# **European Union Summary Risk Assessment Report**

# **COAL-TAR PITCH, HIGH TEMPERATURE**

CAS No: 65996-93-2 EINECS No: 266-028-2

# **RISK ASSESSMENT**

GENERAL NOTE

This report contains different documents:

- **Environment** Version May 2008 (pages 55)

- Human Health Version April 2008 (pages 41)

# **COAL-TAR PITCH, HIGH TEMPERATURE**

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# SUMMARY RISK ASSESSMENT REPORT

Environment

Final report, May 2008

The Netherlands

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## PREFACE

This report provides a summary, with conclusions, of the risk assessment report of the substance COAL-TAR PITCH, high temperature that has been prepared by The Netherlands in the context of Council Regulation (EEC) No. 793/93 on the evaluation and control of existing substances.

For detailed information on the risk assessment principles and procedures followed, the underlying data and the literature references the reader is referred to the comprehensive Final Risk Assessment Report (Final RAR) that can be obtained from the European Chemicals Bureau<sup>1</sup>. The Final RAR should be used for citation purposes rather than this present Summary Report.

#### **Outline of the risk assessment**

Coal tar pitch, high temperature (CTPHT) possibly contains thousands of substances that may all be relevant for the receiving environment. It is however the Rapporteurs' opinion that the assessment should be focused on the risk of the emission of polycyclic aromatic hydrocarbons (PAHs) only, since this was the main reason to put CTPHT on the 3<sup>rd</sup> priority list. Moreover, based on the available information, it is only for the EPA 16 homocyclic PAHs that sufficient effect - and exposure data are available. It is for this reason that the risk assessment of CTPHT is restricted to this group of PAHs and regards them as representative for the total emission of PAH, accepting that the potential risk of CTPHT might be underestimated.

Since so many unintentional sources contribute to the total emission of PAHs into the environment, which by extension are not related to production and use of CTPHT, the risk assessment will only be focussed on the PAHs that are emitted by producers and the down stream users of CTPHT on a local scale. To put this emission into perspective, the calculated local concentrations have been related to the background levels measured in urban and rural areas.

<sup>&</sup>lt;sup>1</sup> European Chemicals Bureau – Existing Chemicals – http://ecb.jrc.it

# CONTENTS

1	GEI	VERAL SUBSTANCE INFORMATION	3
	1.1	IDENTIFICATION OF THE SUBSTANCE.	3
	1.2	PURITY/IMPURITIES, ADDITIVES	
	1.3	PHYSICO-CHEMICAL PROPERTIES	4
	1.4	CLASSIFICATION	8
2	GEI	VERAL INFORMATION ON EXPOSURE	9
3	EN	VIRONMENT	12
	3.1	ENVIRONMENTAL EXPOSURE	12
	3.2	EFFECTS ASSESSMENT	32
	3.3	RISK CHARACTERISATION         3.3.1 Aquatic compartment (incl. sediment)         3.3.1.1 Production         3.3.1.2 Industrial use/processing         3.3.1.3 Regional background in fresh and marine surface water (including sediment)         3.3.2 Sewage treatment plant         3.3.3 Terrestrial compartment         3.3.4 Production         3.3.5 Secondary poisoning	35 36 37 40 41 41 41 42 44 44 45
		<ul><li>3.3.6 PBT assessment</li></ul>	
4	HU	MAN HEALTH	48
5	RES	SULTS	49
	5.1	ENVIRONMENT	49
	5.2	HUMAN HEALTH	
		<ul> <li>r! Bookmark not defined.</li> <li>5.2.2 Human health (risks from physico-chemical properties)</li> <li>r! Bookmark not defined.</li> </ul>	

# TABLES

Table 1.1 PAH content in CTPHT (16 EPA PAH and other aromatic hydrocarbons). Method used is DIN 5	1920
for softening point and ISO 6998 for coking value	. 3
Table 1.2 Physico-chemical properties of CTPHT	. 4
Table 1.4. Physico-chemical properties of various PAHs	
Table 2.1 Use pattern for coal tar pitch. Sales in the EU in 2003.	. 9
Table 3.1. Ranking of PAH in different classes	. 13

Table 3.2. Suggested half-life classes of PAHs in various environmental compartments (Mackay et al., 199).	
Table 3.3 The log Koc for the 16 EPA PAHs based on the equation of Karickhoff et al. (1979)	
Table 3.4 Estimation of removal of the 16 EPA in STP according to EUSES 2.0	
Table 3.5 Local concentration during emission episode in surface water $(ng.l^{-1})$ for the production sites	
Table 3.6 Local concentration during emission episode in sediment ( $\mu g.kg_{dwt}^{-1}$ ) for the production sites	
Table 3.7 Local concentrations during emission episode in sea water, marine sediment, fresh water, and fre	
water sediment for ferro-alloy producing industry	. 17
Table 3.8 Local concentrations in water (fresh and marine) during the emission episode (ng.l <sup>-1</sup> ) for primary aluminium production and anode baking facilities.	. 19
Table 3.9 Local concentrations in sediment (fresh and marine) during the emission episode ( $ug kg_{dyt}^{-1}$ ) for	
primary aluminium production and anode baking. Table 3.10 Local concentrations in agricultural soil averaged over 30 days (ng.kg <sub>dwt</sub> <sup>-1</sup> ) for the production sit	. 20
Table 3.10 Local concentrations in agricultural soil averaged over 30 days (ng.kg <sub>dwt</sub> <sup>-1</sup> ) for the production sin	tes. 22
Table 3.11 Local concentrations (total) in grassland averaged over 180 days (ng.kg <sub>dwt</sub> <sup>-1</sup> ) for the production	sites.22
Table 3.12 Local concentrations in agricultural soil over 30 days (ng.kg <sub>dwt</sub> <sup>-1</sup> ) for primary aluminium produc	tion
and anode baking.	. 24
and anode baking	and
anode baking	. 26
anode baking. Table 3.14 Local concentrations in agricultural soil and grassland (µg.kg <sub>wwt</sub> <sup>-1</sup> ) for the ferro-alloy and graphi	te
production industry	27
Table 3.15 Local concentrations in air at 100 m from the point source (ng.m <sup>-3</sup> ) at the production sites	. 28
Table 3.16 Local concentrations in air, at 100 m from point source (ng.m <sup>-3</sup> ) for ferro-alloy and graphite	
production industry	. 29
Table 3.17 Local concentrations in air (ng.m <sup>-3</sup> ) for the primary aluminium production and anode baking	
facilities	. 30
Table 3.18 Concentrations STP effluent (ng.1 <sup>-1</sup> ) for the relevant production sites.	
Table 3.19. The PNEC for the various PAHs for fresh and marine water organisms	
* For benzo(b)fluoranthene the PNEC is the same as for benzo(k)fluoranthene after read-across with this	
compound	. 33
Table 3.20. The PNEC for the various PAHs for fresh and marine sediment organisms	
Table 3.21. The PNEC for the various PAHs for soil organisms	
Table 3.22 Clocal/PNEC for surface water and marine water (*) for the different CTPHT production sites	
Table 3.23 Clocal/PNEC for sediment for the different CTPHT production sites.	
Table 3.24 Clocal/PNEC for water and sediment for the ferro-alloy industry.	
Table 3.25 CLocal/PNEC in water (marine and fresh) for primary aluminium production and anode baking	
Table 3.26 CLocal/PNEC for sediment (marine and fresh) at primary aluminium production and anode bak	
sites.	
Table 3.27 Ratio between the COMMPS monitoring data and PNEC for surfacewater and sediment organi	
Table 3.28 Ratio between the OSPAR monitoring data and PNEC for marine water and sediment organism	
Table 3.29 Clocal/PNEC for agricultural soil for the different CTPHT production sites.	
Table 3.30 Clocal/PNEC for agricultural soil and grassland for the ferro-alloy and graphite industry.	
Table 3.31 CLocal/PNEC agricultural soil at primary aluminium production and anode baking sites	
Table 3.32 Ratio between the background concentration in different soils presented by Wilcke (2000) PNE	
soil organism	

# 1 GENERAL SUBSTANCE INFORMATION

#### 1.1 IDENTIFICATION OF THE SUBSTANCE

CAS Number:65996-32-2EINECS Number:266-028-2IUPAC Name:Coal Tar Pitch, High temperature

#### 1.2 PURITY/IMPURITIES, ADDITIVES

The content of the sixteen EPA PAHs in pitch used for impregnation and binding is presented in Table 1.1. Most relevant for the risk assessment is the composition for binder pitch, as it is the main source for the production of anodes and electrodes.

	Impregnation Pitch	Binder Pitch
	[mg/kg]	[mg/kg]
Aromatic hydrocarbons		
Acenaphthene	390	432
Fluorene	144	472
2-Methylfluorene	50	112
1-Methylfluorene	n.d.	61
Phenanthrene	3874	6299
Anthracene	737	1311
Cyclopenta[def]phenanthrene	918	821
Fluoranthene	17389	10789
Acephenanthrylene	828	386
Pyrene	14849	9449
Benzo(a)fluorene	4509	1974
Benzo(b)fluorene	4306	2456
Benz(a)anthracene	15008	7715
Chrysene	14041	8053
Benzo(b)fluoranthene	17408	12131
Benzo(k)fluoranthene	8704	6065
Benzo[e]pyrene	11891	8976
Benzo(a)pyrene	12924	10021
Perylene	5014	3167
Dibenz(a,h)anthracene	2209	1749
Indeno(1,2,3-cd)pyrene	11106	9061
Benzo(ghi)perylene	9945	8664
Anthantrene	4581	3464
Tar acids / phenolics	n.d.	n.d.
Tar bases / nitrogen-containing heterocycles		
Acridine	242	264
Carbazole	1556	1664
Sulfur-containing heterocycles		

Table 1.1 PAH content in CTPHT (16 EPA PAH and other aromatic hydrocarbons). Method used is DIN 51920 for softening point and ISO 6998 for coking value

	Impregnation Pitch	Binder Pitch
	[mg/kg]	[mg/kg]
Dibenzothiophene	269	438
Oxygen-containing heterocycles / furans		
Dibenzofuran	n.d.	215
Total	162.892	116.209

#### **1.3 PHYSICO-CHEMICAL PROPERTIES**

The physico-chemical characteristics of pitch are presented in Table 1.2.

