the range from 100 mg/kg to 1,000 mg/kg.

CSTEE (2004) has listed a little different range of concentrations for PAHs in tyres, but the order is in accordance with the findings made by Baumann's in his study. It has to be mentioned that CSTEE (2004) state that a fairly good correlation exists between the total amount of PAHs in the tyres and the content of benz(a)pyrene (BaP).

2 Collection of tyres

The consumer's pattern for the use of tyres as playground equipment has been revealed by making interviews with dealers for playground equipment, responsible persons for playgrounds e.g. inspectors and companies who offers turnkey solutions for playgrounds. A representative number of tyres which are used as playground equipment was purchased based on the information obtained regarding the consumer's pattern for the use of tyres for playgrounds. The samples purchased included different types of tyres (passenger car tyres, lorry tyres and tractor tyres) and tyres produced by different manufactures. Both worn and brand new tyres were purchased. In supplement to the tyres impact absorbing playground surfacing based on granulated worn tyres were purchased as well.

In the collection / purchase phase it was checked up on the possibility to get information with regard to the use of plasticizers based on high aromatic mineral oils in the tyres. If such information is not easily accessed a screening for PAHs was performed.

2.1.1 Content of PAHs in the collected tyres – knowledge available

The contacts made to the dealers of tyres made it clear that they in fact did not know the meaning of PAHs or high aromatic mineral oils (HA). To get information about the formularies of the rubber compounds used for the tyres from the dealers was as one can imagine not possible. On the Nordic Rubber Conference 2004 (NRC 2004) in Tampere, Finland Nokia informed that new tyres with reduced and low content of PAHs would be labelled in such a way that the consumers would know if they were going to purchase a "Green tyre". Nokia was in a process to substitute the high aromatic mineral oil based plasticizers with low aromatic oils. Nokia still had problems with the substitution in summer tyres due to problems with the functional properties of the formularies. This is in accordance with information (HA oils in automotive tyres, 2003). From this information one knows that Gislaved Däck AB produced a HA free winter tyre already in 1997. The source explains that the problem with summer tyres is that the braking distance on wet road is 75 80 % longer than on dry surface. It has to be compared with the best HA plasticized summer tyres where the difference in braking distance only was 20 - 25 % between summer and winter tyres.

2.1.2 Consumer's pattern

Based on the interviews with suppliers of playground equipment it must be concluded that the biggest amount of tyres used in playgrounds is worn passenger tyres. Typically the tyres have a rim diameter to either 13" or 14" tyres and they are 140-170 mm in width. One is informed that the tyres are washed down before use. It is also controlled that the steel wire reinforcement of the tyres do not penetrate the tread due to excessive worn. The tyres are often painted with a water based painting. As the painting after some time flake off the suppliers have chosen to follow an advice from Danish Technological Institute. The advice is to paint the tyres with a black painting

in stead of the blue and red colours previously used. By doing this it makes the flake off less visible as the tyres are black themselves due to the carbon black.

A certain use of new tyres for playgrounds also takes place. The new tyres are cheap passenger car tyres often produced in the Far East. Bridgestone and Continental passenger car tyres have been mentioned. The rim diameter is 13'' and the profile height is 65% compared to the width.

It was stressed that tyres are popular as swings because one can avoid damages to the teeth's. Such damages are well known accidents from swings base don wood.

Lorry tyres are used only in limited amounts for swings. In those cases they are used for more than one child at the same time. More common is the use of lorry tyres for tight rope walking and crawl tunnels. Only worn lorry tyres are used and in general they are purchased for free.



Tractor tyres in limited amounts are used for sand pits. These tyres are all worn. One of the interviewed dealers of tractor tyres informed that it mainly were men which purchased tractor tyres for sand pits. Women were less interested because the child's clothes might be smudged due to rubber dust.

2.2 Purchased tyres and impact absorbing playground surfacing

Based on the information obtained from the interviews of playground equipment suppliers and playground inspectors with regard to the consumer pattern of the use of tyres and falling protection tiles for playgrounds Danish Technological Institute has purchased the below in Table 2.1 listed samples of tyres. In the table is listed the type of tyre, the country where production of the tyre took place, worn or new and where the sample has been cut for the analysis. If more than one sample has been taken from the same tyre a separate laboratory marking has been made.

Table 2.1. Samples of tyres and impact absorbing playground surfacing for screening analysis

Sample no.	Mark	Type	Country	New/worn	Sample taken
1	Continental	Lorry	Germany	New	Tread
2	Continental	Lorry	Belgium	Worn	Tread
3	Michelin	Lorry		Worn	Side wall
4	Pirelli	Lorry		Worn	Side wall
5	Ergo Floor	Impact absorbing playground surfacing	Denmark	New	Upper face
6	Bilgutex	Impact absorbing playground surfacing	Denmark	New	Upper side
7	Taurus	Tractor	Hungary	New	Side wall
8	Pirelli	Tractor	Italy	New	Side wall
9	Roadstone	Passenger car	Korea	New	Side wall
10	Roadstone	Passenger car	Korea	Worn	Side wall
11	Roadstone	Passenger car	Korea	Worn	Tread
12	Nokia	Passenger car	Finland	New	Side wall
13	Nokia	Passenger car	Finland	New	Tread
14	Continental	Passenger car	Germany	New	Tread
15	Michelin	Passenger car	Great Britain	New	Tread
16	Michelin	Passenger car	Germany	Worn	Tread
17	Continental	Passenger car	South Africa	Worn	Tread
18	MarixGlacial	Passenger car	Italy	Worn	Tread
19	Barum Brilliant	Passenger car	Czech Republic	Worn	Tread
20	Hankook	Passenger car	Korea	Worn	Tread
21	Kumho Powerstar	Passenger car	Korea	Worn	Tread
22	Good Year	Passenger car	Italy	Worn	Tread

The amount and the types of PAHs in the tyres can differ depending on the supplier and the mineral oil used for the manufacturing of the tyre. The time for production and the location of the manufacturing plant (Europe or The Far East) might also influence the PAH pattern and amount in the tyre.

3 Chemical analysis

3.1 Analytical methods and sample preparation

3.1.1 Introduction

Methods based on gas chromatography, high pressure liquid chromatography or thin layer chromatography are suitable for the analysis of PAHs and aromatic amines in tyres or in fall protection tiles as well as migration of these substances to a contact medium. To perform the analysis a suitable sample preparation is needed (downsizing of the tyre, extraction and concentration). Selection of method depends on the selectivity and detection limits of the method. All the three mentioned chromatographic methods could be used without problems (e.g. detection limits) so far the analysis is to be performed directly on the tyres. It is however judged that the highest selectivity is obtained in the quantitative analysis for individual chemical substances in the tyres and as migrants in the contact media by using GC/MS analysis with deuterated internal standards added. For this reason GC/MS analysis has been the chosen method for all PAH analysis. The same has been the case for the analysis of p-phenylenediamines and aromatic amines. In the initial screening phase for aromatic amines thin layer chromatography combined with identification based on colour reaction with iodine has been the method used due to its simplicity.

3.1.2 Sample preparation and methods of analysis

3.1.2.1 *Sample preparation*

Tyres contain high amounts of steel cord as reinforcement. This makes sampling rather difficult. For the passenger car tyres it was possible to cut the samples by mean of a big band saw with diamond coated blade. Samples from the side wall of tractor and lorry tyres were cut by mean of a drilling machine with a special saw bit. The last samples were circular with a average diameter of 70 mm.

Samples from the tread from tractor and lorry tyres were cut by mean of a hobby knife.

The samples cut for the screening analysis and the quantitative analysis was pulverized after the rubber was cut free from the steel reinforcement with a hobby knife. The pulverization was made in a Tekmar A-10 laboratory mill. Before the milling the rubber samples were cut into small bites and cooled with liquid nitrogen. Further cooling was made by pouring a small amount of liquid nitrogen in the milling chamber before the milling bladders were activated. By this milling procedure a very fine rubber powder is obtained because the rubber at the low temperature get stiff and due to the stiffness easily is pulverized by the rotating milling bladders.



Passenger car tyre, sampling from tread



Tractor tyre, sampling from side wall

3.1.2.2 Extraction and cleaning up

The pulverized rubber samples from the tyres or the contact medium (sand, artificial sweat) were extracted one hour at 30 °C with dichloromethane (CH_2Cl_2) in an ultrasound bath. This extraction was followed by an extraction with a mixture of dichloromethane and acetone (volume percent 50/50). These solvents are used on a routine base for the extraction of PAH and other polycyclic hydrocarbons from soot particles and organic aerosols (Feilberg, 1999; Feilberg et al., 2001). Due to the experience with this procedure it was adapted to the extraction of the tyres. The addition of acetone is made to assure that the more polar chemical components are efficiently extracted. The internal standards were added in the first extraction step. Two deuterated PAHs, pyrene- d_{10} and benzo(a)pyrene- d_{12} were used. The combined extracts were concentrated by means of stream of N_2 at 40°C to a final volume of approximately 1 ml. Then 2 ml cyclohexane was added and the extract was once again concentrated to 1 ml. This concentrate can be used directly for the analysis of aromatic amines as well as of the dominating PAHs. The analysis of other PAHs among these the most genotoxic e.g. benzo(a)pyrene demands a further cleaning up of the concentrate due to interfering substances in the complex matrix. To remove the interferences from the initial tyre extracts the following method based on a liquid-liquid extraction was used (Feilberg, 1999; Feilberg et al., 2001):

The concentrated cyclohexane extract was extracted with a mixture of dimethylformamide (DMF) and water (volume percent 90/10). By this first extraction step the PAHs and semi polar as well as polar chemical substances are separated from the most apolar substances (hydrocarbons). In the next step the DMF/water mixture is adjusted to a water content of 50 % by further addition of water. The PAH-fraction in this solvent mixture will enter the cyclohexane phase. The more polar chemical substances will remain in the DMF/water mixture. Each step in the procedure is carried out three times. The combined cyclohexane extracts are concentrated to a convenient volume (typically 1 ml). The concentrate (1 μl) is then injected into the injection port of the GC-MS instrument.

The recovery of PAHs for the method has formerly been determined to be in the range 75-100 % (Feilberg, 1999). The internal standards added in the first extraction step compensated for losses during the dedicated purification/concentration method.

The extracts were used for the screening analysis as well as for the quantitative investigations (see below).

The concentrations of the aromatic amines are so high, that it is not necessary to carry out a purification of this fraction. The analysis for aromatic amines was accordingly made directly on the crude solvent extracts of the tyres.

3.1.2.3 Gas chromatography with mass spectroscopic detection (GC-MS)

Equipment and parameters used:

GC: HP 6890
Capillary column: 30 m x 0.25 mm x 0.25 μm RTX-5 (poly(di(5% phenyl)/95 %methyl)siloxane))
Temperature programme: 80 °C (1.0 min.), ramp to 320 °C at 10 °C/min., hold for 5 min.
Injection temperature: 280 °C

Injection volume: 1 μ l
Interface: 270 $^{\circ}$ C
Carrying gas: Helium, constant flow: 1.5 ml min⁻¹
MS: HP 5973
Detection: m/z 50-350

The PAHs were identified and quantified based on their molecular-ion and by comparison of the retention times with retention times of authentic standards. The aromatic amines were identified and quantified based on the dominant ion (molecular ion or fragmentation ion).

Calibration has been made based on standard solutions of the chemical substances analysed in different concentrations within the measuring interval. Internal standards were added. The calibration curves obtained all showed a satisfactory linearity with regression coefficients (R²) > 0.99. The analytical results are reported with an estimated uncertainty equal to 10%.

The detection limits for pure solutions were on the instrument used for the analysis in the order of 1-20 pg substance injected. This corresponds to detection limits in the range 0.1-2 ng/ml for concentrated samples with a final volume of 100 μ l. The detection limit for an amount of sample equal to 500 mg tyre will be in the range 0.2-4 μ g/kg. Theoretically it is possible to obtain lower detection limits by extracting a higher amount of tyre rubber or by further concentration of the final volume to an even smaller volume (e.g. 10 μ l). From a practical point of view the gain in detection limits will depend on the purity and complexity of the sample.

The detection limits for the different types of samples are estimated from the actual samples and thus compensate for the purity, composition and concentration steps as well as the amount of sample extracted. The individual detection limits are stated in the following section with the presentation of the results. The actual detection limits are estimated from the concentration which equals a signal – noise ratio of 3.

3.1.2.4 TLC with Iodine visualisation

The rubber powder (2 g) is weighed. The powder is transferred to a 100 ml glass bottle and is extracted with 50 ml dichloromethane for one hour after transfer of the bottle to a shaking bath. The extract is decanted from the rubber powder and further 10 ml dichloromethane is added to the bottle which is shaken for a short time. The dichloromethane is decanted and combined with the first extract.

The dichloromethane extract is concentrated by means of a rotational evaporator at maximum 30 $^{\circ}$ C to approximately 1 ml. The concentrate is transferred to a little test tube, which can be sealed with a tight lid. The original glass bottle is flushed with a little dichloromethane and transferred to the test tube. The amount is adjusted to 2 ml in final volume.