Table 1.2 Physico-chemical properties of CTPHT						
Value	Comment / Reference					
black solid						
65 - 150 °C	softening range; CCSG 2006*					
>360 °C	at 1013 hPa					
1.15 - 1.40	at 20 °C; ASTM D 71; CCSG					
	2006*					
< 0.1	at 20 °C;					
< 10	at 200 °C; OECD 104; CCSG					
	2006*					
~0.040	16 EPA PAHs, at a loading of					
	10 g/L at 22 °C; RÜTGERS					
	VFT 1999					
-	not applicable					
>250	ISO 2719; CCSG 2006*					
>450	ignition point at 1013 hPa; DIN					
	51794;					
	CCSG 2006*					
not explosive	CCSG 2006*					
not oxidizing	CCSG 2006*					
	Value black solid 65 - 150 °C >360 °C 1.15 - 1.40 < 0.1 < 10 ~0.040  >250 >450 not explosive					

Table 1.2 Physico-chemical properties of CTPHT

\*CCSG 2006: Internal communication, Coal Chemicals Sector Group/CEFIC 2006

#### Water solubility

Within the scope of a comprehensive analytical programme on the availability of PAH from pitch in water (RÜTGERS VFT 1999), a column containing 10 g of finely powdered pitch (20 - 200  $\mu$ m) was force-perculated by 1.1 l of tap water (water recycling for 1 wk). Each experimental period was terminated by withdrawal of 1 l of the extract and renewal of the volume by fresh-water exchange of 1 l each. After the first run, 36.5  $\mu$ g PAH/l were found; after 15 cycles, the PAH decreased to 11.8  $\mu$ g/l, and after 39 cycles to 0.9  $\mu$ g/l. The first water-soluble fraction was dominated by the presence of acenaphthene, phenanthrene, fluoranthene, and pyrene, followed by naphthalene and fluorene. All other PAHs were

distinctly below 1  $\mu$ g/l. The total cumulative amount of water-extractable EPA PAHs amounted to approx. 370  $\mu$ g/10g (= ~0.004 %).

Substance	CAS nr	Molecular	Molecular weight	Melting point	Boiling point	Water solubility	Log Kow	Vapour pressure	Density	Henry's constant
		formula	(g.mol <sup>-1</sup> )	(°C)	(°C)	(µg.l-¹)*	(-)	(Pa at 25 °C)	(kg.l <sup>-1</sup> )_	(Pa m³/mol at 25 °C)
Naphthalene	91-20-3	C <sub>10</sub> H <sub>8</sub>	128.2	81	217.9°	31900ª	3.34°	11.2 <sup>g</sup>	1.154	50 <sup>1</sup>
Acenaphthene	208-96-8	C <sub>12</sub> H <sub>8</sub>	154.2	96	278	3910 <sup>₅</sup>	4.00 <sup>e</sup>	3.3 x 10 <sup>-1h</sup>	0.899	14.3 <sup>i</sup>
Acenaphthylene	91-20-3	C <sub>12</sub> H <sub>10</sub>	150.2	92	279	16100 <sup>b</sup>	3.62 <sup>f</sup>	4.8 x 10 <sup>-1i</sup>	1.024	11.5 <sup>,</sup>
Fluorene	86-73-7	C <sub>13</sub> H <sub>10</sub>	166.2	115-116	295°	1800ª	4.22 <sup>e</sup>	8.3 x 10 <sup>-2i</sup>	1.203	8.5 <sup>i</sup>
Anthracene	120-12-7	C <sub>14</sub> H <sub>10</sub>	178.2	216.4	342°	47a	4.68 <sup>d</sup>	9.4 x 10 <sup>-4i</sup>	1.283	4.3
Phenanthrene	85-01-8	C <sub>14</sub> H <sub>10</sub>	178.2	100.5	340	974ª	4.57 <sup>d</sup>	2.6 x 10 <sup>-2i</sup>	0.980	3.71
Fluoranthene	206-44-0	C <sub>16</sub> H <sub>10</sub>	202.3	108.8	375	200ª	5.20 <sup>d</sup>	1.2 x 10 <sup>-3h</sup>	1.252	1.1º
Pyrene	129-00-0	C <sub>16</sub> H <sub>10</sub>	202.3	156	360	125ª	4.98 <sup>e</sup>	1.0 x 10 <sup>-3i</sup>	1.271	1.4 <sup>n</sup>
Benzo(a)anthracene	56-55-3	C18H12	228.3	160.7	435	10.2ª	5.91d	7.6 x 10 <sup>-6i</sup>	1.226	0.81 <sup>p</sup>
Chrysene	218-01-9	C18H12	228.3	253.8	448	1.65ª	5.81 <sup>d</sup>	5.7 x 10 <sup>-7j</sup>	1.274	0.079 <sup>q</sup>
Benzo(a)pyrene	50-32-8	C <sub>20</sub> H <sub>12</sub>	252.3	175	496	1.54ª	6.13 <sup>d</sup>	7.3 x 10 <sup>-7j</sup>	1.35	0.034° <sup>(20 °C)</sup>
Benzo(b)fluoranthene	205-99-2	C <sub>20</sub> H <sub>12</sub>	252.3	168.3	481	1.28ª	6.12 <sup>f</sup>	3.3 x 10 <sup>-6k</sup>	-	0.051° <sup>(20 °C)</sup>
Benzo(k)fluoranthene	207-08-9	C <sub>20</sub> H <sub>12</sub>	252.3	217	480	0.93ª	6.11 <sup>d</sup>	1.3 x 10 <sup>-7k</sup>	-	0.043° <sup>(20 °C)</sup>
Benzo(ghi)perylene	191-24-2	C <sub>22</sub> H <sub>12</sub>	276.3	277	545 <sup>i</sup>	0.14ª	6.22 <sup>d</sup>	1.4 x 10 <sup>-8 j</sup>	1.329	0.027° <sup>(20 °C)</sup>
Dibenzo(a,h)anthracene	53-70-3	C <sub>22</sub> H <sub>14</sub>	278.4	266.6	524	0.82 <sup>b</sup>	6.50e	3.7 x 10 <sup>-10j</sup>	1.282	1.3.10 <sup>-4q</sup>
Indeno(1,2,3-cd)pyrene	193-39-5	C22H12	276.3	163.6	536	0.1*	6.58 <sup>f</sup>	1.7 x 10 <sup>-8k</sup>	-	0.046 <sup>q</sup>

Table 1.4. Physico-chemical properties of various PAHs

The data presented in the table were taken form Mackay et al. (1992) The selected values for water solubility were preferably based on generated column methods (a) and in absent on shakeflask (b) using geometric means (\* for indeno(1,2,3-cd)pyrene no data were available, a default value of 0.1  $\mu$ g/l was used). The selected values for log Kow were preferably based on slowstirring/generator column (c) or slow-stirring methods (d) using average values. If absent the log Kow values were based on the shake-flask method (e), or in absent of data calculated using ClogP model (f). The selected values for vapour pressure were based on manometry/gas saturation (g), gas saturation (h), gas saturation/effusion (i), effusion method (j) using geometric means or estimated using EPIWIN (k). The selected values for the Henry's constant were based on batch/gas stripping/wetted-wall column (l), batch stripping/wetted-wall column (m), batch/gas stripping (n), gas stripping (o), batch column (p) using geometric means or when no data were available, constants were calculated using EUSES 2.0 (q).

#### 1.4 CLASSIFICATION

Proposed Classification and Labelling for the Environment:

Symbols: N

R-phrases: R50/53

S-phrases: S60, 61

CTPHT is a complex mixture containing many compounds, such as homo- and heterocyclic aromatic hydrocarbons. As a consequence, it is very difficult to classify CTPHT on the basis of the individual compounds. In addition, not all the substances can be analyzed when diluted in water. Furthermore, the different CTPHT components influence each others solubility in the water phase and consequently the composition in the water phase will not be the same at different loadings. Therefore, the WAF approach is considered most appropriate to classify CTPHT, as recommended for oil products and products such as creosote in the OECD Guidance document on aquatic toxicity testing of difficult substances and mixtures (series on testing and assessment Number 23). It was however concluded that limited data is available on the preparation and aquatic toxicity testing of WAFs of CTPHT. Hence, it proved to be impossible to draw any definitive conclusions on the aquatic classification and labelling of CTPHT taking the preferred WAF approach. Therefore, it was decided to base the aquatic classification and labelling of CTPHT upon the rules laid down in the Dangerous Preparations Directive (DPD) (1999/45/EEC), which is the first choice as a suitable alternative in this case. CTPHT is considered as a 'preparation' in this perspective. In the last Adaptation to Technical Progress of the DPD (2006/8/EC) concentration limits are provided for classification of preparations containing substances that are very toxic to the aquatic environment (N;R50/53). The 16 individual EPA PAHs were analysed with respect to their acute aquatic effects data and the lowest available EC50 or LC50 was chosen as a point of departure for aquatic hazard classification.

# GENERAL INFORMATION ON EXPOSURE

### Production

2

Within the European Union, high temperature coal tar pitch is produced by ten companies at eleven sites in nine countries. The total European Union production capacity in 2004 was 1,127,000 tonnes. The actual production output of coal tar pitch in that year was about 817,800 tonnes. Import from outside the EU was reported to be about 91,600 tonnes per year and export was about 355,600 tonnes per year. The total consumption of coal tar pitch in the EU from these figures is estimated to be about 554,000 tonnes per year

### Uses

Coal tar pitch is mainly used as a binding agent in the production of carbon electrodes, anodes and Søderberg electrodes for instance for the aluminium industry. It is also used as a binding agent for refractories, clay pigeons, active carbon, coal briquetting, road construction and roofing. Furthermore small quantities are used for heavy duty corrosion protection, see Table 2.1

Application	Industry category <sup>1)</sup>	Use category <sup>2)</sup>	Quantity (tonnes/year)	Percentage of total sales
Anodes	8	2	322 500	71.3
Electrodes	8	2	81 400	18.0
Refractories	0	2	22 500	5.0
Road construction	16	2	800	0.2
Active carbon	0	2	7 900	1.7
Heavy duty corrosion protection	14	2/39	4 700	1.0
Roofing	16	2	3 200	0.7
Clay pigeons	0	2	5 800	1.3
Coal briquetting	9	2	3 700	0.9
Total			452 400	100

 industrial category 0 is others, industrial category 8 metal extraction, refining and processing industry, industrial category 9 is mineral oil and fuel industry, industrial category 14 is paints, lacquers and varnishes industry, industrial category 16 is engineering industries: civil and mechanical

2) use category 2 is adhesives and binding agents and use category 39 is non-agricultural biocides

The exposure assessment has been focussed on the emission of PAHs on a local scale for production of coal tar pitch and the main applications, primarily because lower emissions for the other sources are expected. Moreover, the amounts of coal tar pitch used for roofing and road paving decrease as it is replaced by petroleum pitch on account of the lower PAH content (worker hygiene). Some manufacturers claim to produce "environmentally" friendly clay pigeons by applying petroleum pitch in order to meet the EEC environmental protection directives, or apply no binder at all.

The emission of PAHs at coke ovens are not considered because coal tar is produced at this process. Coal tar is used as a feedstock for the production of coal tar pitch and therefore the coke ovens are not part of the life cycle of coal tar pitch which actually starts at the production stage of coal tar pitch.

With respect to the main applications of coal tar pitch, the following point sources are considered:

- Anode production
- Aluminium production applying prebakes (with and without) anode baking.
- Aluminium production using Søderberg technology
- Graphite electrode production
- Production of steel, silicon, etc., applying electric arc furnaces with Søderberg electrodes.

#### <u>Trends</u>

The future consumption of pitches depends not only on human health risks and environmental hazards but also on economics due to progress of science and technology.

Since more than ten years a new technology has been developed at benchscale based on inert anodes to replace CTPHT-bound carbonated anodes but this technology is still immature and costly. Therefore, it can be expected that CTPHT will be used for more than decades in the primary aluminium smelters.

For refractories, the pitch industry now proposes pitches with a higher softening point resulting in a benzo(a)pyrene (B(a)P) content of 300 ppm compared to currents levels in pitches ranging up to 20,000 ppm.

Most of the European countries have banned CTPHT in the road construction by law or agreement between trade unions and road building companies. In fact only very particular applications such as kerosene proof coatings for parking lots, airfields and taxi ways still use pitch as an emulsion. This market is decreasing and represents only 200 tonnes of pitch per year.

Pitch bound active carbons are more and more produced outside the EU and are anyway processed in closed vessels where the pitch is pyrolyzed to pure carbon with controlled emissions.

Roofing and corrosion protection with CTPHT-based products are declining dramatically and a phasing out of these artefacts is predicted in the next few years. However, information provided by industry contradicts the assumption that the use of CTPHT in heavy duty corrosion protection has been reduced significantly and that in the short term this application will be phased out.

The use of pitch bound coal briquettes is forbidden in some countries (Germany and Scandinavia). This market is also linked to dedicated and captive users in mining countries (France and Belgium) where retired miners have rights on solid fuels provided by the former state owned companies. Capacities of 2,000 ktonnes/year of briquettes existing in the early 80's in Europe are now decreased to 150 ktonnes/year, also using more environmental

friendly binders like starch and molasses. Also here a full phasing out of the use of CTPHT can be expected in the next few years. However, recent information provided by industry contradicts the assumption that the use of CTPHT in coal briquetting will be phased out.

Clay pigeons manufacturers, claiming environmental protection, displaced carbopitch by petrochemical binders for more than 80% of their production and the former clay pigeons being exported outside the European Union. However, information provided by industry contradicts the assumption that the use of CTPHT in clay pigeons has been reduced significantly and that in the short term this application will be phased out.

In summary, the pitch market, decreasing in Europe for economical reasons, will remain only for electrodes, anodes and graphite artefacts



## **3 ENVIRONMENT**

#### 3.1 ENVIRONMENTAL EXPOSURE

#### Environmental releases

PAH may enter the environment from both natural (forest fires, volcanoes) and anthropogenic sources. The latter includes production and use of coal tar pitch itself, but PAH is also formed as a by-product during other industrial processes (e.g. coke plants). The emissions of PAH from other sources are mainly characterised by combustion processes and by particular industrial processes using PAH-containing compounds such as coal, crude oil, creosote, coal-tar or bitumen. Important non-industrial sources of PAH emissions are the combustion of solid fuels, like wood, peat and coal and the use of all automotive fuels but in particular diesel oil. Natural sources of PAH include the accidental burning of forests, woodland, heath etc. Another natural PAH source is volcanic activity, but no data is available regarding these emissions. A recent overview of the PAH emissions to air in the EU is not available and the data available is only based on a few EU countries. Nevertheless, it seems that the largest emission sources to air are non-industrial, like domestic combustion, the use of coal tar-based products and road transport. For the emission sources of PAH. Compared to (industrial) point source data, the emission via atmospheric deposition seems more important.

Site specific data was available for the CTPHT producing companies, anode production and primary aluminium production applying Søderberg and prebake anodes. The risk assessment for the other applications of CTPHT is based on generic (realistic worst case) scenarios. For most of the production sites complete emission profiles for all EPA 16 PAHs were provided for both water and air. If absent, the emission rates were related to sites with comparable operational management. With respect to the application of CTPHT, emission rates were either provided by industry (production of anodes and electrodes, aluminium production) or obtained from literature. For all applications the information was limited to only a number of PAHs, not specified PAH totals or to B(a)P only. Therefore, emission rates for the rest of the 16 EPA PAHs were determined using typical profile of the 16 EPA PAHs for the process of concern. For the anode and graphite production and aluminium production based on Søderberg technology these profiles were provided by industry, if needed completed with information found in literature. For production of ferro-alloys profiles were obtained from open literature.

Coal tar pitch is produced from coal tar at coal tar processing facilities. At these facilities many other products, essentially different kinds of oils are produced. All these different production steps contributed to the total release of PAHs by the facility. As coal tar pitch is the final product, which remains after several distillation steps it is difficult to consider it separate from all the other production steps in coal tar processing. Therefore it should be noted that the reported figures do not concern the production of coal tar pitch per se, but the whole process of coal tar processing.

### Environmental fate

## Degradation

A detailed description of the biodegradation of PAHs is given in the RAR. On the basis of model calculations, Mackay *et al.* (1992) ranked the 16 EPA PAH according to their persistence in, water, soil and sediment in different classes (Table 3.1) which correspond to a specific half-live in these compartments (Table 3.2). For the risk assessment these values are used.

Compound	Water	Soil	Sediment
Naphthalene	3	5	6
Acenaphthene <sup>*)</sup>	3	5	6
Acenaphthylene <sup>*)</sup>	3	5	6
Fluorene	4	6	7
Anthracene	4	6	7
Phenanthrene	4	6	7
Fluoranthene	4	7	8
Pyrene	5	7	8
Benzo(a)anthracene	5	7	8
Chrysene	5	7	8
Benzo(a)pyrene	5	7	8
Benzo(b)fluoranthene <sup>*)</sup>	5	7	8
Benzo(k)fluoranthene	5	7	8
Benzo(ghi)perylene*)	5	7	8
Dibenzo(a,h)anthracene	5	7	8
Indeno(1,2,3-cd)pyrene	5	7	8

Table 3.1. Ranking of PAH in different classes

Table 3.2. Suggested half-life classes of FARS in various environmental compartments (mackay et al., 1332).	Table 3.2. Suggested half-life classes of PAHs in various environmental compartment	s (Mackay et al., 1992).
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Class	Half-life (h)				
	Mean		Range		
1	17		10-30		
2	55		30-100		
3	170		100-300		
4	550		300-1000		
5	1700		1000-3000 (42 -125 days)		
6	5500		3000-10000 (125 - 420 days)		
7	17000		10000-30000 (420 – 1250 days)		
8	55000		> 30000		

#### Adsorption

Many studies have been performed to determine the organic carbon-water partition coefficient  $(K_{oc})$  of aromatic hydrocarbons, both monoaromatic and polycylic compounds. A well known relationship between  $K_{oc}$  and  $K_{ow}$  is the following equation of Karickhoff *et al.* (1979) based on experiments with 10 compounds of which 8 are non-halogenated aromatic compounds, mostly PAHs, in three sediments.

The last years, more evidence becomes available that sorption of organic chemicals into soils and sediments can be better described by a two-phase model. Research in this field is still ongoing. To be able to use this two-phase sorption model, it is important to know the fraction of black carbon and the fraction of amorphous organic carbon. It should also be noted that the quantification of carbonaceous materials still suffers from operational shortcomings (Cornelissen et al., 2005). Thus, although the two-phase model seems to be an improvement over the one-phase model, in practice it can only be used when black carbon is measured. This is very site-specific. Moreover, care should be given to the fact that when partition coefficients for the 'pure' OC phases are combined, this exceeds the actual, experimentally measured sorption. Thus,  $K_{BC}$  values for pure BC are not necessarily valid under in situ conditions, probably due to attenuation effects by DOM molecules (Koelmans et al., 2006). For the purpose of the RAR the one-phase model as proposed by Karickhoff et al. (1979), which incorporates field-derived sediments with mixtures of all types of organic carbon (including both black carbon and amorphous organic carbon), is used to derive 'general'.

Koc values for the different PAHs (see Table 3.3).

Compound	Log Kow	Log Koc
Naphthalene	3.34	3.13
Acenaphthene	4.00	3.79
Acenaphthylene	3.62	3.41
Fluorene	4.22	4.01
Anthracene	4.68	4.47
Phenanthrene	4.57	4.36
Fluoranthene	5.20	4.99
Pyrene	4.98	4.77
Benzo(a)anthracene	5.91	5.70
Chrysene	5.81	5.60
Benzo(a)pyrene	6.13	5.92
Benzo(b)fluoranthene	6.12	5.92
Benzo(k)fluoranthene	6.11	5.90
Benzo(ghi)perylene	6.22	6.01
Dibenzo(a,h)anthracene	6.50	6.29
Indeno(1,2,3-cd)pyrene	6.58	6.37

Table 3.3 The log Koc for the 16 EPA PAHs based on the equation of Karickhoff et al. (	1979)

#### Factors influencing the sorption and bioavailability of PAHs

Several studies indicate that bioavailability decreases with increasing residence time. The extent of aging seems to be dependent on the organic carbon content. As no ageing effect were found at an organic carbon content of standard soil (2%) and the fact that this phenomenon is insufficiently quantifiable, aging is not considered in the risk assessment. The adsorption and desorption of PAHs to carbonaceous materials can show a high degree of variation, likely as a result of the origin of the organic carbon to which the PAHs are associated. Consequently, strong sorbing carbonaceous materials may limit the bioavailability of PAHs to soil and sediment species. However, the implication for risk assessment of coal tar pitch is as yet difficult to interpret. In addition, the effect of the sorption on carbonaceous materials on uptake of PAHs by biota is still unclear. Where some studies show that uptake of PAHs is significantly decreased in the presence of carbonaceous materials, others show that this effect is not present or negligible.

Based on these considerations and the uncertainties on this topic, it was decided not to include a correction for binding to soot-like materials in the risk assessment.

#### Precipitation

This information on precipitation is in conformity with the estimated distribution using EUSES 2.0, which was used for the current risk assessment

#### Distribution in sewage treatment plants

The distribution of the 16 EPA PAHs in sewage treatment plants has been calculated using the model SIMPLETREAT integrated in EUSES (EC, 2004) based on the Koc values and the Henry's low constants presented in Table 3.3 and Table 1.6, respectively. They are presented as an example in Table 3.4.

nr	PAH compound	% to air	% to water*	% to sludge	% degraded	% removal
1	Naphthalene	38.7	47.2	12.6	1.5	52.8
2	Acenaphthene	11.0	47.4	40.3	1.3	52.6
3	Acenaphthylene	12.4	62.8	22.9	1.8	37.2
4	Fluorene	5.7	41.6	52	0.3	58.4
5	Anthracene	1.5	25.2	73.1	0.2	74.8
6	Phenanthrene	1.6	29	69.2	0.2	71.0
7	Fluoranthene	0.1	14.3	85.5	0.1	85.7
8	Pyrene	0.3	18	81.7	0.0	82.0
9	Benzo(a)anthracene	0.0	9.3	90.7	0.0	90.7
10	Chrysene	0.0	9.6	90.3	0.0	90.4
11	Benzo(a)pyrene	0.0	8.8	91.2	0.0	91.2
12	Benzo(b)fluoranthene	0.0	8.8	91.2	0.0	91.2
13	Benzo(k)fluoranthene	0.0	8.8	91.2	0.0	91.2
14	Benzo(ghi)perylene	0.0	8.7	91.3	0.0	91.3
15	Dibenzo[a.h]anthracene	0.0	8.3	91.7	0.0	91.7
16	Indeno(1,2,3-cd)pyrene	0.0	8.3	91.7	0.0	91.7

Table 3.4 Estimation of removal of the 16 EPA in STP according to EUSES 2.0

\* % to water is equal to parameter Fstp used in section 3.1.5.1

#### **Bioaccumulation**

An evaluation of the available data on bioaccumulation of PAHs in fish and mussels has been made. For fish the following reliable range of BCF values were found: Naphthalene: 302 - 999; Acenaphthene: 387; Fluorene: 1050 - 3500; Anthracene: 900 - 6760; Phenanthrene: 700 - 6760; Fluoranthene: 3388 - 14836; Pyrene: 50 - 11300; Benzo(a)-anthracene: 200 - 265; Benzo(a)pyrene: 608.