The thinlayer chromatographic screening for antiozonants has been performed according to the principles in ISO 4645 (1995) "Rubber and rubber products - Guide to the identification of antidegradants - Thin layer chromatographic methods". The elution solvent used corresponds to method A in the standard: n-heptane:ethylacetate 90:10 (volume percent). The thin layer plates used for the analysis are Merck (article 1.11798) 20 x 20 cm Silica gel 60 F 254 with concentration zones. 5 μ l of the solutions and

standards listed below are put on the plates. After the plates have been developed in the chosen elution solvent, the solvent is allowed to evaporate in a hood before visual judgement.

The TLC plates are first judged under UV light, then visually after one hour and finally after treatment with iodine in a chromatographic developing tank. The results from the visual inspection and the iodine treated TLC plates were documented as photos.

The references used for the TLC screening of aromatic amines are listed in Table 3.1.

Table 3.1. References used for the TLC-screening

Sample mark	CAS-number	Short name	Chemical name
A	26603-23-6	ODPA	Oktylated diphenylamine
B	-		Bisdiphenylamine
C	106-50-3		P-Phenylendiamine
D	93-46-9	DNPD	N,N'-di-beta-naphtyl-p-phenylen-diamine
E	74-31-7	DPPD	N,N'-diphenyl- p-phenylenamine
F	793-24-8	6PPD	(1,3-dimethyl-butyl) N'-isopropyl-N'-phenyl-p-phenylendiamine
E	101-72-4	IPPD	N'-isopropyl-N'-phenyl-p-phenylendiamine
F	90-30-2	PAN	1- Naphtyl phenyl amine
G	-	TMQ	2,2,4-trimethyl-1,2-dihydroquinoline

The reference substances were dissolved in dichloromethane as 1% solutions (0.1 g /10 ml).

3.2 Screeningsanalysis

3.2.1 GC/MS analysis. Results

The relative amounts determined of three typical PAHs from the screening analysis of the tyres are listed in the Figure 3.1 below.

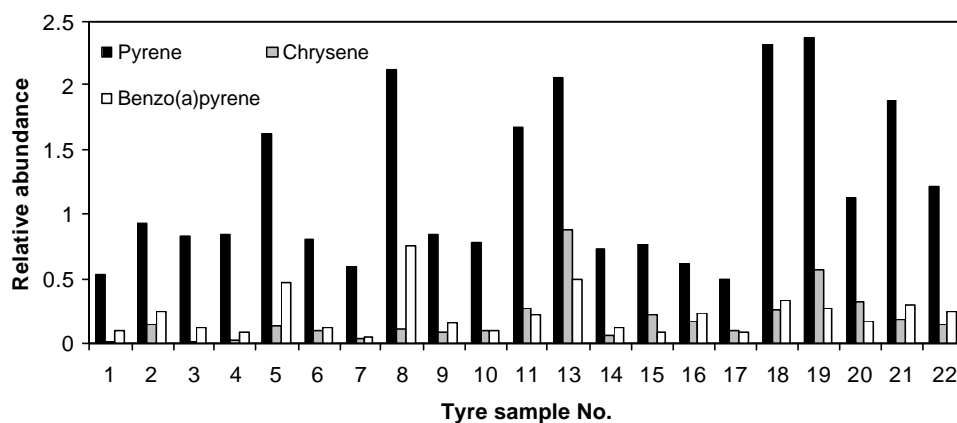


Figure 3.1. Relative amounts of selected PAHs in samples taken from the investigated tyres

A number of PAHs as well as aromatic amines were identified in all samples from the tyres.

The PAHs and aromatic amines identified and detected in this investigation are listed in Table 3.1 below.

Table 3.1. Statistics on identified and detected PAHs and aromatic amines

Chemical substance	Number of samples
Fluoranthene	21
Pyrene	21
Benzo(a)fluorine	0
Benz(a)anthracene	20
Chrysene	21
Benzo(b+j+k)fluoranthene	20
Benzo(e)pyrene	21
Benzo(a)pyrene	21
Indeno(1,2,3-cd)pyrene	16
Benzo(ghi)perylene	21
Dibenz(ah)anthracene	4
Dibenz(aj)anthracene	0
Aniline	0
p-Phenylendiamine	0
N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylendiamine (6PPD)	21
N-isopropyl-N'-phenyl-p-phenylendiamine (IPPD)	18
N,N'-diphenyl-p-phenylendiamine (DPPD)	9
1-naphthyl-phenyl-amine (PAN)	1
N,N'-di-beta-naphthyl-p-phenylen-diamine (DNPD)	0

To get a better judgement of the relative content of PAHs in the tyres and to help the selection of tyres for quantitative analysis internal standards were added to the samples at the first extraction step. For selected PAHs the relative amount is presented as the chromatographic signal (the area below the peak) divided with the signal from the internal standard. The relationship is shown in Table 3.1. The most volatile components among the investigated PAHs i.e. fluoranthene og pyrene (molecular weight 202), are found in the highest concentrations. Dibenz(ah)anthracene is identified in 4 of the 21 samples investigated. Benzo(a)fluorene and dibenz(aj)anthracene has not been detected in any of the samples investigated.

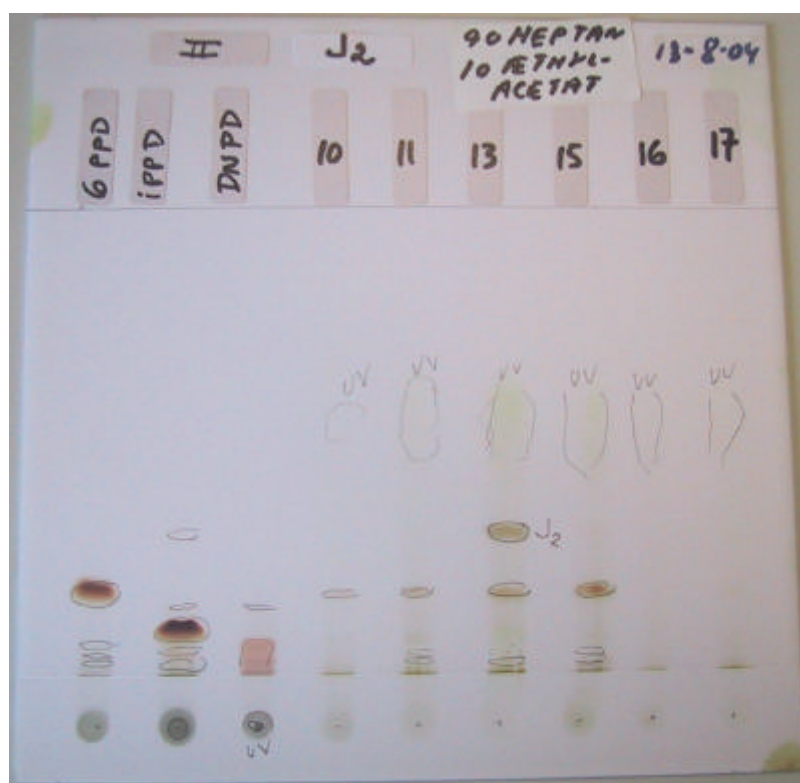
The following aromatic amines were in addition detected in the tyre solvent extracts: 6PPD, IPPD, DPPD, PAN. The most significant chemical component was 6PPD, while IPPD was present in most of the samples. For a few samples a higher signal was obtained for IPPD than for 6PPD.

3.2.2 TLC analysis, results

The results from the thin layer chromatographic screening are in accordance with the results from the GC/MS screening, both with regard to the concentration level and identity of the chemical substances. In total 13 screenings were performed by TLC. The photos below illustrate results from the screening.



TLC screening for aromatic amines before iodine treatment



TLC screening for aromatic amines after iodine treatment

3.3 Quantitative analysis

3.3.1 Selection of tyres for quantitative analysis

Based on the results from the initial screening analysis the following samples were selected for the quantitative analysis for content of PAHs and aromatic amines.

Table 3.2. Selected samples for quantitative analysis

Sample mark	Sample No.
Continental lorry, worn, tread	2
Ergofloor faldunderlagsflise, new	5
Roadstone, passenger car. worn, side wall	10
Roadstone, passenger car. worn, tread	11
Nokia, passenger car. new, tread	13
Barum Brilliant, passenger car, worn, tread	19

3.3.2 Results

The quantitative results for content of PAHs and aromatic amines in tyres are presented in Table 3.3.

The results for three selected PAHs, pyrene, chrysene og benzo(a)pyrene as well as the total amount of PAHs are illustrated graphically in Figure 3.2.

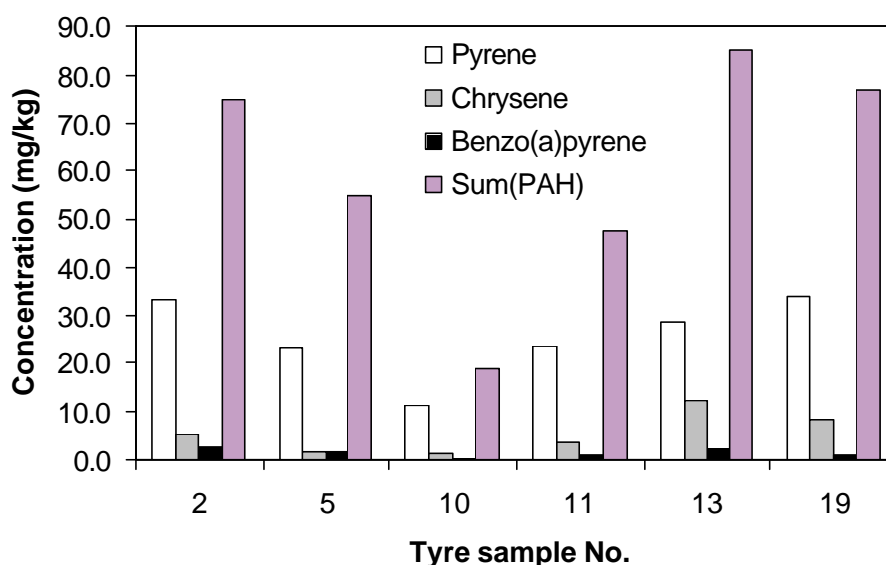


Figure 3.2. Concentration of selected PAHs and the sum of all the PAHs in the 6 samples taken from tyres for quantitative analysis.

The quantitative analysis confirms that the dominating PAHs are the ones who have a relative low molecular weight. Pyrene alone counts for approximately 50% of the total amounts of PAHs detected. The highest concentration of ? PAHs is recognised in a new passenger car tyre (sample no. 13). The lowest concentration is detected in side wall rubber from a worn passenger car tyre (sample no.10).

The aromatic amines are present in much higher concentrations. This finding is not very surprising because these substances are added to the tyres in high concentrations to prevent degradation of the rubber. The dominant chemical substance is in general 6PPD, but IPPD is also present in considerable amounts. The highest concentration of 6PPD has been measured in a new

passenger car tyre (sample no. 13). The lowest amounts of aromatic amines has been measured in an impact absorbing playground surfacing (sample no. 5).

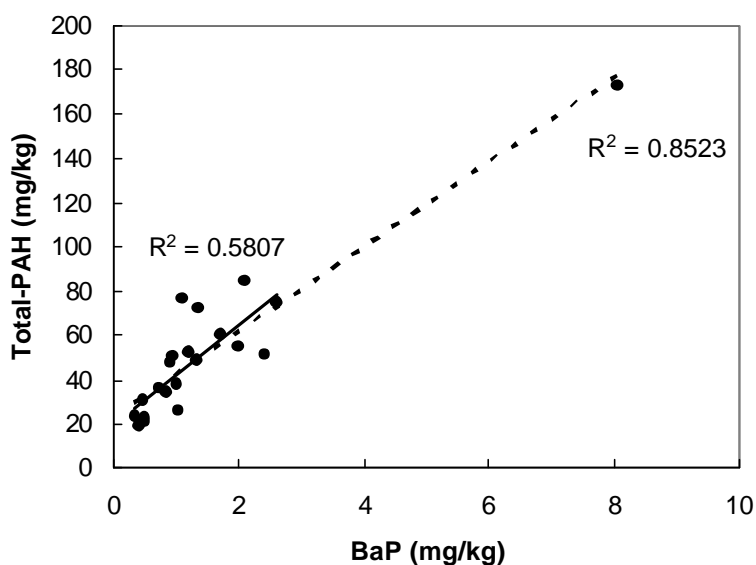
Table 3.3. Found concentrations of individual chemical substances in tyres (mg/kg)

Sample no.	2	5	10	11	13	19	Detection limit
Fluoranthene	15.4	10.6	2.1	4.7	16.0	13.4	0.02
Pyrene	33.2	23.2	11.4	23.6	28.8	34.0	0.02
Benz(a)fluorene	ID	ID	ID	ID	ID	Id	0.02
Benz(a)-anthracene	0.9	1.2	0.2	1.0	ID	0.8	0.07
Chrysene	5.3	2.0	1.4	3.7	12.3	8.2	0.07
Benz(b+j+k)fluoranthene ^a	2.1	3.0	0.3	1.9	1.9	1.7	0.04
Benz(e)pyrene	5.9	4.1	0.9	3.8	9.6	9.2	0.04
Benz(a)pyrene	2.6	2.0	0.4	0.9	2.1	1.1	0.06
Dibenz(a,j)anthracene	ID	ID	ID	ID	ID	ID	0.13
Dibenz(a,h)anthracene	0.8	ID	ID	ID	1.3	ID	0.13
Indeno(1,2,3-c,d)pyrene	1.0	1.4	0.2	0,7	2.0	1.1	0.08
Benz(ghi)perylene	7.3	7.0	2.1	6.9	10.7	7.0	0.15
DPPD	0.0	7.7	ID	ID	1.2	37.6	1 ^b
6PPD	259.0	235.7	1957.3	1297.3	2477.6	262.6	1 ^b
IPPD	340.6	3.6	39.2	19.5	3.2	355.5	1 ^b
PAN	IP	4.3	IP	IP	IP	IP	1 ^b

^aBenz(b+j+k)fluoranthene represents the sum of benz(b)fluoranthene, benz(j)fluoranthene and benz(k)fluoranthene.