For mussels the following reliable range of BCF values were found: Anthracene: 345 - 380189; Phenanthrene: 1240 - 1280; Fluoranthene: 5920 - 4120 ; Pyrene: 1054 - 43000; Benzo(a)-anthracene: 41000 - 142000.

It was concluded that the EP can be considered to estimate the maximum amount that can be taken up by earthworms, but the total variation in body residues and uptake kinetics may be driven by differences in assimilation efficiencies between soils, as well as differences in desorption kinetics of PAHs from soils. The BCF values calculated based on the equation presented are therefore considered as a reasonable worst case for earthworms

There are several indications that biomagnification of PAHs does not occur in both the aquatic and terrestrial environment, partly being the result of the relatively high rates of

metabolism and excretion of PAHs in vertebrates and some invertebrates. Nevertheless, species from the lower trophic levels that are not able to effectively metabolize these compounds may exhibit food web transfer.

#### Environmental concentrations

#### Water compartment

In view of the strong contribution of the unintentional sources to the regional background concentration, it was decided to present Clocal and PEC regional separately to get a better understanding of the additional risk that is caused by the emission sources under investigation. As sufficient monitoring data are available no separate calculation of the regional PECs had been performed. Since the different PAH emission sources are already mapped by several authorities it is not expected that a comparison between calculated regional PECs and monitoring data would elucidate that a significant emission source is overlooked.

#### Production

The local concentration in surface water and sediment for the different production sites are given in Table 3.5 and Table 3.6, respectively. For all sites, except site 3 and 5, site specific information on river flow is available. For these sites the dilution factor is set accordingly. For site 3 and 5 de default dilution factor as recommended in the EU TGD (2003) is applied: 10 for fresh water and 100 for marine water. When the reported on-site emissions are discharged to off-site wastewater treatment facilities (STP) the STP-model is used in the calculations with the appropriate effluent flow of the off-site STP (site 1, 3, 5 and 7).

Substance/Site	1*	3**	4*	5*	6*	7*	8*	9*
Naphthalene	0.0045	0.27	0.7	2.1	0.68	0.037	2.9	1.0
Acenaphthene	0.00086	0.03	0.4	0.72	0.35	0.0081	2.5	0.5
Acenaphthylene	n.d.	0.07	1.6	3.7	0.046	0.010	2.3	0.5
Fluorene	0.0006	0.03	0.4	0.69	0.19	0.015	0.3	0.5
Anthracene	0.00011	0.05	0.7	0.81	0.22	0.0045	0.1	0.5
Phenanthrene	0.0010	0.03	1.1	0.016	0.58	0.069	0.4	0.5
Fluoranthene	0.00034	0.02	5.0	0.25	0.49	0.021	0.5	0.4
Pyrene	0.0019	0.08	3.9	0.22	0.31	0.024	0.6	0.5
Benzo(a)anthracene	0.000024	0.004	2.6	0.024	0.045	0.0043	0.1	0.6
Chrysene	0.000027	0.005	2.4	0.0034	0.046	0.0048	0.1	0.6
Benzo(a)pyrene	0.000017	0.006	7.6	0.0022	0.041	0.0031	0.0	0.9
Benzo(b)fluoranthene	0.000018	0.003	12.0	0.0023	0.031	0.0048	0.0	0.5
Benzo(k)fluoranthene	0.000018	0.003	3.8	0.0023	0.028	0.0016	0.0	0.5
Benzo(ghi)perylene	0.000015	0.002	4.2	0.0019	0.018	0.0023	0.0	0.8
Dibenzo(a,h)anthracene	0.000009	0.0	0.8	0.0012	0.014	0.00037	0.0	0.5
Indeno(1,2,3-cd)pyrene	0.000008	0.001	2.6	0.0010	0.011	0.0015	0.0	0.5

Table 3.5 Local concentration during emission episode in surface water (ng.I-1) for the production sites.

\*) concentration in fresh water; \*\*) concentration in marine water

Substance/Site	1*	3**	4*	5*	6*	7*	8*	9*
Naphthalene	0.00064	0.0003	0.10	0.83	0.10	0.0060	0.45	0.14
Acenaphthene	0.00055	0.022	0.27	1.2	0.23	0.0055	1.7	0.31
Acenaphthylene	n.d.	0.020	0.46	2.7	0.013	0.0029	0.64	0.13
Fluorene	0.00060	0.035	0.44	2.0	0.21	0.017	0.35	0.51
Anthracene	0.00033	0.19	2.4	6.9	0.69	0.015	0.31	1.4
Phenanthrene	0.0024	0.065	2.8	0.10	1.4	0.17	1.1	1.1
Fluoranthene	0.0034	0.26	55	6.9	5.1	0.23	5.1	4.3
Pyrene	0.012	0.53	26	3.7	2.0	0.16	3.9	2.7
Benzo(a)anthracene	0.0012	0.23	147	3.5	2.4	0.23	6.4	29
Chrysene	0.0011	0.21	110	0.38	2.0	0.21	4.6	25
Benzo(a)pyrene	0.0015	0.27	736	0.51	3.7	0.29	2.8	78
Benzo(b)fluoranthene	0.0015	0.23	1104	0.51	2.7	0.43	2.9	38
Benzo(k)fluoranthene	0.0015	0.23	345	0.51	2.3	0.14	2.9	38
Benzo(ghi)perylene	0.0016	0.30	506	0.55	2.0	0.26	2.0	83
Dibenzo(a,h)anthracene	0.0019	0.36	166	0.64	2.9	0.078	1.5	101
Indeno(1,2,3-cd)pyrene	0.0020	0.37	690	0.69	2.8	0.38	1.7	106

Table 3.6 Local concentration during emission episode in sediment (µg.kgdwt<sup>-1</sup>) for the production sites.

\*) concentration in freshwater sediment; \*\*) concentration in marine sediment

#### Industrial/professional use

With respect to the industrial uses considered the emissions are specified in the fraction dissolved and bound to particles. Based on the considerations given above and the uncertainties on this topic, it was decided not to include a correction for binding to soot-like materials in the current risk assessment. Therefore, the calculation of the concentration in surface water and sediment will be based on the total concentration in effluent and the partitioning based on the coefficients presented above.

The concentration in sea/fresh water and marine/fresh water sediment for the Ferro-alloy production plants is given in Table 3.7. As mentioned in section 3.1.3.2.2 the release of PAHs from graphite is considered negligible. For primary aluminium production and anode baking facilities these are presented in Table 3.8 and Table 3.9, respectively.

Table 3.7 Local concentrations during emission episode in sea water, marine sediment, fresh water, and fresh water
sediment for ferro-alloy producing industry.

Substance	Sea water (ng.l <sup>-1</sup> )	Marine sediment (µg.kgdwt <sup>-1</sup> )				
Naphthalene	0.5	0.1				
Acenaphthene	2.8	1.7				
Acenaphthylene	0.5	0.1				
Fluorene	1.6	1.7				

Substance	Sea water (ng.I <sup>-1</sup> )	Marine sediment (µg.kgdwt <sup>-1</sup> )
Anthracene	33	10.0
Phenanthrene	18.8	42.0
Fluoranthene	27.5	266.5
Pyrene	17.4	107.2
Benzo(a)anthracene	2.8	140.5
Chrysene	5.9	240.5
Benzo(a)pyrene	1.0	79.7
Benzo(b)fluoranthene	1.9	153.5
Benzo(k)fluoranthene	NA	NA
Benzo(ghi)perylene	0.4	42.0
Dibenzo(a,h)anthracene	0.1	21.7
Indeno(1,2,3-cd)pyrene	0.2	53.6

Ferro-alloy: Ferro-alloy production (including paste preparation)

Use category	Site	Naphthalene	Acenaphthene	Acenaphthylene	Fluorene	Anthracene	Phenanthrene	Fluoranthene	Pyrene	Benz(a)anthracene	Chrysene	Benzo(a)pyrene	Benzo(b)fluoranthene	Benzo(k)fluoranthene	Benzo(ghi)perylene	Dibenzo(a,h)anthracene	Indeno(1,2,3-cd)pyrene
VSS II	S1			5.8E+00		In the second			Loop and so house have								2.2E+00
	S3	1.7E+00	7.2E+00	1.7E+00	4.5E+00	6.0E+00	5.5E+01	7.6E+01	4.8E+01	8.2E+00	1.6E+01	2.5E+00	7.6E+00		1.1E+00	3.0E-01	6.4E-01
	S4			1.8E+02				1									6.6E+01
				Ziminipipipipi	10 100 100 100					2			NE	NE	NE	NE	NE
VSS I			1000			A Verse foot of too loop							NE	NE	NE	NE	NE
	20													NE	NE	NE	NE
PB+Anode I				1.0E+01			Terror and a second control to								4.0E+00	3.4E+00	3.0E+00
PB+Anode I				1.6E+01													4.7E+00
PB+Anode I	-							4	NE		NE	NE	NE	NE	NE	NE	NE
PB+Anode I	PA4	NE	NE	NE	NE	NE	NE	NE	NE	NE	NE	NE	NE	NE	NE	NE	NE
PB+Anode I			00100100	6.7E+01	00A 1005001000	010013/ 000	000102										2.0E+01
PB+Anode I	PA6	NE	NE	NE	NE	NE	NE	NE	NE	NE	NE	NE	NE	NE	NE	NE	NE
PB+Anode I				4.5E+00													1.3E+00
PB+Anode I	PA8	NE				r								NE	NE	NE	NE
PB+Anode I	PA9												NE	NE	NE	NE	NE
PB+Anode I	-			1.1E+00											4.3E-01	3.7E-01	3.2E-01
PB+Anode I	PA11	4.0E-01	1.7E+00	4.0E-01	1.0E+00	1.3E+01	4.8E+01	2.7E+01	2.1E+01	3.2E+00	2.7E+00	5.9E-01	1.3E+00		1.6E-01	1.4E-01	1.2E-01
PB+Anode I	PA12 <sup>1)</sup>			3.2E-01											1.2E-01	1.1E-01	9.2E-02
PB+Anode I	PA13	2.7E+01	1.1E+02	2.7E+01	7.1E+01	8.9E+02	3.2E+03	1.8E+03	1.4E+03	2.2E+02	1.9E+02	4.0E+01	8.5E+01		1.1E+01	9.1E+00	7.9E+00
PB+Anode I	PA14	2.5E+02	1.0E+03	2.5E+02	6.3E+02	8.0E+03	2.9E+04	1.7E+04	1.3E+04	1.9E+03	1.7E+03	3.6E+02	7.7E+02		9.6E+01	8.2E+01	7.1E+01
PB+Anode I	PA15	8.1E-03	3.3E-02	8.1E-03	2.1E-02	2.6E-01	9.6E-01	5.5E-01	4.2E-01	6.4E-02	5.5E-02	1.2E-02	2.5E-02		3.2E-03	2.7E-03	2.3E-03
Anode I	A1 <sup>1)</sup>	3.1E+02	1.3E+03	3.1E+02	8.1E+02	1.0E+04	3.7E+04	2.1E+04	1.6E+04	2.5E+03	2.1E+03	4.6E+02	9.8E+02		1.2E+02	1.0E+02	9.1E+01