^bThe detection limits for the aromatic amines are based on the not concentrated samples as the capacity of the instrument is exceeded, if these substances are analysed after concentration.

"IP" means "not detected"



Figur 3.2 Correlation between the sum of PAH's and benz(a)pyrene. The stiplede line represents a linear regression base don all numbers while the solid line represents a linear regression, where the sample with the highest concentrations is excluded.

It is often assumed that benz(a)pyrene is a PAH-indicator of relevance. A statistical investigation has been made to confirm if this is also the case for the content of PAHs in rubber formulations for tyres. In Figur 3.2 a plot of the concentrations of analysed PAHs from all 21 samples analysed has been made. The total PAH has been plotted against the corresponding concentrations of benzo(a)pyrene. The correlations found are statistical signifkant ($P < 0,005$; $n = 20/21$), either one omit the sample with a very high

amount of PAH (tractor tyre) or include the sample in the statistic. The correlation between the individual PAHs and benzo(a)pyren is also significant ($P < 0,05$; $n = 15-21$). It must be concluded that benzo(a)pyrene is useful as indicator for the PAH content in tyres.

3.4 Migration tests

3.4.1 Selection of tyres for the migration tests

Based on the results from the initial screening analysis the following samples were selected for the migration studies. The selection was done not only due to the screening analysis but also based on the results from the quantitative analysis. The migration study includes the migration of PAHs as well as aromatic amines.

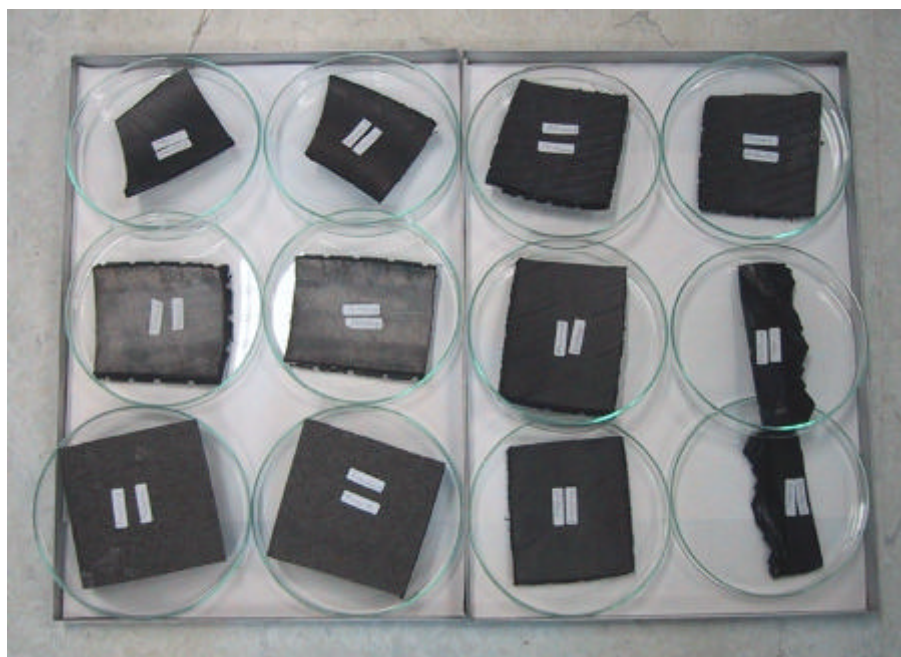
Table 3.4. Samples selected for migration tests

Sample name	Sample number
Continental lorry, second-hand, tread	2
Ergofloor impact absorbing playground surfacing, new	5
Roadstone, passenger car. Second-hand, tread	10
Roadstone, passenger car. Second-hand, tread	11
Nokia, passenger car. New, tread	13
Barum Brilliant, passenger car, second-hand, tread	19

It was decided at an early stage that the second-hand tractor tyre from Pirelli should be used for the full scale experiment.

3.4.1.1 Experimental details

A known area of the sample was exposed to artificial sweat for one hour at 30 C. The artificial sweat was prepared according to ISO 12870:1997 (E) "Øjenoptik, Brillestel, Grundlæggende krav og prøvningsmetoder pkt. 8.5.1.5 Artificial sweat solution. The artificial sweat is composed of 50 g lactic acid and 100 g sodium chloride dissolved in 900 ml water according to quality 3 i ISO 3696 and diluted to a 1 l final volume. The area/volume of artificial sweat during contact exposure was in a ratio as specified in Table 3.5 below. As the tyres have different pattern and geometries the ratio has been determined in such a way that the contact was one-sided. After the exposure period the rubber surface was rinsed with artificial sweat and finally with demineralised water. The amounts of rinsing liquids used are listed in Table 3.5. The experiments were conducted as double determinations.



Contact experiments with artificial sweat

The combined fractions of artificial sweat and distilled water are washed to a final volume according to the scheme below, are filtered through a filter paper and extracted twice with 2 times 30 – 50 ml of methylenechloride. The methylenechloride phase is dried over dry sodium sulphate for 2 hours. After filtration the methylenechloride phase is concentrated to a final volume of 1 ml internal standard is added to the first extract.

Table 3.5. Experimental parameters for the migration tests

Sample mark	Sample number	Weight, g	Area, cm ²	Contact-sweat, ml	Rinsing-sweat, ml	Rinsing-water, ml
Continental lorry, second-hand, tread	2	59.25 61.61	59.7 65.8	60 60	50 50	50 50
Ergofloor falling protection tiles, new	5	553.43 532.32	141.5 137.8	60 60	50 50	50 50
Roadstone, passenger car. Second-hand, sidewall	10	66.28 60.74	83.6 80.0	100-120 100-120	30 30	50 50
Roadstone, passenger car. Second-hand, tread	11	152.41 167.25	125.0 135.1	120 120	40 40	50 50
Nokia, passenger car. new, tread	13	179.90 174.44	125.4 123.3	200 200	50 50	50 50

Sample mark	Sample number	Weight, g	Area, cm ²	Contact-sweat, ml	Rinsing-sweat, ml	Rinsing-water, ml
Barum Brilliant, passenger car, second-hand, tread	19	153.82 151.53	122.2 116.9	100 100	30 30	50 50

The combined fractions for each sample of contact sweat, rinsing sweat and rinsing water were filtered through filter paper to remove loose rubber particles. The filtrate was extracted twice with two times 30-50 ml methylenechloride. The methylenechloride phase was dried two hours over dehydrated sodium sulphate.

The methylenechloride phase was filtered from the sodium sulphate and concentrated to a final volume of 1 ml. The concentrate was analysed for PAHs and aromatic amines after addition of internal standard to the original extract.

3.4.1.2 Results

The concentrated extract was quantitatively analysed for content of PAHs and aromatic amines. The results are recorded in Table 3.6 below:

Table 3.6. Migration of identified chemical substances. Found concentrations (ng cm⁻²) and with corresponding detection limits (DL). The results are reported as a mean value of two samples \pm 1 standard deviation.

Sample no.	2	5	10	11	13	19	DL
Fluoranthene	0.033 \pm 0.012	0.029 \pm 0.009	0.052 \pm 0.009	0.033 \pm 0.004	0.277 \pm 0.074	0.049 \pm 0.006	0.0006
Pyrene	0.036 \pm 0.020	0.032 \pm 0.006	0.082 \pm 0.039	0.059 \pm 0.008	0.487 \pm 0.021	0.066 \pm 0.008	0.0009
6PPD	0.948 \pm 0.120	5.083 \pm 0.232	19.267 \pm 8.678	44.101 \pm 32.277	49.496 \pm 20.282	0.735 \pm 0.063	0.005
IPPD	5.817 \pm 0.187	0.502 \pm 0.035	0.401 \pm 0.042	ID	0.118 \pm 0.167	10.197 \pm 0.773	0.005

"ID" means "not detected"

Table 3.6 illustrates that measurable amounts of the following chemical substances has been detected:

- Fluoranthene
- Pyrene
- 6PPD
- IPPD

Other PAHs and aromatic amines were not detected.

The results reveal that a significant higher migration of the more water soluble amines takes place in comparison with the PAHs. This finding is not only due to a higher amount of amines in the tyres, but also due to the higher solubility of the aromatic amines in water. The water solubility is higher as a consequence of the two nitrogen atoms in the molecules.

3.4.2 Full scale experiment

3.4.2.1 Experiment details

The tractor tyre was after a sample was taken for quantitative analysis for PAHs and aromatic amines installed in a cement tile based sun yard. The sun yard was situated in Hoejbjerg, south of Aarhus approx. 35 m from a not very busy road. The traffic is not very frequent as "bumps" prevent usually traffic. The road is due to the bumps mainly used by the inhabitants along the road.

The rubber from the tractor tyre was analysed quantitatively for content of PAHs and aromatic amines. The results are presented in Table 3.7.

Table 3.7. Content of PAHs and aromatic amines in Pirelli tractor tyre.

Chemical substance	Concentration mg/kg
Fluoranthene	37.4
Pyrene	75.6
Benz(a)anthracene	2.8
Chrysene	4.1
Benzo(b+j+k)fluoranthene	8.0
Benzo(e)pyrene	10.3
Benzo(a)pyrene	8.1
Indeno(1,2,3-cd)pyrene	4.4
Benzo(ghi)perylene	21.5
? (PAH)	172.7
N-(1,3-dimethylbutyl)-N'-phenyl-p-phenyldiamine (6PPD)	535.8
N-isopropyl-N'-phenyl-p-phenyldiamine (IPPD)	5.9
N,N'-diphenyl-p-phenyldiamine (DPPD)	36.4

The tractor tyre was filled with sand until approx. 15 cm from the upper edge. A sample blind was drawn from the sand before start of the experiment. Half part of the sandpit was covered by a PE foil with the aim of being able to draw reference samples not influenced by rainfall.



Full scale test experimental set-up

Samples of the sand were then taken for analysis of the migration of PAHs and aromatic amines during the exposure period. The samples were drawn at the edge of the tractor tyre, where it was easily seen that rain water has dripped and made marks in the sand. The size of the samples of sand drawn for analysis was approximately 500 g sand for the individual samples drawn. In total three samplings were made. The experiment was initiated 4 July 2004 and the samples were drawn 11 July, 4 Th. August and 15Th. August 2004. When the samples were drawn 11 July, the PE foil was not protecting the ½ part of the sand pit due to a heavy storm. For this reason no reference sample could be drawn this day. The exposure period was very rainfull. From DMI information on the precise amount of rain has been obtained during the exposure experiment. I hele perioden faldt der 84 mm of rain has been measured on DMI's weather station 22361, renseanlægget, Viby J. The station is located within a radius of 5 km from Højbjerg. In the first exposure period 4/7-11/7 2004 the rainfall was 56 mm. From 11/7-4/8 2004 the rainfall was 24 mm. In the last period of exposure a rainfall of 4 mm was recorded. The 3.2 mm of the 4 mm was registered shortly before the sampling (13/8 2004).

Influence from sun and heat also influence the migration. On one hand the sun might in a photochemical way influence the migration; on the other hand heat will promote the migration of PAHs as well as of aromatic amines.

The analytical results are presented in Table 3.8 below:

Table 3.8. Found values for content of individual chemical substances in sand ($\mu\text{g kg}^{-1}$ (wet weight)) with corresponding detection limits (DL).

	Ref. start	Sample 11/7	Sample 4/8	Ref. 4/8	Sample 15/8	Ref. 15/8	DL
Fluoranthene	1.67	3.78	2.76	5.40	10.12	2.89	0.002
Pyrene	1.12	6.01	4.20	6.31	12.57	3.64	0.004
Benz(a)anthracene	0.25	0.42	0.33	0.47	1.02	0.50	0.008
Chrysene	1.42	1.15	1.08	1.71	2.27	1.96	0.008
Benz(b+j+k)fluoranthene	0.10	0.19	0.15	0.22	0.25	0.22	0.002
Benz(e)pyrene	0.06	0.11	0.07	0.13	0.18	0.14	0.002
Benz(a)pyrene	0.03	0.09	0.06	0.07	0.09	0.07	0.002
Dibenz(ah)anthracene	IP	IP	0.01	IP	IP	0.01	0.001
Indeno(1,2,3-cd)pyrene	0.02	0.06	0.05	0.05	0.08	0.05	0.001
Benz(ghi)perylene	0.03	0.12	0.09	0.12	0.15	0.11	0.001
6PPD	IP	33.44	21.91	5.88	109.84	IP	0.1
IPPD	IP	2.47	0.71	0.43	4.56	IP	0.1

In Figure 3.3 A-C. the change in concentration of PAHs and aromatic amines with time is illustrated for pyrene, benzo(a)pyrene and 6PPD.

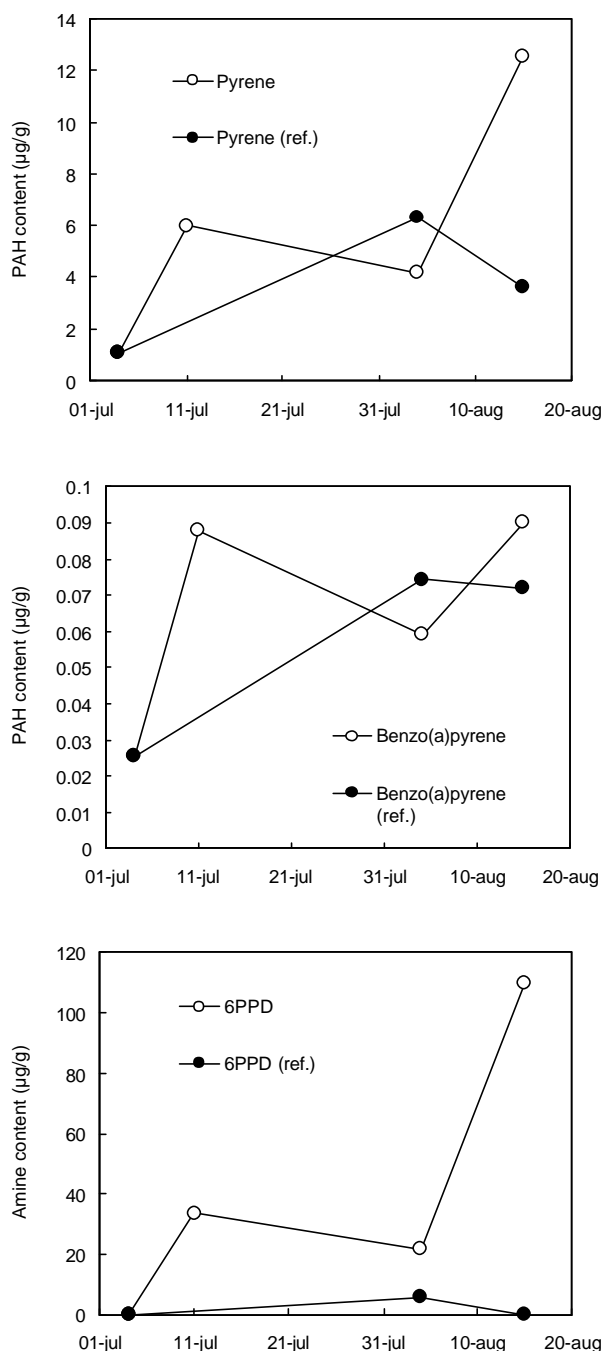


Figure 3.3 A-C. Change in concentration (wet weight) of selected PAHs and 6PPD with time in the sand covered by PE foil sand. \circ Represents samples of sand exposed to rain, while \bullet represents samples protected against rain with PE foil (ref.).

From the figures it can be seen that a rise in the concentration of the PAHs and aromatic amines happens when one compares the actual concentrations with the initial concentrations. As can be seen a rise in the concentration of PAHs and amines happens in all cases when one compares with the initial concentration. Aromatic amines were as expected not detected in the sand before exposure to the tractor tyre. In the case of PAHs a rise in concentration is observed both for the sample taken where the sand is uncovered and where the sand was protected with PE foil against exposure to rain.

In principle three ways for the contamination of the sand with PAHs are possible: migration from the tractor tyre, atmospheric dry deposition and atmospheric wet deposition (rain water).

The observation made that a rise in concentration in both covered and uncovered sand however indicates that the content of PAH in the sand during exposure is not explained by migration of PAHs from the tyre. The rise in the concentration can not alone be explained as due to wet deposition from the atmosphere.

A more detailed information regarding PAH sources is obtained by a study of the mutual concentrations of PAHs with the same molecular weight. They will possess approximately the same volatility and water solubility. The mutual concentrations of fluoranthene and pyrene, benz(a)anthracene and chrysene, benzo(a)pyrene and benzo(e)pyrene, benzo(b+j+k)fluoranthene and benz(e)pyrene, indeno(1,2,3-cd)pyrene and benzo(ghi)perylene is illustrated in Figure 3.4. In Figure 3.4 one can see that the mutual concentrations of PAHs in the tyre deviates from the mutual concentrations in the sand. The mutual concentrations of PAHs in the samples drawn from the sand are similar, if one excludes benz(a)anthracene and chrysene. If the migration from the tyre should be the only or dominating source for the contamination of the sand the concentrations in Figure 3.4 should be comparable with the PAH profile for the tyre. It is easily seen that this is not the case. It should be mentioned that the uncertainty in the PAH profile for the same sample can be neglected as most of the uncertainties from the sample preparation is not existing due to the addition of deuterated internal standards. The results depicted in Figure 3.4 underline that the PAH contamination of the sand primarily is due to deposition and only to a minor degree if any to the migration from the tyre.

Based on all the results of the experiment it is judged that atmospheric dry position is the most important source for the PAHs.

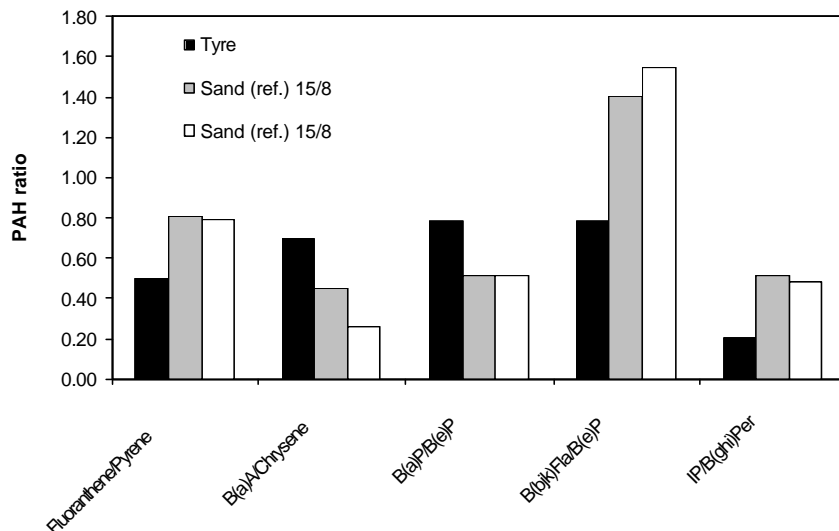


Figure 3.4. PAH ratio in full scale experiment

It must be stressed that a final conclusion regarding the contribution from the different sources mentioned above demands a more comprehensive investigation and more analytical measurements.

The concentrations of the two aromatic amines detected in the sand 6PPD and IPPD are in all measurements considerable higher in the sand exposed to rain in comparison to the sand covered by the PE foil (reference sand). As one can exclude atmospheric deposition it must be concluded that the aromatic amines migrate from the tyre to the sand due to the exposure to rain water and heat. This conclusion is a logical consequence of the much higher solubility in water of the aromatic amines compared to the PAHs.

Furthermore the aromatic amines are present in much higher concentrations in the tyre and tailor-made to migrate to the surface of the rubber to protect the rubber against degradation from the weather conditions.

4 Health Assessment

4.1 Introduction

In this section, potential health effects from the detected substances in tyres are assessed. The assessment is based upon these scenarios that were chosen and carried out in phase 1 of the project.

The focus of the assessment is aimed towards toddlers and children, who are the major groups for exposure.

For each of the identified and quantified substances information of the substances identity as well as chemical and physical properties are presented. This will include data on material state, melting point, boiling point, density, vapour pressure and solubility.

A search in the open literature has been performed. Focus has been on the ability of skin absorption and effects by oral intake. The most important test results, the effects and circumstances are presented. The aim was to find data for NOAEL/LOAEL (No or low adverse effect levels) for the selected substances or other relevant data if available. Special focus was on potential long term effects, especially carcinogenic effects.

4.1.1 Scenarios

Regarding exposure, two scenarios are selected:

- A. One scenario, where toddlers and children were exposed by skin contact. It is assumed that parts of the person's arms, hands, legs and feet are exposed for one hour daily, and that the exposed area is 200 cm². As a worst case scenario, a toddler with a body weight of 10 kg was selected.
- B. One scenario, where toddlers are exposed by oral intake of polluted sand. It is assumed that a toddler is able to eat up to 10 grams of polluted sand per day.

The exposure scenarios are defined according to the EU's Technical Guidelines Document (TGD, 2003).

The exposure from scenario A is calculated by:

Intake per day per kg b.w. = $[M \times A \times H \times F] / \text{b.w.}$ {equation 1}

- b.w.: Body weight (kg)
M: Migrated amount of substance (mg/cm²×h)
A: Exposed skin area (cm²)
H: Time of exposure per day (hours)
F: Fraction absorbed

Equation 1 can be reduced to:

Intake per day per kg body weight (mg/kg)

$$= M \times F \times 20 \text{ (mg/kg) \{equation 2\}}$$

Exposure from scenario B can be calculated by:

Intake per day per kg b.w. = $[C \times W \times F] / \text{b.w}$ {equation 3}

b.w.: Body weight (kg)

C: Concentration in sand (mg/kg)

W: Weight of sand eaten (gram)

F: Fraction absorbed

Intake per day per kg b.w. = $C \times F \times 0.001$ (mg/kg) {equation 4}

The variables M and C in equation 2 and 4 are measured (see chapter 3). In scenario A the variable F is assumed to be 10 percent if $\log K_{ow}$ is higher than 4 and 100 percent if $\log K_{ow}$ is equal to or less than 4. For scenario B - oral exposure - F is assumed to 100 percent (TDG, 2003).

Based upon the estimated intake in the two scenarios it will be possible to point out the potential health risks for toddlers and children when they are using tyres on a playground.

4.1.2 Identified substances

In the tests of the sand exposed to a tyre the following substances were identified:

- Fluoranthene
- Pyrene
- 6PPD
- IPPD
- Benzo(a)anthracen
- Chrysene
- Benzo(b+j+k)fluoranthene
- Benzo(e)pyrene
- Benzo(a)pyrene
- Dibenz(ah)anthracene
- Indeno(1,2,3-cd)pyrene
- Benzo(ghi)perylene

In the migration tests the following substances were identified

- Fluoranthene
- Pyren
- 6PPD
- IPPD

The first four substances identified in the sand are also found in the migration test. These are the most important substances and will be assessed both with respect to dermal and oral uptake. These are assessed in section 4.2. The

substance benzo(a)pyrene is also included, because it has been used as a marker for PAH-compounds.

The other substances are detected in the test of the sand in relatively small amounts (see chapter 3). They are evaluated with respect to oral uptake and the potential effects for this group of substances compared with the other four substances. The results are described in section 4.3.

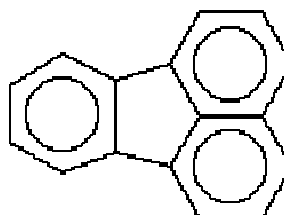
4.2 Selected substances

These substances were both identified in the analysis of sand and in the migration tests.

4.2.1 Fluoranthene

4.2.1.1 Identity

Name	Fluoranthene
CAS-number.	206-44-0
EINECS number.	205-912-4
Molecular formula	C ₁₆ H ₁₀
Molecular structure	



Molecular weight	202.26 grams/mole
Synonyms	1,2-(1,8-Naphthalenediyl)benzene 1,2-(1,8-Naphthylene)benzene 1,2-Benzacenaphthene Benzene, 1,2-(1,8-naphthalenediyl)- Benzene, 1,2-(1,8-naphthylene)- Benzo(jk)fluorine

Fluoranthene exists as pale yellow needles or plates. The substance has a melting point of 111 °C, a boiling point of 375 °C and a density of 1.252 at 0/4 °C (Lide 1995; ATSDR 1990).

Fluoranthene is almost insoluble in water (IARC, 1983), but is soluble in alcohol, ether, benzene and acetic acid (Lide, 1995). It has a vapour pressure of 1.9×10^{-3} mm Hg at 25 °C and a log K_{ow} of 5.2 (U.S.EPA, 1987).