Table 3.8 Local concentrations in water (fresh and marine) during the emission episode (ng.I-1) for primary aluminium proc	oduction and anode baking facilities.
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1) concentration in fresh surface water. NE: no emission to water

Ŭ.	Site	Naphthalene	Acenaphthene	Acenaphthylene	Fluorene	Anthracene	Phenanthrene	Fluoranthene	Pyrene	Benz(a)anthracene	Chrysene	Benzo(a)pyrene	Benzo(b)fluoranthene		Benzo(ghi)perylene		
	S1						the second second second	of the part of the	Exception Front Provide State	COLOR STREET		7.1E+02			3.9E+02	2.0E+02	5.1E+02
	S3											2.1E+02				-	1.5E+02
	-					203	00100100100100			and and and and		2.2E+04					1.5E+04
							100100100100	NE	VI.SSI S		NE	NE	NE	NE	NE	NE	NE
	~		-										NE	NE	NE	NE	NE
							100 100 100		100			NE	NE	NE	NE	NE	NE
PB+Anode I												1.3E+03					7.0E+02
PB+Anode I												2.0E+03				1.1E+03	
PB+Anode I PB+Anode I	-					a sector of the		1.0E-01 NE	1./E-01 NE	2.0E-02 NE	2.5E-02 NE	1.2E-02 NE	1.2E-02 NE	NE	9.8E-03 NE	5.1E-03 NE	4.3E-03 NE
PB+Anode I PB+Anode I			1010									8.2E+03					4.6E+03
PB+Anode I PB+Anode I				1.8E+01 NE				4.4E+04 NE	2.0E+04 NE	2.7E+04 NE	1.8E+04 NE	8.2E+03 NE	1.7E+04 NE	NE	2.7E+03 NE	4.4E+03 NE	4.6E+03 NE
PB+Anode I		60										5.6E+02					3.1E+02
PB+Anode I								3.0 <u>E</u> ∓03 NE	$\frac{1.4E+0.5}{NE}$	NE	NE	3.0E+02 NE	NE	NE	1.8E+02 NE	3.0E+02 NE	NE
PB+Anode I												NE	NE	NE	NE	NE	NE
PB+Anode I												1.4E+02				7.2E+01	
PB+Anode I												4.9E+01				2.6E+01	
PB+Anode I		The second s		Enclosed and and and and and		A TELEVISION OF A						3.9E+01				2.1E+01	
PB+Anode I	PA13											3.3E+03					1.9E+03
PB+Anode I	PA14	3.4E+01	6.3E+02	6.4E+01	6.5E+02	2.4E+04	6.7E+04	1.6E+05	7.5E+04	9.7E+04	6.6E+04	3.0E+04	6.2E+04		9.8E+03	1.6E+04	1.7E+04
PB+Anode I	PA15	1.1E-03	2.1E-02	2.1E-03	2.1E-02	7.8E-01	2.2E+00	5.3E+00	2.5E+00	3.2E+00	2.2E+00	9.9E-01	2.0E+00		3.2E-01	5.3E-01	5.5E-01
Anode I	A1 <sup>1)</sup>	4.3E+01	8.0E+02	8.2E+01	8.3E+02	3.0E+04	8.5E+04	2.1E+05	9.5E+04	1.2E+05	8.5E+04	3.8E+04	7.9E+04		1.2E+04	2.0E+04	2.1E+04

#### Table 3.9 Local concentrations in sediment (fresh and marine) during the emission episode (µg.kgdwt<sup>-1</sup>) for primary aluminium production and anode baking.

1) concentration in fresh surface water

As no monitoring data for the production site are available no comparison between predicted and measured levels can be made. In comparison to the regional concentrations reported in COMMPS database, the water concentrations predicted for site 1 and 5 up to 9 were well lower. For site 4 the predicted water concentrations were comparable to the median values. The marine water concentration for site 3 was comparable to the BRCs reported by OSPAR.

The calculated local concentrations in sediment for site 1 and 5 up to 9 were well below the 90 percentile regional concentrations reported in COMMPS database. The predicted concentration for site 4 were much closer the 90 percentile of the COMMPS database, especially the high molecular PAHs. The predicted marine sediment concentrations for B(a)P, fluoranthene, benzo(b+k)fluoranthene and pyrene at site 3 were comparable or lower than the BRCs used by OSPAR. For the other PAHs no BRCs are given and consequently no comparison can be made.

#### Industrial use

In comparison to the background levels reported by OSPAR and measured on a reference site by Axelman *et al.* (1999), the local concentrations (Clocal) in marine water near anode and VSS plants and ferro alloy plants were much higher. Also the calculated local concentrations in fresh water were much higher in comparison to the mean values in EU rivers, whereas the Clocal in freshwater near ferro alloy plants is comparable to the mean values in the EU rivers, although the calculated local concentrations for fluoranthene were higher. In the absence of monitoring data, no comparison can be made for the Clocal near the emission points of anode plants and ferro-alloy plants. The monitoring data available in sea water in the vicinity for aluminium smelters using web scrubbers (Axelman *et al.*, 1999) were comparable to those predicted when the different forms (dissolved, colloids and particles) are added.

The calculated local concentrations in sediment were for all applications much higher than the regional background concentrations, where the calculated local concentrations near ferro alloy plants were much closer to these values. Like for the water phase the monitoring data for sediment near emission points are limited to aluminium smelters. The Clocal for marine sediment near VSS plants is well within the range of B(a)P concentration measured in the vicinity near different smelters.

#### **Terrestrial**

#### Production

Only for those sites where emissions are directed to a municipal wastewater treatment plant the local concentrations (averaged over 30 days) in grassland and agricultural soil are the result of atmospheric deposition and sludge application. For a number of these sites the sludge is not spread on arable land but incinerated (i.e. site 1 and 3). For site 5 waste water is directed to an onsite industrial STP for which it is assumed that sludge is not used for agricultural purposes. Consequently, sludge-application to arable land is applicable to site 7 only. For the other sites the effluent is treated in on-site wastewater treatment facilities or directly discharged to water. For now it is assumed that for on-site wastewater treatment facilities sludge is treated as chemical waste and sludge is not allowed to be used on agricultural soil.

#### Industrial/professional use

The local concentrations (averaged over 30 days) in grassland and agricultural soil are the result of only atmospheric deposition as no waste water treatment of the (scrubber/cooling

water) effluent was assumed. The route of waste water treatment sludge to agricultural soil therefore is not relevant for the generic scenarios. The concentrations predicted in agricultural soil and grassland at sites near the different downstream users are given in Table 3.12, Table 3.13 and Table 3.14.

Substance/Site	1	3	4	5	6	7 <sup>1)</sup>	8	9
Naphthalene	221	2210	1053	988	121	51	143	130
Acenaphthene	34	88	31	208	18	9	21	21
Acenaphthylene	86	64	23	69	47	20	53	52
Fluorene	56	182	53	1287	30	22	35	34
Anthracene	51	101	20	715	27	17	31	31
Phenanthrene	143	611	72	4420	81	112	91	88
Fluoranthene	273	637	108	4030	156	208	169	169
Pyrene	208	364	70	728	113	169	130	126
Benzo(a)anthracene	442	390	121	819	247	169	273	260
Chrysene	494	780	130	1560	273	182	312	299
Benzo(a)pyrene	1690	1144	416	1014	884	416	1287	988
Benzo(b)fluoranthene	8190	5460	2080	598	4550	1950	5200	5070
Benzo(k)fluoranthene	2990	2600	793	1690	1560	663	1950	819
Benzo(ghi)perylene	702	546	182	923	364	208	416	416
Dibenzo(a,h)anthracene	2730	1950	702	1248	1560	611	2080	1690
Indeno(1,2,3-cd)pyrene	1209	910	312	988	650	338	1170	728

Table 3.10 Local concentrations in agricultural soil averaged over 30 days (ng.kgdwt<sup>-1</sup>) for the production sites.

Table 3.11 Local concentrations (total) in grassland averaged over 180 days (ng.kgdwt <sup>-1</sup> ) for the production sites.
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Substance/Site	1	3	4	5	6	7 <sup>1)</sup>	8	9
Naphthalene	351	3380	1690	1560	195	77	221	208
Acenaphthene	66	169	60	403	36	16	42	40
Acenaphthylene	169	122	44	130	88	36	101	99
Fluorene	109	364	103	2470	60	27	68	65
Anthracene	100	208	40	1430	56	25	62	61
Phenanthrene	299	1196	143	8710	156	95	182	182
Fluoranthene	546	1287	221	8060	299	182	338	325
Pyrene	416	728	143	1430	221	143	260	247
Benzo(a)anthracene	897	780	247	1690	507	221	533	533
Chrysene	1001	1560	260	2990	533	247	611	598
Benzo(a)pyrene	3250	2340	832	2080	1820	728	2600	1950
Benzo(b)fluoranthene	16900	11050	4290	1209	9100	3640	10270	10010
Benzo(k)fluoranthene	5980	5200	1560	3510	3250	1261	3770	1690

Substance/Site	1	3	4	5	6	<b>7</b> <sup>1)</sup>	8	9
Benzo(ghi)perylene	1430	1105	351	1820	741	325	845	819
Dibenzo(a,h)anthracene	5590	3900	1430	2470	2990	1196	4160	3250
Indeno(1,2,3-cd)pyrene	2470	1820	624	1950	1300	546	2340	1430

1) Only for site 7 sludge from the municipal STP is spread on agricultural land.