4.2.1.2 Detected quantities

The test result from the analysis of un-exposed sand showed that the sand contained 1.7 µg fluoranthene per kg. After exposure in 2 month the content of fluoranthene was 10.1 µg per kg. This means that 8.4 µg per kg originates from the tyre.

From the migration test the results showed a migration of about 0.05 ng / (cm² × hour) for most of the samples. One sample showed a migration of 0.28 ng / (cm² × hour).

4.2.1.3 *Function of the substance*

The substance fluoranthene does not have any technical function as such. It is a component in high aromatic oils used as a plasticizer in the rubber mixture.

4.2.1.4 *Classification and TLVs*

Fluoranthene is not classified in the Annex 1 of Directive 67/548/EEC.

No threshold limits for the substance has been found.

4.2.1.5 *Health Effects*

The health effects are described in the report "Toxicity Summary for Fluoranthene" by Faust, 1993. Although this report is relatively old a search in IRIS and HSDB provide the same results.

Acute toxicity

Acute toxicity data for animals include

- an oral test on LD₅₀ of 2000 mg/kg for rats
- a dermal LD₅₀ of 3180 mg/kg for rabbits
- an interavenous LD₅₀ of 100 mg/kg for mice

These data do not indicate any serious health hazard based on acute toxicity.

Fluoranthene has been shown to be photosensitising, enhancing erythema elicited by ultraviolet radiation in guinea pig skin. Also irritation to the eyes of rabbits has been shown.

No data on inhalation were available.

Sub-chronic toxicity

In a sub-chronic study (U.S.EPA, 1988) mice were administered 0, 125, 250 or 500 mg/kg per day for 13 weeks. At doses of 250 mg/kg produced kidney damages, increased liver weights, and increased liver enzyme levels. These effects were also seen at doses of 125 mg/kg but were not considered statistically significant or adverse.

Based on this study NOAEL and LOAEL were determined to:

NOAEL: 125 mg/kg/day

LOAEL: 250 mg/kg/day

To derive the sub-chronic Reference dose, RfD an uncertainty factor of 300 is used, reflecting a factor of 10 for intra- and interspecies variation and a factor of 3 for lack of reproductive/developmental toxicity and data for a second species.

RfD, sub-chronic, oral: 0.4 mg per kg per day.

No information regarding inhalation or dermal exposure was available.

Chronic toxicity

Fluoranthene is not classified as carcinogen to humans, because of no human data and inadequate data from animal tests.

The primary target organs are the kidneys and the liver. Information on other target organs was not available.

The sub-chronic study has been used for determination of a chronic RfD using a safety factor of 3000, - where a safety factor of 10 is used for using a sub-chronic test.

RfD, chronic, oral: 0.04 mg per kg per day = 40 µg per kg per day

In IRIS it is stated that the confidence in the RfD is low, because of medium confidence in the principal study and low confidence in the database.

Some tests where animals were painted with a fluoranthene solution are reported and showed no development of skin tumours. The tests are, however, judged inadequate, because no increases in tumour incidences were observed and the tested group sizes were small.

4.2.1.6 Exposure scenarios

Here is assumed 100percent absorption (F) for oral intake and 10 percent for dermal exposure based on a high log K_{ow} (5.2).

A child will by oral intake be exposed to:

$$\begin{aligned} \text{Intake per day per kg b.w.} &= C \times F \times 0.001 \\ &= 10.1 \mu\text{g/kg} \times 1 \times 0.001 \\ &= 0.01 \mu\text{g/kg} \end{aligned}$$

By dermal exposure is assumed that the intake will be:

$$\begin{aligned} \text{Intake per day per kg b.w.} &= M \times F \times 20 \\ &= 0.28 \text{ ng/kg} \times 0.1 \times 20 \\ &= 0.56 \text{ ng/kg} \end{aligned}$$

4.2.1.7 Assessment

The substance fluoranthene causes a potential health risk related to long term exposure. This is based on test with mice where damages to liver and kidneys have been observed. Fluoranthene is a substance, which does not cause any acute health effects, or irritations based on the available information.

A reference dose of 40 µg per kg b.w. per day by oral intake has been determined. The scenarios showed:

- oral intake by children will not exceed 0.01 µg per kg b.w. per day
- dermal uptake by children will not exceed 0.0005 µg per kg b.w. per day

Compared with the NOAEL a margin of safety (MOS) can be estimated to more than 1.000.000.

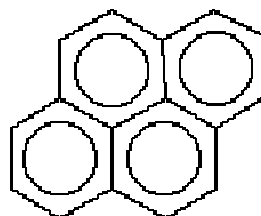
Conclusion

It can be concluded that the potential health risk from fluoranthene is insignificant.

4.2.2 Pyrene

4.2.2.1 Identity

Name	Pyrene
CAS-number.	129-00-0
EINECS number.	204-927-3
Molecular formula	C ₁₆ H ₁₀
Molecular structure	



Molecular weight	202.26 grams/mole
Synonyms	Benzo(def)phenanthrene CCRIS 1256 Pyren [German] beta-Pyrene

Pure pyrene is colourless crystals with a melting point of 151°C and a boiling point of 404 °C. The density of the substance is 1.271 grams/cm³ at 23°C (Lide, D.R. 1995).

The vapour pressure of the substance is 8.92×10^{-5} mmHg at 25°C (Piat, 1996).

The partition coefficient log K_{ow} is 4.88 (Hansch *et al.*, 1995) and the solubility in water is 0.135 mg/litre at 25°C (Mackay and Shiu, 1977). The substance is soluble in alcohol, ether, benzene, carbon disulphide and toluene.

4.2.2.2 Detected quantities

The test result from the analysis of sand shows that the sand contained 1.1 µg pyrene per kg. After exposure in 2 month the content of pyrene was 12.6 µg per kg. This means that 11.5 µg per kg originates from the tyre.

From the migration test the results showed a migration of about 0.06 ng / (cm² × hour) for most of the samples. One sample showed a migration of 0.49 ng / (cm² × hour).

4.2.2.3 Function of the substance

The substance does not have any technical function as such. It is a component in high aromatic oils that are used as a plasticizer in the rubber mixture.

4.2.2.4 Classification and TLV's

Pyrene is not classified in the Annex 1 of Directive 67/548/EEC.

OSHA (1994) has issued a threshold limit value of 0.2 mg per m³ at 8 hours.

4.2.2.5 Health Effects

Acute toxicity

Limited data regarding acute toxicity has been found. These show that pyrene has a mild irritating effect and may be toxic by ingestion.

Rabbit, skin, 24 H	500 mg, Mild irritation	Marhold, 1972
Rat, oral, LD ₅₀	2700 mg/kg	Gigiena Truda, 1971
Mouse, oral, LD ₅₀	800 mg/kg	Gigiena Truda, 1971
Rabbit, inhalation, LC ₅₀	170 mg/m ³	Gigiena Truda, 1971

In Lewis, 1996, pyrene is also mentioned as an irritant to skin. Persons with existing skin disorders may be more susceptible to the effects of coal tar pitch volatiles (Mackison *et al.*, 1981).

Sub-chronic toxicity

In the IRIS data base is presented a 13 week-test on sub-chronic toxicity for mice (U.S. EPA, 1989). In the test a group of 20 males and 20 females were gavaged with 0, 75, 125 or 250 mg/kg/day. Damages to the kidneys (nephropathy) were observed in all dosage groups. The kidney lesions were described as minimal or mild in all dosage groups. Based on the results of this study, NOAEL was considered to be 75 mg/kg/day and LOAEL were 125 mg/kg/day.

Chronic toxicity

Pyrene is not classifiable as to human carcinogenicity (classification D) based on no human data and inadequate data from animal tests (U.S. EPA, 2000).

Data for chronic RfD is derived based on the sub-chronic study described above (U.S. EPA, 1989). An uncertainty factor of 3000 reflects 10 each for intra- and interspecies variability, 10 for the use of a sub-chronic study for chronic RfD derivation, and an additional 3 to account for the lack of both toxicity studies in a second species and developmental/reproductive studies. The value for RfD is 0,03mg/kg/day, and the value is assessed having low confidence.

Compared with this, the average daily intake of pyrene for women in Japan has been estimated as 0.98 ug/day (Tamakawa K *et al.*, 1987).

Regarding dermal exposure a 0.3% solution of pyrene obtained by synthesis was applied in benzene twice weekly on the back skin of 40 mice (strain, age and sex unspecified). The longest observation time was 680 days. No skin lesion was reported. A 5% solution of pyrene (purity unspecified; solvent not indicated) was applied three times weekly for one year to mouse skin (strain, age and sex unspecified). No skin tumour was observed. A 5% solution of pyrene was also applied for one year on mouse skin previously treated with a tumour initiating dose of benzo(a)pyrene. No skin tumour was observed (IARC. 1983).

4.2.2.6 Exposure scenarios

It is assumed that 100 percent is absorbed by oral intake and 10 percent by dermal exposure based on a high value for log K_{ow} (4.9). A child will by oral intake be exposed to:

$$\begin{aligned}\text{Intake per day per kg b.w.} &= C \times F \times 0.001 \\ &= 12.6 \mu\text{g/kg} \times 1 \times 0.001 \\ &= 0.013 \mu\text{g/kg}\end{aligned}$$

By dermal exposure it is assumed that the intake will be:

$$\begin{aligned}\text{Intake per day per kg b.w.} &= M \times F \times 20 \text{ (mg/kg)} \\ &= 0.49 \text{ ng/kg} \times 0.1 \times 20 \\ &= 0.98 \text{ ng/kg}\end{aligned}$$

4.2.2.7 Assessment

Pyrene is not classified as a carcinogen (classification D). No data were available for other effects such as reproductive effects or mutagenicity. Pyrene may be toxic by ingestion and may cause mild irritations to skin.

A reference dose of 30 µg per kg b.w. per day by oral intake has been determined. The scenarios showed:

- Oral intake by children will not exceed 0.01 µg per kg b.w. per day
- Dermal uptake by children will not exceed 0.0001 µg per kg b.w. per day

Compared with the NOAEL of 75 mg/kg per day MOS is more than 1.000.000.

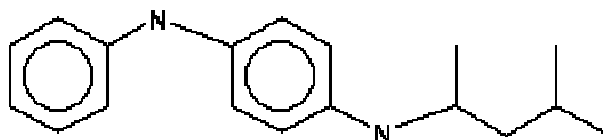
Conclusion

It can be concluded that the potential health risk from pyrene is insignificant.

4.2.3 6PPD

4.2.3.1 Identity

Name	1,4-Benzenediamine, N-(1,3-dimethylbutyl)-N'-phenyl-
CAS-number.	793-24-8
EINECS number.	212-344-0
Molecular formula	C ₁₈ H ₂₄ N ₂
Molecular structure	



Molecular weight	268.40 grams/mole
Synonyms	6PPD N-(1,3-Dimethylbutyl)-N'-phenyl-1,4-phenylene-diamine Santoflex 13 Santoflex N-Phenyl-N'-(1,3-dimethylbutyl)-p-phenylene-diamine

6PPD is a dark, violet solid substance at room temperature. Its melting point is 50°C (Lewis, 1997). The boiling point is given by Bayer AG in a data sheet to 230°C at 13.3 hPa. The density of the substance is 1.07 (Lewis, 1997).

The vapour pressure is given at 200°C to 8.7 hPa and at 300°C 93 hPa (IUCLID, 2000).

The partition coefficient log K_{ow} is estimated to 5.4 (IUCLID, 2000).

Data on solubility is very limited. In water the solubility of 6PPD is given to 1.1 ppm. Data on solubility in other media has not been found (IUCLID, 2000).

4.2.3.2 *Detected quantities*

The test result from the analysis of sand shows that the sand contained no 6PPD before exposure to the tyre. After exposure in 2 month the content of 6PPD was 110 µg per kg.

From the migration test the results showed a migration of amounts from 0.74 ng/(cm² × hour) to 49.5 ng/(cm² × hour).

4.2.3.3 *Function of the substance*

6PPD is added to the rubber mixture to prevent ozonation reactions.

4.2.3.4 *Classification and TLV's*

6PPD is not classified in the Annex 1 of Directive 67/548/EEC.

No threshold limit value has been found.

4.2.3.5 *Health Effects*

Information on 6PPD has been found in the IUCLID dataset and in the databases in TOXNET.

Acute toxicity

A number of data for acute oral and dermal toxicity is given by IUCLID.

The lowest data for LD₅₀, oral, rat is 2,500 mg/kg.

For skin exposure on rabbits, LD₅₀ > 7940 mg/kg and a LD₀ of 3160-5010 mg/kg were reported.

No data on inhalation was found.

Bayer has reported some Draize tests, where rabbits were exposed for 24 hours and examined after 72 hours. Doses of 12.5 and 125 mg 6PPD dispersed in 0.5 gram vaseline caused slightly irritation where as 25 mg 6PPD in 0.5 ml olive oil caused moderate irritation. Tests showed also slightly eye irritations (IUCLID, 2000).

From the above-mentioned data it is seen that 6PPD causes no serious health effects by oral intake or dermal exposure. The substance may be an irritant to skin.