Anode I

Anode I

PA15 A1<sup>1)</sup>

#### Dibenzo(a,h)anthracene Indeno(1,2,3-cd)pyrene Benzo(b)fluoranthene Benzo(k)fluoranthene Benzo(ghi)perylene Benz(a)anthracene Acenaphthylene Benzo(a)pyrene Acenaphthene Phenanthrene Fluoranthene Naphthalene Anthracene Chrysene Fluorene Pyrene Site Use cat. **S**1 6.7E+02 1.4E+02 3.3E+02 1.3E+03 4.2E+02 3.6E+03 5.7E+03 2.6E+03 3.4E+03 7.9E+03 7.7E+03 1.5E+04 4.7E+03 2.0E+03 5.0E+03 VSS II 1.7E+03 3.5E+02 8.5E+02 3.4E+03 1.1E+03 9.3E+03 1.5E+04 6.7E+03 8.7E+03 2.0E+04 2.0E+04 3.7E+04 VSS II S3 1.2E+04 5.2E+03 1.3E+04 VSS II S4 1.8E+03 3.7E+02 9.0E+02 3.6E+03 1.1E+03 9.9E+03 1.6E+04 7.1E+03 9.3E+03 2.2E+04 2.1E+04 4.0E+04 1.3E+04 5.5E+03 1.4E+04 P7 3.9E+00 2.9E+00 6.8E+02 2.5E+02 5.5E+02 9.6E+02 6.0E+02 3.7E+02 7.0E+02 3.9E+02 1.7E+02 2.5E+02 SWPB 1.0E-02 VSS I S5 1.9E+03 4.0E+02 9.4E+02 3.7E+03 8.3E+02 4.2E+03 6.2E+03 4.2E+03 8.8E+03 2.1E+04 2.2E+04 5.6E+04 1.6E+04 2.9E+03 1.4E+04 VSS I S6 1.8E+03 3.8E+02 9.1E+02 3.5E+03 8.0E+02 4.1E+03 6.0E+03 4.1E+03 8.5E+03 2.0E+04 2.1E+04 5.5E+04 1.5E+04 2.8E+03 1.4E+04 7.0E+02 1.3E+02 6.1E+00 7.9E+02 7.2E+02 4.1E+03 6.0E+03 3.0E+03 6.1E+03 1.4E+04 5.7E+03 2.6E+04 5.5E+03 5.8E+03 5.8E+03 Anode I PA1 PA2 3.0E+02 5.5E+01 2.6E+00 3.4E+02 3.1E+02 1.7E+03 2.5E+03 1.3E+03 2.6E+03 6.1E+03 2.4E+03 1.1E+04 2.3E+03 2.5E+03 2.5E+03 Anode I PA3 Anode I 2.7E-01 5.0E-02 2.3E-03 3.1E-01 2.8E-01 1.6E+00 2.3E+00 1.2E+00 2.4E+00 5.6E+00 2.2E+00 1.0E+01 2.1E+00 2.2E+00 2.2E+00 PA4 3.1E+01 5.7E+00 2.7E-01 3.5E+01 3.2E+01 1.8E+02 2.6E+02 1.3E+02 2.7E+02 6.3E+02 2.5E+02 1.1E+03 2.4E+02 2.6E+02 2.6E+02 Anode I PA5 1.9E+02 3.5E+01 1.6E+00 2.1E+02 1.9E+02 1.1E+03 1.6E+03 8.1E+02 1.7E+03 3.9E+03 1.5E+03 7.0E+03 Anode I 1.5E+03 1.6E+03 1.6E+03 2.8E+01 5.1E+00 2.4E-01 3.1E+01 2.8E+01 1.6E+02 2.4E+02 1.2E+02 2.4E+02 5.7E+02 2.2E+02 1.0E+03 Anode I PA6 2.2E+02 2.3E+02 2.3E+02 1.8E+03 3.4E+02 1.6E+01 2.1E+03 1.9E+03 1.1E+04 1.6E+04 7.8E+03 1.6E+04 3.7E+04 1.5E+04 6.7E+04 Anode I PA6 1.4E+04 1.5E+04 1.5E+04 PA7 5.1E+00 2.4E-01 3.1E+01 2.8E+01 1.6E+02 2.4E+02 1.2E+02 2.4E+02 5.7E+02 2.2E+02 1.0E+03 2.2E+02 2.3E+02 2.3E+02 Anode I 2.8E+01 1.2E+00 5.8E-02 7.6E+00 6.9E+00 4.0E+01 5.8E+01 2.9E+01 5.9E+01 1.4E+02 5.5E+01 2.5E+02 Anode I PA8 6.7E+00 5.3E+01 5.6E+01 5.6E+01 PA9 Anode I 1.6E+04 2.9E+03 1.4E+02 1.8E+04 1.6E+04 9.3E+04 1.3E+05 6.8E+04 1.4E+05 3.3E+05 1.3E+05 5.8E+05 1.2E+05 1.3E+05 1.3E+05 3.2E+01 1.5E+00 2.0E+02 1.8E+02 1.0E+03 1.5E+03 7.6E+02 1.5E+03 3.6E+03 1.4E+03 6.5E+03 1.4E+03 1.5E+03 1.5E+03 1.7E+02 Anode I PA10 6.7E+02 1.2E+02 5.8E+00 7.6E+02 6.9E+02 3.9E+03 5.7E+03 2.9E+03 5.9E+03 1.4E+04 5.4E+03 2.5E+04 5.2E+03 5.6E+03 5.6E+03 Anode I PA11 1.9E+01 3.5E+00 1.6E-01 2.1E+01 1.9E+01 1.1E+02 1.6E+02 8.2E+01 1.7E+02 3.9E+02 1.5E+02 7.0E+02 Anode I PA12 1.5E+02 1.6E+02 1.6E+02 Anode I PA13 2.4E+03 4.5E+02 2.1E+01 2.7E+03 2.5E+03 1.4E+04 2.1E+04 1.0E+04 2.1E+04 5.0E+04 2.0E+04 9.0E+04 1.9E+04 2.0E+04 2.0E+04 1.8E+03 3.4E+02 1.6E+01 2.1E+03 1.9E+03 1.1E+04 1.6E+04 7.8E+03 1.6E+04 3.7E+04 1.5E+04 6.7E+04 Anode I PA14 1.4E+04 1.5E+04 1.5E+04

#### Table 3.12 Local concentrations in agricultural soil over 30 days (ng.kg<sub>dwt<sup>-1</sup></sub>) for primary aluminium production and anode baking.

6.3E+00 6.7E+00 6.7E+00

7.7E+04 8.2E+04 8.2E+04

8.1E-01 1.5E-01 7.0E-03 9.2E-01 8.3E-01 4.7E+00 6.9E+00 3.5E+00 7.1E+00 1.7E+01 6.6E+00 3.0E+01

9.9E+03 1.8E+03 8.6E+01 1.1E+04 1.0E+04 5.8E+04 8.4E+04 4.3E+04 8.7E+04 2.0E+05 8.0E+04 3.7E+05



Anode I

A1

#### Dibenzo(a,h)anthracene Indeno(1,2,3-cd)pyrene Benzo(k)fluoranthene Benzo(b)fluoranthene Benzo(ghi)perylene Benz(a)anthracene Acenaphthylene Benzo(a)pyrene Acenaphthene Phenanthrene Fluoranthene Naphthalene Anthracene Fluorene Chrysene Pyrene Site Use cat. **S**1 1.1E+03 2.7E+02 6.2E+02 2.6E+03 8.5E+02 7.4E+03 1.1E+04 5.1E+03 6.6E+03 1.6E+04 1.5E+04 2.8E+04 9.5E+03 4.0E+03 1.0E+04 VSS II 2.7E+03 7.0E+02 1.6E+03 6.6E+03 2.2E+03 1.9E+04 2.9E+04 1.3E+04 1.7E+04 4.1E+04 3.9E+04 7.3E+04 VSS II S3 2.5E+04 1.0E+04 2.6E+04 2.6E+04 1.1E+04 2.8E+04 VSS II S4 2.9E+03 7.5E+02 1.7E+03 7.0E+03 2.3E+03 2.0E+04 3.1E+04 1.4E+04 1.8E+04 4.3E+04 4.2E+04 7.8E+04 P7 7.4E+00 5.7E+00 1.4E+03 5.1E+02 1.1E+03 1.9E+03 1.2E+03 7.4E+02 1.4E+03 SWPB 1.6E-02 7.6E+02 3.3E+02 5.1E+02 VSS I S5 2.9E+03 7.7E+02 1.8E+03 7.3E+03 1.6E+03 8.5E+03 1.3E+04 8.5E+03 1.8E+04 4.2E+04 4.2E+04 1.1E+05 3.2E+04 5.8E+03 2.8E+04 VSS I S6 2.8E+03 7.4E+02 1.7E+03 7.1E+03 1.6E+03 8.2E+03 1.2E+04 8.2E+03 1.7E+04 4.1E+04 4.1E+04 1.1E+05 3.1E+04 5.6E+03 2.7E+04 1.1E+03 2.6E+02 1.1E+01 1.5E+03 1.4E+03 7.9E+03 1.2E+04 6.1E+03 1.2E+04 2.9E+04 1.2E+04 5.2E+04 1.1E+04 1.2E+04 1.2E+04 Anode I PA1 PA2 4.6E+02 1.1E+02 4.8E+00 6.4E+02 6.1E+02 3.4E+03 5.2E+03 2.6E+03 5.2E+03 1.2E+04 4.9E+03 2.2E+04 4.6E+03 4.9E+03 4.9E+03 Anode I PA3 Anode I 4.2E-01 1.0E-01 4.4E-03 5.8E-01 5.5E-01 3.1E+00 4.7E+00 2.3E+00 4.7E+00 1.1E+01 4.4E+00 2.0E+01 4.2E+00 4.4E+00 4.4E+00 4.8E+02 5.1E+02 5.1E+02 PA4 1.1E+01 5.0E-01 6.7E+01 6.3E+01 3.5E+02 5.4E+02 2.7E+02 5.4E+02 1.3E+03 5.1E+02 2.3E+03 4.8E+01 Anode I PA5 2.9E+02 7.0E+01 3.0E+00 4.1E+02 3.9E+02 2.1E+03 3.3E+03 1.6E+03 3.3E+03 7.8E+03 3.1E+03 1.4E+04 2.9E+03 3.1E+03 3.1E+03 Anode I 1,0E+03 2,5E+02 1,1E+01 1,5E+03 1,4E+03 7,6E+03 1,2E+04 5,8E+03 1,2E+04 2,8E+04 1,1E+04 5,0E+04 Anode I PA6 1.0E+04 1.1E+04 1.1E+04 2.8E+03 6.7E+02 2.9E+01 3.9E+03 3.7E+03 2.1E+04 3.2E+04 1.6E+04 3.2E+04 7.5E+04 3.0E+04 1.3E+05 Anode I PA6 2.8E+04 3.0E+04 3.0E+04 PA7 1.0E+01 4.5E-01 6.0E+01 5.7E+01 3.1E+02 4.8E+02 2.4E+02 4.8E+02 1.1E+03 4.6E+02 2.0E+03 4.3E+02 4.6E+02 4.6E+02 Anode I 4.3E+01 2.5E+00 1.1E-01 1.5E+01 1.4E+01 7.6E+01 1.2E+02 5.8E+01 1.2E+02 2.8E+02 1.1E+02 5.0E+02 Anode I PA8 0E+01 L0E+021.1E+021.1E+02 PA9 Anode I 2.4E+04 5.8E+03 2.6E+02 3.4E+04 3.2E+04 1.8E+05 2.8E+05 1.4E+05 2.8E+05 6.5E+05 2.6E+05 1.2E+06 2.4E+05 2.6E+05 2.6E+05 PA10 2.7E+02 6.5E+01 2.8E+00 3.8E+02 3.6E+02 2.0E+03 3.1E+03 1.5E+03 3.1E+03 7.2E+03 2.9E+03 1.3E+04 2.7E+03 2.9E+03 2.9E+03 Anode I 1.0E+03 2.5E+02 1.1E+01 1.4E+03 1.4E+03 7.6E+03 1.2E+04 5.8E+03 1.2E+04 2.8E+04 1.1E+04 5.0E+04 1.0E+04 1.1E+04 1.1E+04 Anode I PA11 2.9E+01 7.0E+00 3.1E-01 4.1E+01 3.9E+01 2.1E+02 3.3E+02 1.6E+02 3.3E+02 7.8E+02 3.1E+02 1.4E+03 2.9E+02 3.1E+02 3.1E+02 Anode I PA12 Anode I PA13 3.7E+03 9.0E+02 3.9E+01 5.2E+03 5.0E+03 2.7E+04 4.2E+04 2.1E+04 4.2E+04 1.0E+05 4.0E+04 1.8E+05 3.7E+04 4.0E+04 4.0E+04 2.8E+03 6.7E+02 2.9E+01 3.9E+03 3.7E+03 2.1E+04 3.2E+04 1.6E+04 3.2E+04 7.5E+04 3.0E+04 1.3E+05 Anode I PA14 2.8E+04 3.0E+04 3.0E+04 1.2E+00 3.0E-01 1.3E-02 1.7E+00 1.7E+00 9.2E+00 1.4E+01 7.0E+00 1.4E+01 3.3E+01 1.3E+01 6.0E+01 Anode I PA15 1.2E+01 1.3E+01 1.3E+01