Sub-chronic toxicity

In a 13 week test with rats oral doses of 19, 75 and 188 mg/kg were administered daily. Mild anemia was seen in mid- and high-dose rats. Reduction in white blood cell counts were seen in females at all levels. Elevations in serum proteins and cholesterol as well as body weight depressions were noted in the mid- and high-dose rats. (IUCLID, 2000).

Chronic toxicity

Data from IUCLID indicate that 6PPD is a potential sensitizing substance. Some people, previously exposed to rubber samples, reacted positive in a patch-test. One reported test included 50 human volunteers, who were patch-tested with 50 % w/v 6PPD in dimethylphthalate; - 5 of the 50 individuals

showed reactions in the 3-week induction phase and 5 of 5 showed reactions in the challenge phase.

In a two years study with rats oral doses of 8, 23 and 75 mg/kg were administered daily. The results showed reduced body weight for both sexes at the high dose level and increased kidney and spleen weights for females at the high dose level (Stevens *et al.*, 1981).

In a 12 month study, rats were given 4, 20 or 120 mg/kg (oral feed) daily. The NOEL for chronic toxicity was determined to be 4 mg/kg based on decrease in body weight and haematological changes at the mid- and high- dose level. A NOEL for oncogenic effects was determined to be at least 120 mg/kg (IUCLID, 2000).

The reproductive and developmental toxicity was tested by a Japanese Pharmaceutical Laboratory. The test showed that NOAEL for reproduction is at least 1.000 mg/kg.

- In one test male and female rats were orally given doses of given 40, 200 and 1000 mg/kg per day. Males were treated 42 or 49 days including 28 days before mating and females were treated for 14 days before mating, through the mating period and until 7 days of gestation. Neither the foetuses nor the parents were affected. The NOAEL for reproductivities and fetal development was determined to be 1000 mg/kg (Chihara *et al.*, (1), 1998).
- In a similar test pregnant rats were exposed orally from day 7 through day 17 of gestation. No effects on the foetuses were observed and the NOAEL for dams and foetuses was determined to be 1000 mg/kg (Chihara *et al.*, (2), 1998).
- In another similar test the effects on the rats and their offspring's were examined, when the mothers were orally exposed from day 7 of gestation through day 21 of lactation. No effects on the offspring were observed and the NOAEL on development of the offspring was determined to be 1000 mg/kg (Chihara *et al.*, (3) 1998).

4.2.3.6 Exposure scenarios

Here is assumed 100 percent absorption by oral intake and 10 percent by dermal exposure because of a high value for log K_{ow} (5.4).

A child will by oral intake be exposed to:

$$\begin{aligned} \text{Intake per day per kg b.w.} &= C \times F \times 0.001 \\ &= 110 \mu\text{g/kg} \times 1 \times 0.001 \\ &= 0.11 \mu\text{g/kg} \end{aligned}$$

By dermal exposure is assumed that the intake will be:

$$\begin{aligned}\text{Intake per day per kg b.w.} &= M \times F \times 20 \text{ (mg/kg)} \\ &= 50 \text{ ng/kg} \times 0.1 \times 20 \\ &= 0.10 \text{ } \mu\text{g/kg}\end{aligned}$$

4.2.3.7 Assessment

The substance 6PPD may be irritating to skin and eyes and is a potential sensitizer to skin. The substance has a low acute toxicity by oral and dermal exposure.

The following values for chronic effects have been found:

NOEL for effects on blood	4 mg/kg
NOEL for oncogenic effects	more than 120 mg/kg
NOAEL for reproduction	more than 1.000 mg/kg

No other data, as for instance on carcinogenicity, has been found.

The scenarios showed:

- Oral intake by children will not exceed 0.1 μg per kg b.w. per day
- Dermal uptake by children will not exceed 0.1 μg per kg b.w. per day

Compared with the NOEL of 4 mg/kg per day MOS is more than 10.000.

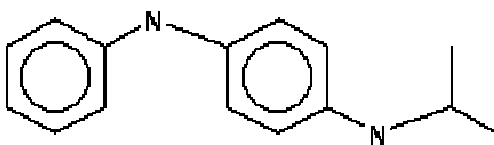
Conclusion

It can be concluded that the potential health risk from 6PPD is insignificant.

4.2.4 IPPD

4.2.4.1 Identity

Name	N-isopropyl-N'-phenyl-4-phenylenediamine
CAS-number.	101-72-4
EINECS number.	202-969-7
Molecular formula	$\text{C}_{15}\text{H}_{18}\text{N}_2$
Molecular structure	



Molecular weight	226.35 grams/mole
Synonyms	IPPD 1,4-Benzenediamine, N-(1-methylethyl)-N'-phenyl- 4-Isopropylaminodiphenylamine Santoflex 36

The substance IPPD is dark grey to black flakes. It has a melting point of 75°C (Ashford, 1994). The boiling point is determined by Bayer to be 161°C at 1 mmHg (IUCLID, 2000).

The density is 1.07 g/cm³ at 20°C. The vapour pressure is 0.00093 hPa at 50°C and 2.1 hPa at 180°C. Log K_{ow} is measured to be 3.9 (IUCLID, 2000).

The only available data on solubility is that IPPD is soluble in aromatic solvents and insoluble in water.

4.2.4.2 *Detected quantities*

The test result from the analysis of sand shows that the sand contained no IPPD before exposure to the tyre. After exposure in 2 month the content of IPPD was 4.6 µg per kg.

From the migration test the results showed a migration of 0 to 10.2 ng/(cm² × hour).

4.2.4.3 *Function of the substance*

IPPD is added to the rubber mixture to prevent ozonation reactions.

4.2.4.4 *Classification and TLV's*

The substance is included in the Annex 1 of Directive 67/548/EEC with the classification:

Xn;R22-R43	Harmful; Harmful if swallowed - May cause sensitization by skin contact
N;R50/53	Dangerous to the environment; Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment

No TLV's or other standards have been found.

4.2.4.5 *Health Effects*

Information on IPPD has been found in the IUCLID dataset and in the databases in TOXNET.

Acute effects

The following information was found in IUCLID.

Several tests to determine an oral LD₅₀ has been reported. The data varies from 555 to 1,620 mg/kg for rats and 1,122 to 3,030 mg/kg for mice.

No data is given for inhalation.

The acute dermal toxicity for rabbits LD₅₀ is found to be more than 7,500 mg/kg. A test regarding adsorption showed no skin penetration after immersing the tails of mice ¾ in a 50% oil solution.

A patch test on human volunteers showed that 20 out of 50 persons showed skin irritation after repeated skin contact. The dose level was not indicated. Moderate eye irritation was observed on rabbits after exposure to 100 mg in 24 hours.

Sub-chronic effects

An inhalation study on rats for 15 days with an exposure of 300-400 mg/m³ in 2 hours daily is reported in IUCLID. Observations showed unchanged body weight, some changes in the nervous system and malfunction of the liver.

In another study rats were orally fed for 90 days with doses of 0, 180 mg/kg, 360 mg/kg and 720 mg/kg. Lower body weight gains were observed in the high-exposure group of males. In the mid- and high exposure groups of males and in all females increased liver weight were noted. Increased spleen and kidney weights were observed in high-exposure females and mild anaemia was found in mid- and high-exposure animals. Based on the observed organ

weight changes, a NOEL was not established, while a NOEL for treated males was 180 mg/kg.

In a 4 week study dose levels of 0, 500, 1000, 1750 and 2500 mg/kg was tested. The species used were not mentioned. The result showed that at dose levels of 1000 mg/kg and above decreases in body weight gain, haematological effects, evaluations in total serum protein as well as increased liver and spleen weights were noted. The NOEL was considered to be approximately 500 mg/kg.

Chronic effects

In IUCLID, tests on sensitization has been reported. Humans with contact dermatitis caused by rubber reacted positive with IPPD in varies tests.

Regarding genetic toxicity a number of Ames test has been reported in the CCRIS data base as well as in the IUCLID data set, - all except one showing a negative result.

Tests on carcinogenicity and reproduction have not been found.

Data for developmental toxicity has been given in a test on rats. Female rats were exposed from day 6 to day 15 of gestation with the dose levels 0, 12.5, 62.5 and 125 mg/kg per day. The test method followed OECD Guide-line 414. At the two highest dose levels decrease in food consumption on day 6-9 of gestation was observed. Increased skeletal findings following fetal examination were observed. The delayed developmental effects noted at 12.5 62.5 mg/kg were not considered to be adverse effects. Based on the findings a NOAEL was determined to be 125 mg/kg per day for maternal effects. For effects on the foetus a LOAEL was determined to be 125 mg/kg and a NOAEL to 62.5 mg/kg per day (IUCLID).

4.2.4.6 Exposure scenarios

Here is assumed 100 percent absorption both for oral and dermal exposure. Log K_{ow} is 3.9, and therefore it can be discussed if F for dermal exposure should be less than 100 percent.

A child will by oral intake be exposed to:

$$\begin{aligned} \text{Intake per day per kg b.w.} &= C \times F \times 0.001 \\ &= 4.6 \mu\text{g/kg} \times 1 \times 0.001 \\ &= 4.6 \text{ ng/kg} \end{aligned}$$

By dermal exposure is assumed that the intake will be:

$$\begin{aligned} \text{Intake per day per kg b.w.} &= M \times F \times 20 \text{ (mg/kg)} \\ &= 10.2 \text{ ng/kg} \times 1 \times 20 \\ &= 204 \text{ ng/kg} \end{aligned}$$

4.2.4.7 Assessment

IPPD may be toxic if swallowed in large quantities. Skin contact may cause sensitization. Data on long term effects, except for developmental toxicity, has not been found. A NOEAL for maternal effects is 125 mg/kg per day and for effects on the foetuses the NAOEL is 62.5 mg/kg.

The value for NOEAL of 62.5 mg/kg per day can be compared with the scenarios:

- Oral intake by children will not exceed 5 ng per kg b.w. per day
- Dermal uptake by children will not exceed 200 ng per kg b.w. per day

Comparing the NOAEL with the scenarios MOS is more than 100.000.

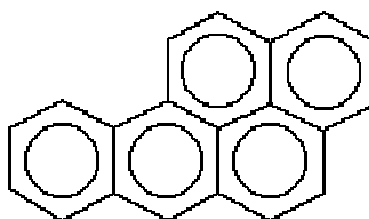
Conclusion

It can be concluded that the potential health risk from IPPD is insignificant.

4.2.5 Benzo(a)pyrene

4.2.5.1 Identity

Name	Benzo(a)pyrene
CAS-number.	50-32-8
EINECS number.	200-028-5
Molecular formula	C ₂₀ H ₁₂
Molecular structure	



Molecular weight	252.32 grams/mole
Synonyms	Benzo(def)chrysene 3,4-Benzopyrene 4,5-Benzpyrene 6,7-Benzopyrene

Benzo(a)pyrene is pale yellow crystals. The melting point is 179°C and the boiling point is 310°C at 10 mmHg. The density is 1.351 g/cm³.

The partition coefficient for benzo(a)pyrene log K_{ow} is 5.97 (Hansch *et al.*, 1995).

The vapour pressure is very low, 5.5 × 10⁻⁹ mm Hg at 25°C (extrapolated value) (Murray JJ *et al.*, 1974).

The solubility for benzo(a)pyrene in water is 1.6 µg/litre at 25°C. The substance is soluble in aromatic hydrocarbons such as benzene, toluene and xylene and sparingly soluble in alcohols.

4.2.5.2 Detected quantities

The test result from the analysis of sand shows that the sand contained 0.03 µg per kg of benzo(a)pyrene before exposure to the tyre. After exposure in 2 month the content was 0.09 µg per kg.

No benzo(a)pyrene was detected in the migration test.

4.2.5.3 Function of the substance

The substance benzo(a)pyrene does not have any technical function as such. It is a component in high aromatic oils used as a plasticizer in the rubber mixture.

4.2.5.4 Classification and TLV's

The substance is included in the Annex 1 of Directive 67/548/EEC (29. amendment) with the classification:

Carc2;R45	Toxic; May cause cancer
Mut2;R46	Toxic; May cause heritable genetic damage
Rep2;R60-61	Toxic; May impair fertility. May cause harm to the unborn child
R43	May cause sensitization by skin contact (included in 29.ATP)
N;R50/53	Dangerous to the environment; Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment

The Danish TLV for polyaromatic hydrocarbons (particles, soluble in benzene) is 0.2 mg/m³ (At-vejledning C.0.1). The regulation from OSHA states as well a TWA of 0.2 mg/m³ (1994). Other countries have issued a lower limit, for instance Norway 0.04 mg/m³ (1999), Poland 0.003 mg/m³ (1999), and Finland 0.01 mg/m³ (1999).

4.2.5.5 Health effects

Data regarding benzo(a)pyrene has been found SCF's report on Polycyclic Aromatic Hydrocarbons in food (SCF, 2002), HSDB, IRIS and other databases.