#### Table 3.13 Local concentrations in grassland over 180 days (ng.kg<sub>dwt</sub>-1) for primary aluminium production and anode baking.

1.5E+05 1.6E+05 1.6E+05

1.5E+04 3.7E+03 1.6E+02 2.1E+04 2.0E+04 1.1E+05 1.7E+05 8.5E+04 1.7E+05 4.1E+05 1.6E+05 7.3E+05

	agricult	ural soil	gras	sland		
Substance/Scenario	Ferro-Alloy	Graphite	Ferro-Alloy	Graphite		
Naphthalene	0.9	1.1	1.4	1.8		
Acenaphthene	0.2	0.6	0.4	1.1		
Acenaphthylene	0.5	0.3	0.9	0.6		
Fluorene	2.1	0.7	4.0	1.3		
Anthracene	1.0	0.6	2.0	1.2		
Phenanthrene	6.2	8.3	12.5	16.9		
Fluoranthene	10.3	15.6	20.8	31.2		
Pyrene	4.9	7.8	9.9	15.6		
Benzo(a)anthracene	6.6	7.2	13.0	14.3		
Chrysene	14.3	23.4	27.3	48.1		
Benzo(a)pyrene	11.8	2.6	23.4	5.3		
Benzo(b)fluoranthene	23.4	14.3	46.8	29.9		
Benzo(k)fluoranthene	-	18.6	-	28.6		
Benzo(ghi)perylene	6.8	3.0	13.0	6.0		
Dibenzo(a,h)anthracene	3.3	1.8	6.4	3.5		
Indeno(1,2,3-cd)pyrene	7.2	3.8	14.3	7.7		

Table 3.14 Local concentrations in agricultural soil and grassland (µg.kg<sub>wwt<sup>-1</sup></sub>) for the ferro-alloy and graphite production industry.

Ferro-alloy: Ferro-alloy production (including paste preparation);

Graphite: production of graphite electrodes (including paste preparation) using dry scrubbers;

NA: no information available

#### Comparison with measured data

#### Production

In the absence of local monitoring data, no comparison between the predicted and measured levels can be made. Though, for all sites the predicted concentrations for all 16 EPA PAHs were within the range of the background concentrations reported for arable – and grassland and below those measured in urban areas. The highest concentrations were predicted for site 1 and 3, especially for the PAHs Phenanthrene, fluoranthene, pyrene, Benzo[bjk]fluoranthene and Indeno(1,2,3-cd)pyrene.

#### Industrial use

The Clocal concentrations for anode and VSS production plants are within the range of urban areas reported by Wilcke (2000) or higher. For ferro-alloy plants the local concentrations are comparable to those given for arable- and grassland. The local concentrations for plants using prebaked anodes were negligible in comparison to background concentrations. As no monitoring data has been provided by the industry, no comparison for the local environmental concentrations can be made.

#### Atmosphere

The local concentrations of the EPA 16 PAHs in the atmosphere have been calculated in according to the Technical Guidance Document (EC, 2003). The concentrations in air near the production sites and sites near pitch processing plants uses presented in Table 3.15, Table 3.16 and Table 3.17 do not include the regional background concentration.

The local air compartment receives its input from direct emissions to air, and volatilisation from the sewage treatment plant. The concentration in air at a distance of 100 meters from the point source is estimated with a Gaussian plume model. Degradation and wet and dry deposition of both vapour and aerosol particles are taken into account as the most important fate processes.

#### Production

Local concentrations 100 m from the point source are presented in the following table. Atmospheric release from the waste water treatment plant does not contribute to the local concentration for those sites with reported on-site waste water treatment; either biological or physical (site 4, 6, 8 and 9). This is caused by the facts that in these cases the direct emissions to water are used as input and the STP calculation procedure is not used in the local assessment. In general it can be stated that for CTPHT production sites the contribution from the waste water treatment is not significant with respect to the local air emissions from the production process.

Substance/Site	1	3	4	5	6	7	8	9
Naphthalene	190	1900	900	860	110	42	120	120
Acenaphthene	13	56	20	130	12	4.8	14.0	13.0
Acenaphthylene	57	42	15	45	31	12.0	35	34
Fluorene	12	38	11	260	6.2	2.50	7.1	6.8
Anthracene	10	20.0	3.9	140	5.4	2.1	6.1	6.0
Phenanthrene	29	120	14	870	16	6.3	18.0	18.0
Fluoranthene	20	47	7.8	290	11	4.3	12.0	12.0
Pyrene	17	29	5.6	59	9.1	3.8	10.00	10.0
Benzo(a)anthracene	5.1	4.5	1.4	9.4	2.9	1.10	3.0	3.0
Chrysene	4.5	7.2	1.2	14	2.4	0.98	2.8	2.70
Benzo(a)pyrene	7.7	5.5	2.0	4.9	4.1	1.60	6.1	4.6
Benzo(b)fluoranthene	63	42	16	4.6	34	14.0	39	38
Benzo(k)fluoranthene	12	10.0	3.2	7.0	6.5	2.50	7.6	3.3
Benzo(ghi)perylene	2.7	2.1	0.66	3.5	1.4	0.55	1.6	1.50
Dibenzo(a,h)anthracene	10	6.7	2.4	4.4	5.2	2.10	7.1	5.7
Indeno(1,2,3-cd)pyrene	4.3	3.2	1.1	3.5	2.3	0.91	4.1	2.50

Table 3.15 Local concentrations in air at 100 m from the point source (ng.m-3) at the production sites.

#### Industrial/professional use

Local concentrations 100 m from the point source are presented in the following table. Atmospheric release from the waste water treatment plant does not contribute to the local concentration because it was assumed that the wet scrubber effluent and cooling water effluent is not treated in the local STP.

The calculations in EUSES 2.0.3 are based on an included OPS (Operational priority substances) model assuming 100 metres from one point source at an emission height of 10 m. According to EAA, a more realistic assumption for the aluminium smelters would be an emission from multiple sources at a height higher than 10 m. This has been modelled by NILU for two Norwegian aluminium smelters, where it is shown that the atmospheric fluor and PAH concentrations are significantly lower than those calculated with EUSES 2.0.3. Therefore for the VSS plants the air concentration has been adjusted using OPS-Pro 4.1 based on a higher emission height (25 m) and a larger emission surface (500 by 500 m).

Table 3.16 Local concentrations in air, at 100 m from point source (ng.n	n <sup>-3</sup> ) for ferro-alloy and graphite production
industry.	

Substance/Scenario	Ferro-Alloy	Graphite
Naphthalene	820	970
Acenaphthene	140	360
Acenaphthylene	310	210
Fluorene	420	140
Anthracene	190	120
Phenanthrene	1200	1700
Fluoranthene	750	1100
Pyrene	400	630
Benzo(a)anthracene	75	81
Chrysene	130	220
Benzo(a)pyrene	56	13
Benzo(b)fluoranthene	180	110
Benzo(k)fluoranthene		58
Benzo(ghi)perylene	25	11
Dibenzo(a,h)anthracene	11	6.1
Indeno(1,2,3-cd)pyrene	25	13

Ferro-alloy: Ferro-alloy production (including paste preparation);

Graphite: production of graphite electrodes (including paste preparation) using dry scrubbers