Acute toxicity

Very few data on acute toxicity is given. In RTECS, the following data is found:

TDL ₀	Rat, intraperitoneal	40 mg/kg	(1968)
TDL ₀	Rat, intraperitoneal	100 mg/kg	(1979)
TDL ₀	Mouse, intraperitoneal	80 mg/kg	(1979)
TDL ₀	Rat, oral	100 mg/kg	(2001)

Subacute toxicity

In a 90-days study on rats liver weight was identified as the critical effect and a NOAEL of 3 mg/kg b.w. was determined (Kroese *et al.*, 2001 SCF, 2002).

Treatment of male rats by gavage for 35 days with 3, 10, 30 or 90 mg/kg b.w. induced various immunotoxic effects such as decrease in thymus and lymph nodes weight, decreased absolute and relative B cell numbers in the spleen and decreased numbers of red and white blood cells. The NOAEL for immunotoxicity of benzo(a)pyrene was 3 mg/kg b.w. per day (De Jong *et al.*, 1999).

Chronic toxicity

IARC (1987) has classified the substance as probably carcinogenic to humans (group 2A) based on sufficient evidence of carcinogenicity in animals. The U.S. EPA has included benzo(a)pyrene in the IRIS data-base and here the substance is classified B2: Probable human carcinogen.

In a report from RIVM (Baars *et al.*, 2001) on re-evaluation of human-toxicological maximum permissible risk levels the following data on benz(a)pyrene is provided

- RIVM developed an oral cancer risk estimate CR (oral) for benzo(a)pyrene of 0.5 µg/kg × day. This value was based on tumour development in a variety of organs and tissue (Kroese *et al.*, 2001) in a two year study with Wistar rats. The result is converted to a risk specific dose (RSD) of 0.05 µg/kg × day.

- Based upon occupational inhalation exposure to PAH-mixtures respiratory effects were noted in humans and a LOAEL for non-carcinogenic effects were estimated to 0.1 µg/m³.

Among other PAHs benzo(a)pyrene was considered genotoxic with positive results in assays *in vitro* and *in vivo*. Positive results were also shown at germ cell level (SCF, 2002).

Data from animals and humans regarding reproductive and developmental effects are insufficient for risk assessment. Although adverse effects in animals have generally been seen only at relatively high doses of benzo(a)pyrene the values of NOAEL have not been established (SCF, 2002).

4.2.5.6 Exposure scenarios

Only the scenario regarding oral intake is relevant while the substance was not detected in the migration tests.

A child will by oral intake be exposed to:

$$\begin{aligned}
 \text{Intake per day per kg b.w.} &= C \times F \times 0.001 \\
 &= 0.09 \mu\text{g/kg} \times 1 \times 0.001 \\
 &= 0.1 \text{ ng/kg}
 \end{aligned}$$

4.2.5.7 Assessment

Benzo(a)pyrene is a substance that may cause cancer as well as genetic and developmental effects.

NOEAL were for a sub-chronic test estimated to 3 mg/kg b.w. per day. Based on oral cancer risk RIVM has estimated a risk specific dose (RSD) of 50 ng/kg b.w. per day.

Comparing the findings in the test of the sand with the RSD it is seen that the RSD is about 500 times higher than the findings. Compared with the NOAEL of 3 mg/kg, a MOS of more than 1.000.000 is estimated.

Conclusion

The potential health risk from exposure of benzo(a)pyrene is insignificant.

4.3 Other identified substances

4.3.1 Identification

4.3.1.1 Detected quantities

Besides the substances described in the previous section a number of other substances have been identified and quantified in the sand exposed to tyres. These substances are presented in Table 4.1..

Table 4.1. Additional substances identified in sand

Name	CAS-number	Max-content µg/kg wet weight	Content at start µg/kg wet weight
Benz(a)anthracene	56-55-3	1.02	0.25
Dibenz(a,h)anthracene	53-70-3	-	-
Benz(e)pyrene	192-97-2	0.18	0.06
Benz(b)fluoranthene	205-99-2	0.25	0.10
Benz(j)fluoranthene	205-82-3		
Benz(k)fluoranthene	207-08-9		
Benz(ghi)perylene	191-24-2	0.15	0.03
Crysene	218-01-9	2.27	1.42
Indeno(1,2,3-cd)pyrene	193-39-5	0.08	0.02

Because dibenz(a,h)anthracene was not detected in the analysis, this substance is omitted in the following assessment.

4.3.1.2 Identity

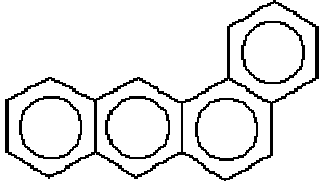
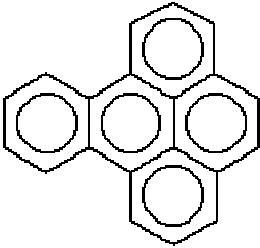
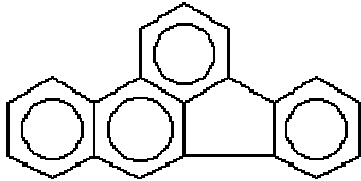
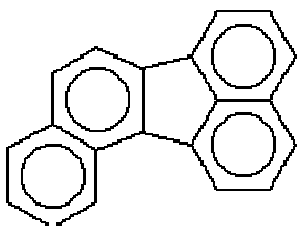
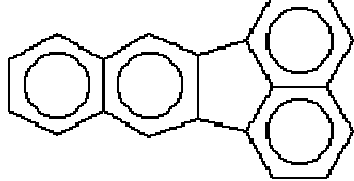
In Table 4.2 basic data for the selected substances are shown. Compared to benzo(a)pyrene the structure of the substances in Table 4.2 is similar.

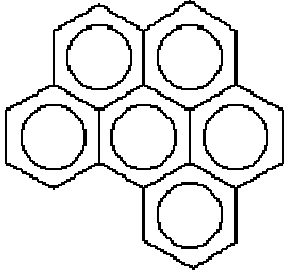
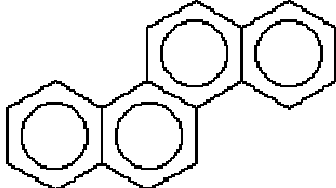
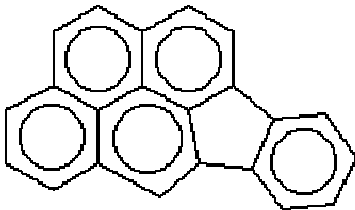
Benzo(a)pyrene consist of five aromatic rings. It is the same for benzo(e)pyrene. Benz(a)anthracene and crysene consists of 4 aromatic rings and benz(ghi)perylene of six aromatic rings. The fluoranthenes consist of 4 aromatic rings and a 5-ring and indeno(1,2,3-cd)pyrene of 5 aromatic rings and a 5-ring.

As can be seen from Table 4.2 the molecular weight for the substances is about 250 gram per mole, the melting point is above 150°C and log K_{ow} is above 5 for the substances where data for this parameter were found. These values are equivalent to the data for benzo(a)pyrene.

Regarding classification most of the substances are classified Carc. Cat. 2; R45 N;R50/53. Crysene is also classified for mutagenicity, Cat. 3. Benz(g,h,i)perylene is only classified with respect to the environment and indeno(1,2,3-cd)pyrene were not included in the Annex I of Directive 67/548/EEC. This indicates, that, based on classification, none of the substances included in Table 4.2 are more hazardous than benzo(a)pyrene.

Table 4.2. Properties of selected substances identified in sand

Name and properties		Formula
Name	Benz(a)anthracene	
CAS-number	56-55-3	
EINECS no.	200-280-6	
Molecular weight	228.29 gram per mole	
Melting point	160 °C	
Log K _{OW}	5.79	
Classification	Carc.Cat.2;R45 N;R50/53	
Name	Benzo(e)pyrene	
CAS-number	192-97-2	
EINECS no.	205-892-7	
Molecular weight	252.32 gram per mole	
Melting point	179 °C	
Log K _{OW}	5.97	
Classification	Carc.Cat.2;R45 N;R50/53	
Name	Benzo(b)fluoranthene	
CAS-number	205-99-2	
EINECS no.	205-911-9	
Molecular weight	252.32 gram per mole	
Melting point	168 °C	
Log K _{OW}	6.60	
Classification	Carc.Cat.2;R45 N;R50/53	
Name	Benzo(j)fluoranthene	
CAS-number	205-82-3	
EINECS no.	205-910-3	
Molecular weight	252.32 gram per mole	
Melting point	166 °C	
Log K _{OW}	NA	
Classification	Carc.Cat. 2;R45 N;50/53	
Name	Benzo(k)fluoranthene	
CAS-number	207-08-9	
EINECS no.	205-916-6	
Molecular weight	252.32 gram per mole	
Melting point	217 °C	
Log K _{OW}	6.84 (estimated)	
Classification	Carc.Cat.2;R45 N;R50/53	

Name	Benzo(ghi)perylene 1,12-Benzoperylene	
CAS-number	191-24-2	
EINECS no.	205-883-8	
Molecular weight	276.34 gram per mole	
Melting point	277 °C	
Log K _{ow}	6.63	
Classification	N;R50/53 ×1	
Name	Crysene	
CAS-number	218-01-9	
EINECS no.	205-923-4	
Molecular weight	228.29 gram per mole	
Melting point	258.2 °C	
Log K _{ow}	5.73	
Classification	Carc.Cat.2;R45 Mut.Cat.3;R68 N;R50/53	
Name	Indeno(1,2,3-cd)pyrene	
CAS-number	193-39-5	
EINECS no.	205-893-2	
Molecular weight	276.35 gram per mole	
Melting point	163.6 °C	
Log K _{ow}	NA	
Classification	NA	

NA: Not available

×1): From the Advisory List on Self-classification from the Danish Environmental Protection Agency, 2001

4.3.2 Evaluation

4.3.2.1 Screening of health effects

In Baars *et al.* (2001) data for some of the most common PAHs is provided.

In Table 4.3. an overview of the genotoxicity and carcinogenicity for selected PAHs is given. No data were available for benz(e)pyrene.

Table 4.3. Genotoxicity and carcinogenicity for selected PAHs (Baars *et al.*, 2001)

Substance	CAS no.	Genotoxicity IPCS (1998)	Carcinogenicity IPCS(1998)	Carcinogenicity IARC(1983)
Benzo(a)pyrene	50-32-8	+	+	2A
Benz(a)anthracene	56-55-3	+	+	2A
Benzo(b)fluoranthene	205-99-2	+	+	2B
Benzo(j)fluoranthene	205-82-3	+	+	2B
Benzo(k)fluoranthene	207-08-9	+	+	2B
Benzo(g,h,i)perylene	191-24-2	+	-	3
Crysene	218-01-9	+	+	3
Indeno(1,2,3-c,d)pyrene	193-39-5	+	+	2B

IPCS classification

+ positive

- negative

IARC classification:

2A compound is probably carcinogenic to humans

2B compound is possibly carcinogenic to humans

3 compound is not classifiable as to its carcinogenicity to humans

IARC has assessed benzo(e)pyrene (IARC, 1987) and found inadequate evidence of carcinogenicity. It was placed in group 3.

In the conclusion (Baars *et al.*, 2001) a table of risk estimation for selected PAHs using the parameter MPR, maximum permissible risk is shown as a measure of the potential risk. The data is provided in Table 4. for the actual substances except benz(e)pyrene, which were not included in the Dutch study.

Table 4.4. Value for Maximum Permissible Risk (Baars *et al.*, 2001)

Substance	CAS no.	Maximum Permissible Risk, MPR	
		Type	Value
Benzo(a)pyrene	50-32-8	CRoral	0.5
Benz(a)anthracene	56-55-3	CRoral	5
Benzo(b)fluoranthene	205-99-2	CRoral	5
Benzo(j)fluoranthene	205-82-3	CRoral	5
Benzo(k)fluoranthene	207-08-9	CRoral	5
Benzo(g,h,i)perylene	191-24-2	TDI	30
Crysene	218-01-9	CRoral	50
Indeno(1,2,3-c,d)pyrene	193-39-5	CRoral	5

CRoral : 1:10⁴ excess lifetime cancer risk for oral exposure; µg/kg b.w. per day

TDI: tolerable daily intake ; µg/kg b.w. per day

As can be seen from Table 4. the MPR is the lowest for benzo(a)pyrene and 10 to 100 times higher for the other substances.

No values for NOAEL have been found for the substances included in Table 4..

The data in Table 4.3. and Table 4. indicates that benzo(a)pyrene is more toxic than the other PAH-substance described in this section.

4.3.2.2 Exposure scenario

In the analysis of the sand altogether 13 PAHs were identified and quantified. The 3 substances, fluoranthene, pyrene and benzo(a)pyrene has already been assessed. In Table 4.5. is shown the amount of these substances and the sum of the other substances.

Table 4.5. Amount of PAHs in sand

Substance	CAS no.	Maximum Amount
Fluoranthene	206-44-0	10 µg/kg
Pyrene	129-00-0	12.6 µg/kg
Benzo(a)pyrene	50-32-8	0.1 µg/kg
Other PAHs	-	4 µg/kg

If it is assumed that a child will be exposed to 10 grams of sand per day with the content of 4 µg/kg of different PAHs, a child will by oral intake be exposed to:

$$\begin{aligned}
 \text{Intake per day per kg b.w.} &= C \times F \times 0.001 \\
 &= 4 \mu\text{g/kg} \times 1 \times 0.001 \\
 &= 4 \text{ ng/kg}
 \end{aligned}$$

4.3.2.3 Assessment

Most of the identified PAHs are potential carcinogenic. Of the nine substances two are classified as group 2A (probably carcinogenic) four in group 2B (possible carcinogenic) by IARC and three in group 3 (inadequate evidence of carcinogenicity). Crysene is as well a potential mutagenic substance.

The data found for the nine PAHs indicate that these have the same type of effects as benzo(a)pyrene, but that the risk is lower.

The NOAEL level for benzo(a)pyrene is determined to be 3 mg/kg b.w. per day based on a sub-chronic study. RIVM has estimated a risk specific dose (RSD) of 50 ng/kg b.w. per day.

Comparing the result of the exposure scenario, where the nine PAHs are added together, with the NOAEL for benzo(a)pyrene gives a MOS of 750.000. The RSD of 50 ng/kg per day is higher than the values estimated from the scenarios.

Conclusion

Taking into account, as most of the nine PAHs has a risk level lower than benzo(a)pyrene it can be concluded that the potential health risk from the actual exposure to these PAHs in the observed amounts is insignificant.

4.4 Conclusion

Some PAHs and amino-compounds have been found in two scenarios. One was sand exposed to discarded tyres and the other was migration tests, where artificial sweat was exposed to discarded tyres. The substances have been identified and quantified in the performed tests.

The following substances were identified:

In migration tests		In test of exposed sand
Fluoranthene	Fluoranthene	Benzo(b+j+k)fluoranthene
Pyrene	Pyrene	Benzo(e)pyrene
6PPD	6PPD	Benzo(a)pyrene
IPPD	IPPD	Dibenz(ah)anthracene
	Benzo(a)anthracene	Indeno(1,2,3-cd)pyrene
	Chrysene	Benzo(ghi)perylene

It was expected to find more PAHs in the migration test. On the other hand, there has been no focus on the amino-compounds, 6PPD and IPPD, with respect to migration from used tyres before.

The four substances found in the migration test and benzo(a)pyrene was assessed. A screening including the other substances was performed.

The assessment showed:

- Fluoranthene causes no acute health effects. Related to long term exposure damages to liver and kidneys have been seen in animal studies. A child may be exposed to 10 ng per day per kg b.w. and with a NOAEL of 125 mg/kg this results in a MOS of more than a million.
- Pyrene may be toxic by ingestion and causes mild irritation to skin. Pyrene is not classified as a carcinogen. No data on reproduction or mutagenicity was available. A child may be exposed to 13 ng per day per kg b.w. and with a NOAEL of 75 mg/kg it results in a MOS of more than a million.
- 6PPD may be irritating to skin and a potential sensitizer. Long term effects such as haematological changes and oncogenic effects as well as effects on reproduction have been observed. A child may be exposed to

100 ng per day per kg b.w. and with a NOEAL of 4 mg/kg, it results in a MOS of 10.000.

- IPPD may be toxic if swallowed in large quantities. Skin contact may cause sensitization. Data on long term effects, except for developmental toxicity, has not been found. A child may be exposed to 200 ng per day per kg b.w. and with a NOAEL of 62.5 mg/kg it results in a MOS of 100.000.
- Benzoe(a)pyrene is a substance that may cause cancer as well as genetic and developmental effects. A child may be exposed to 0.1 ng/kg b.w. per day. Compared with a NOAEL of 3 mg/kg it results in a MOS of more than one million.
- The other identified PAHs causes the same type of health effects as benzoe(a)pyrene but with a lower risk level. A child may be exposed to in total 4 ng/kg b.w. per day of these PAHs. Comparing this with a NOAEL of 3 mg/kg it results in a MOS of 750.000.

From these results it can be concluded that the potential health risk related to use discarded tyres on playgrounds is insignificant.

Although the MOS is high for all the identified components it is notable that the lowest MOS are found for the two identified amino-compounds.

Abbreviation list

Carc	Carcinogen
CCRIS	Chemical Carcinogenesis Research Information System
DL	Detection limit
HA	High aromatic mineral oil
HDSB	Hazardous Substance Data Bank
IP	Not detected
IRIS	Integrated Risk Information System
IUCLID	International Uniform Chemical Information Database
LC ₅₀	Mortality rate concentration 50 percent
LD ₀	Low mortality rate dose
LD ₅₀	Mortality rate dose 50 percent
LOAEL	Lowest adverse effect level
LOEL	Lowest effect level
MOS	Marginal of safety
Mut	Mutagenic effects
NOAEL	No adverse effect level
NOEL	No-effect level
OSHA	Occupational Health and Safety Administration, USA
PAH	Polycyclic aromatic hydrocarbons
Rep	Reproduktive effects
RfD	Reference dose
RFD	Risici specific dose
RTECS	Registry of Toxic Effects of Chemical Substances
TDL ₀	Lowest dose no effect
TLV	Treshold limit values

References

ATSDR, 1990. Toxicological profile for Polycyclic Aromatic Hydrocarbons. Acenaphene, Acenaphthylene, Anthracene, Benzo(a)anthracene, Benzo(a)pyrene, Benzo(b)fluoranthene, Benzo(g,i,h)perylene, Benzo(k)fluoranthene, Crysene, Dibenzo(a,h)anthracene, Fluoranthene, Fluorene, Indeno(1,2,3-c,d)pyrene, Pyrene. Prepared by Clement International Corporation, under Contract No. 205-88-0608. ATSDR/TP-90-20.

At-vejledning C.0.1 (2000) Grænseværdier for stoffer og materialer

Baars, A.J.; Theelen, R.M.C.; Janssen, P.J.C.M.; Hesse, J.M.; van Apeldoorn, M.E.; Meijerink, M.C.M.; Verdam, L.; Zeilmaier, M.J. (2001) Re-evaluation of human-toxicological maximum permissible risk levels. RIVM report 711701 025

Baumann, W.; M. Ismeier, Emmissionen beim bestimmungsgemässen Gebrauch von Reifen, IKT 1997, s. 97

Cedheim, L.; Fagerli, A. K.; Halonen, I.; Møller, S. og Tapper, M. (2001) Sammenfattende metod för at bestämme den totale halten PCA i ekstrakt från däck – ett preliminärt underlag för miljömärkning, Nordtest report TR 469, Nordtest, Finland

Chihara, K.; Yoshioka, M.; Shigematsu, K.; Funabashi H. (1) 1998 Reproductive and developmental toxicity studies of CD-13 (1) - study of fertility and early embryonic development to implantation in rats. Yakuri To Chiryō 1998;26(9):69-76

Chihara, K.; Tateishi, Y.; Funabashi, H. (2) 1998. Reproductive and developmental toxicity studies of CD-13 (2)--study for effects on embryo-fetal development in rats. Yakuri To Chiryō 1998;26(9):77-83

Chihara, K.; Fujioka, M.; Funabashi, H.; Izumi, H. (3) 1998. Reproductive and developmental toxicity studies of CD-13 (4)--study for effects on prenatal and postnatal development, including maternal function. Yakuri To Chiryō 1998;26(9):95-110

Ciullo, P.A.; Hewitt, N. The Rubber Formulary, PDL Handbook Series, 1999

De Jong, W.H.; Kroese, E.D.; Vos, J.G.; Van Loveren, H. 1999. Detection of immunotoxicity of benzo(a)pyrene in a subacute toxicity study after oral exposure in rats. Toxicol. Sci., 50, 214-220

Faust, R. A. (1993) Toxicity Summary for Fluoranthene. Oak Ridge National Laboratory, Oak Ridge, Tennessee

Feilberg, A.; Poulsen, M.; Nielsen, T. og Skov, H. (2001) Occurrence and sources of particulate nitro-polycyclic aromatic hydrocarbons in ambient air in

Denmark. Atmospheric Environment 35 p 353-366

HA oils in automotive tyres, Swedish National Chemical Inspectorate, 2003

Hansch, C.; Leo, A.; Hoekman, D. Exploring QSAR - Hydrophobic, Electronic, and Steric Constants. Washington, DC: American Chemical Society., 1995.

IARC (1983) Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Man. Geneva: World Health Organization, International Agency for Research on Cancer, 1972-PRESENT. (Multivolume work) V32.

IARC (1987) Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Man. Geneva: World Health Organization, International Agency for Research on Cancer, 1972-PRESENT. (Multivolume work) 58 (1987)

IUCLID Dataset for N-1,3-dimethylbutyl-N'-phenyl-p-phenylenediamine. European Chemicals Bureau. Year 2000 CD-Rom edition.

IUCLID Dataset for N-isopropyl-N'-phenyl-p-phenylenediamine. European Chemicals Bureau. Year 2000 CD-Rom edition.

Kroese, E.D.; Muller, J.J.A.; Mohn, G.R.; Dornant, P.M.; Wester, P.W. (2001) Tumorigenic effects in Wistar rats orally administered benzo[a]pyrene for two years (gavage studies). Implications for human cancer risks associated with oral exposure to polycyclic aromatic hydrocarbons. National Institute of Public Health and the Environment, RIVM report no. 658603 010, November 2001. Bilthoven

Lewis, R.J., Sr (Ed.) (1997). Hawley's Condensed Chemical Dictionary. 13th ed. New York, NY: John Wiley & Sons, Inc. 1997.

Lewis, R.J., Sr (Ed.). (1996) Sax's Dangerous Properties of Industrial Materials. Van Nostrand Reinhold, New York

Lide, D.R. (ed.) (1995). CRC Handbook of Chemistry and Physics. 76th ed. Boca Raton, FL: CRC Press Inc.

L. von Meyrinck, Process Oils for the Rubber Industry – Legal Basis and Assessment of Potential Carcinogenicity, Kautchuck Gummi Kunststoffe nr. 7/8 1996, s. 514

Mackay, D.; Shiu, W.Y. J CHEM ENG DATA 22: 399-402 (1977)

Mackison, F. W.; Stricoff, R. S. and Partridge, L. J. Jr. (eds.). NIOSH/OSHA - Occupational Health Guidelines for Chemical Hazards. DHHS(NIOSH) Publication No. 81-123 (3 VOLS). Washington, DC: U.S. Government Printing Office, Jan. 1981.1

Murray, J.J. *et al*; Can J Chem 52: 557-63 (1974)

Opinion of the Scientific Committee on Toxicity, Ecotoxicity and the Environment (CSTEE) on "Questions to the CSTEE relating to scientific evidence of risk to health and the environment from polycyclic aromatic

hydrocarbons in extender oils and tyres". European Commission, Directorate C _ C/ Risk Assessment. Document adopted by the CSTEED during the 40 th plenary meeting of 12–13 November 2004

Miljøstyrelsens vejledende liste for selvklassificering. Miljøstyrelsen 2001

Piat JJ; Environ Sci Technol 30: 751-60 (1996)

Rogge, W. F., Hildemann, L. M., Mazurek, M. A. and Cass, G. R. (1993) Sources of fine organic aerosol. 3. Road dust, tyre debris and organometallic brake lining dust: Roads as sources and sinks. Environmental Science and Technology **27** p 1892-1904

Rubber Handbook, SGF, 10. edition

SCF, 2002 Opinion of the Scientific Committee on Food on the risks to human health of Polycyclic Aromatic Hydrocarbons in food. SCF/CS/CNTM/PAH/29 Final, 4. December 2002. European Commission.

Stevens, M. W. *et al.*, (1981) Toxicologist 1, 58

Tamakawa, K. *et al.*; Eisei Kagaku 33: 66-70 (1987)

TDG, 2003, Technical Guidance Document on Risk Assessment, European Chemicals Bureau, Part 1, app. IVB

US EPA (2000) U.S. Environmental Protection Agency's Integrated Risk Information System (IRIS) on Pyrene (129-00-0) Available from: <http://www.epa.gov/ngispgm3/iris> on the Substance File List as of March 15, 2000

U.S. EPA. 1989. Mouse Oral Subchronic Toxicity of Pyrene. Study conducted by Toxicity Research Laboratories, Muskegon, MI for the Office of Solid Waste, Washington, DC.

U.S.EPA 1987. Heath Effects Assessment for Fluorenes. Prepared for the Office of Solid Waste and Emergency Response by the Environmental Criteria and Assessment Office, Office of Health and Environmental Assessment, Cincinnati, OH. ECAOCIN-OH68.

U.S. EPA. 1988. 13-Week mouse oral subchronic toxicity study. Prepared by Toxicity Research Laboratories, Ltd., Muskegon, Mi for the Office of Solid Waste, Washington, DC.

Wommelsdorff, R. Neue, Kennzeichnungsfrei Mineralölweichmacher, GAK 4 /1999, s. 282