Use cat.	Site	Naphthalene	Acenaphthene	Acenaphthylene	Fluorene	Anthracene	Phenanthrene	Fluoranthene	Pyrene	Benz(a)anthracene	Chrysene	Benzo(a)pyrene	Benzo(b)fluoranthene	Benzo(k)fluoranthene	Benzo(ghi)perylene	Dibenzo(a,h)anthracene	Indeno(1,2,3-cd)pyrene
VSS II	S1			2.2E+02					to the second se			100			1.7E+01	6.9E+00	1.7E+01
VSS II	S3	1.4E+03	2.3E+02	5.6E+02	6.9E+02	2.1E+02	1.9E+03	1.0E+03	5.3E+02	9.8E+01	1.9E+02	9.2E+01	2.8E+02		4.4E+01	1.8E+01	4.4E+01
VSS II	S4	1.5E+03		6.0E+02							Looperter.	100000			4.7E+01		
SWPB	P7	8.7E-03		2.6E+00			100		2.1E+01			10000000		2.9E+00			
VSS I	S5	1.6E+03	2.6E+02	6.4E+02	7.6E+02	1.6E+02	8.3E+02	4.6E+02	3.5E+02	1.0E+02	1.9E+02	1.0E+02	4.1E+02		5.9E+01	1.0E+01	4.9E+01
VSS I	S6	1.6E+03	2.5E+02	6.1E+02	7.3E+02	1.5E+02	8.1E+02	4.4E+02	3.3E+02	9.8E+01	1.9E+02	9.8E+01	4.0E+02		5.7E+01	9.8E+00	4.8E+01
Anode I	PA1	6.1E+02	8.3E+01	4.0E+00	1.6E+02	1.4E+02	8.3E+02	4.3E+02	2.4E+02	7.2E+01	1.3E+02	2.7E+01	1.9E+02		2.1E+01	2.1E+01	2.1E+01
Anode I	PA2	2.6E+02	3.5E+01	1.7E+00	6.8E+01	6.1E+01	3.5E+02	1.8E+02	1.0E+02	3.1E+01	5.6E+01	1.1E+01	8.2E+01		8.7E+00	8.7E+00	8.7E+00
Anode I	PA3	2.3E-01	3.2E-02	1.5E-03	6.2E-02	5.5E-02	3.2E-01	1.7E-01	9.4E-02	2.8E-02	5.1E-02	1.0E-02	7.5E-02		7.9E-03	7.9E-03	7.9E-03
Anode I	PA4	2.7E+01	3.6E+00	1.8E-01	7.1E+00	6.3E+00	3.7E+01	1.9E+01	1.1E+01	3.2E+00	5.9E+00	1.2E+00	8.5E+00		9.0E-01	9.0E-01	9.0E-01
Anode I	PA5	1.6E+02	2.2E+01	1.1E+00	4.3E+01	3.9E+01	2.2E+02	1.2E+02	6.6E+01	1.9E+01	3.6E+01	7.3E+00	5.2E+01		5.5E+00	5.5E+00	5.5E+00
Anode I	PA6	5.8E+02	8.0E+01	3.8E+00	1.5E+02	1.4E+02	8.0E+02	4.1E+02	2.3E+02	6.9E+01	1.3E+02	2.6E+01	1.9E+02		2.0E+01	2.0E+01	2.0E+01
Anode I	PA6	1.6E+03	2.2E+02	1.0E+01	4.2E+02	3.7E+02	2.2E+03	1.1E+03	6.3E+02	1.9E+02	3.5E+02	7.0E+01	5.0E+02		5.3E+01	5.3E+01	5.3E+01
Anode I	PA7	2.4E+01	3.3E+00	1.6E-01	6.3E+00	5.7E+00	3.3E+01	1.7E+01	9.6E+00	2.8E+00	5.3E+00	1.1E+00	7.7E+00		8.1E-01	8.1E-01	8.1E-01
Anode I	PA8	5.9E+00	8.0E-01	3.8E-02	1.5E+00	1.4E+00	8.0E+00	4.2E+00	2.3E+00	6.9E-01	1.3E+00	2.6E-01	1.9E+00		2.0E-01	2.0E-01	2.0E-01
Anode I	PA9	1.4E+04	1.9E+03	9.0E+01	3.6E+03	3.2E+03	1.9E+04	9.7E+03	5.5E+03	1.6E+03	3.0E+03	6.1E+02	4.4E+03		4.6E+02	4.6E+02	4.6E+02
Anode I	PA10	1.5E+02	2.1E+01	1.0E+00	4.0E+01	3.6E+01	2.1E+02	1.1E+02	6.1E+01	1.8E+01	3.3E+01	6.8E+00	4.9E+01		5.1E+00	5.1E+00	5.1E+00
Anode I	PA11	5.8E+02	7.9E+01	3.8E+00	1.5E+02	1.4E+02	8.0E+02	4.1E+02	2.3E+02	6.9E+01	1.3E+02	2.6E+01	1.9E+02		2.0E+01	2.0E+01	2.0E+01
Anode I	PA12	1.6E+01	2.2E+00	1.1E-01	4.3E+00	3.9E+00	2.2E+01	1.2E+01	6.6E+00	1.9E+00	3.6E+00	7.3E-01	5.2E+00		5.5E-01	5.5E-01	5.5E-01
Anode I	PA13	2.1E+03	2.9E+02	1.4E+01	5.6E+02	5.0E+02	2.9E+03	1.5E+03	8.4E+02	2.5E+02	4.6E+02	9.4E+01	6.7E+02		7.1E+01	7.1E+01	7.1E+01
Anode I	PA14	1.6E+03	2.2E+02	1.0E+01	4.2E+02	3.7E+02	2.2E+03	1.1E+03	6.3E+02	1.9E+02	3.5E+02	7.0E+01	5.0E+02		5.3E+01	5.3E+01	5.3E+01
Anode I	PA15	7.0E-01	9.6E-02	4.6E-03	1.9E-01	1.7E-01	9.6E-01	5.0E-01	2.8E-01	8.3E-02	1.5E-01	3.1E-02	2.2E-01		2.4E-02	2.4E-02	2.4E-02
Anode I	A1	8.6E+03	1.2E+03	5.6E+01	2.3E+03	2.0E+03	1.2E+04	6.1E+03	3.4E+03	1.0E+03	1.9E+03	3.8E+02	2.7E+03		2.9E+02	2.9E+02	2.9E+02

Table 3.17 Local concentrations in air (ng.m<sup>-3</sup>) for the primary aluminium production and anode baking facilities.

#### Comparison with measured data

#### Production

The calculated air concentrations near all production sites are all close to the upper range or higher than those measured in urban areas. Though most of PAHs concentrations were within the range reported for industrial areas. Only the concentration predicted for site 5 were higher.

#### Industrial use

The data obtained by Hagen (2002) showed that the B(a)P concentrations in air in the vicinity of plants using Søderberg technology are between 0.1 and 10  $ng/m^3$ . The calculated concentration for the plants using this technology are between 30 and 100  $ng/m^3$ , which is one to two orders of magnitude higher. For the plant located a Karmøy (site S3), where the measured and predicted concentrations are related to the same distance (i.e. 100 m distance), the predicted air concentrations seem to be two orders of magnitude higher. For other plants the concentration measured at 1 km distance. When it is assumed that roughly the concentration at 100 m are 10 times higher than at 1 km, the concentrations for the other sites shown in Table 3.64 seems to deviate to much lesser extent from the predicted concentrations than for Karmøy.

For site PA2 (Sunndalsøra), more recent data shows that the concentration B(a)P at 500 m distance from the plant is a factor of 70 lower than estimated at 100 m distance (0.16  $ng/m^3$  versus 11  $ng/m^3$ ). For site S4 recent measurements indicate that the B(a)P concentration at 200 m distance were a factor of 40 lower than estimated (2.5  $ng/m^3$  versus 98  $ng/m^3$ ). It is unknown to which extent the actual concentrations for the other PAHs deviate from those predicted.

For site PA7, measured HF data at a point 100m from the plant is 0.5  $\mu$ g HF/m3. The corresponding modelled value is 9.4 $\mu$ g/m3.

Overall, the measured data shows that the modelled air concentration can be considered as a conservative prediction. However, a more accurate measure of air concentration can only be obtained by local measurements at a relevant distance and direction from the emission source.

#### STP

Some CTPHT production plants discharge their waste water to a municipal STP or off-site biological waste water treatment plant. For these sites the sewage treatment model has been applied to calculate the fate in the STP. The emission from the production site and the effluent flow rate of the external waste water treatment facility are required as input. The model calculates the emission from the sewage treatment plant to air, the concentration in sewage sludge and the concentration in the effluent. A detailed description of the STP model is given in the Technical Guidance Document (EC, 2003). The highest PEC for total PAH in the effluent which is considered relevant for the risk assessment is 114  $\mu$ g/l at site 4. The concentrations in the effluent of the other production sites were  $\leq 2 \mu$ g/l (Table 3.18).

Substance/Site	1 <sup>1)</sup>	<b>3</b> <sup>1)</sup>	<b>4</b> <sup>2)</sup>	5 <sup>1)</sup>	6 <sup>2)</sup>	<b>7</b> <sup>1)</sup>	<b>8</b> <sup>3)</sup>	<b>9</b> <sup>3)</sup>
Naphthalene	0.73	73	750	60	74	1.3	n.r.	n.r.
Acenaphthene	0.14	48	433	20	38	0.3	n.r.	n.r.
Acenaphthylene	n.d.	92	1783	105	5	0.4	n.r.	n.r.
Fluorene	0.094	152	435	20	21.5	0.6	n.r.	n.r.
Anthracene	0.018	37	867	24	24.5	0.2	n.r.	n.r.
Phenanthrene	0.17	88	1267	0.46	65.5	2.5	n.r.	n.r.
Fluoranthene	0.06	91	6592	8.0	61.5	0.9	n.r.	n.r.
Pyrene	0.33	73	4842	6.9	36.5	0.9	n.r.	n.r.
Benzo(a)anthracene	0.0067	30	5075	1.2	8.5	0.3	n.r.	n.r.
Chrysene	0.0070	31	4433	0.15 <sup>4)</sup>	8	0.3	n.r.	n.r.
Benzo(a)pyrene	0.0064	13	19608	0.14 <sup>4)</sup>	10	0.2	n.r.	n.r.
Benzo(b)fluoranthene	0.0064	156	29333	0.14 4)	7.5	0.4	n.r.	n.r.
Benzo(k)fluoranthene	0.0064	52	9533	0.14 4)	6.5	0.1	n.r.	n.r.
Benzo(ghi)perylene	0.0063	64	11992	0.14 4)	5	0.2	n.r.	n.r.
Dibenzo(a,h)anthracene	0.0060	17	3325	0.13 4)	6	0.1	n.r.	n.r.
Indeno(1,2,3-cd)pyrene	0.0060	73	13350	0.13 4)	5.5	0.2	n.r.	n.r.

Table 3.18 Concentrations STP effluent (ng.I<sup>-1</sup>) for the relevant production sites.

1) discharged from these sites is directed to off-site (public) sewage treatment plants. Sludge from these STPs goes to agricultural soil. These effluent concentrations have been calculated applying the STP model in EUSES (EC, 2003); 2) on-site waste water treatment, reported effluent concentration; 3) these sites have no on-site biological (activated sludge) wastewater treatment theefore the table does not give effluent data for these sites, indicated with n.r.; 4) detection limit is 0.01 µg/l,

3.2

## EFFECTS ASSESSMENT

In the effect assessment the ecotoxicity data has been evaluated for the 16 EPA PAHs separately and subsequently PNEC for the individual PAHs will be derived (see Table 3.19, Table 3.20 and Table 3.21). The data from both literature and other EU RARs are used.

PAHs can be toxic via different mode of actions, such as non-polar narcosis and phototoxicity. The phototoxic effects can be observed after a short period of exposure, which explains why for PAHs like anthracene, fluoranthene and pyrene, where photoxicity is most evident, the acute toxicity values are even lower than the chronic toxicity values.

Although it is recognized that at present time, the ability to conduct PAH-photoactivated risk assessment of acceptable uncertainty is limited by comprehensive information on species exposure to PAH and UV radiation during all life stages, it is thought that the phototoxic effects can not be ignored in the present risk assessment. Therefore these effects are also considered in deriving the PNECs for aquatic species. It should be noted that the UV exposure levels of the selected studies did not exceed the UV levels under natural sun light conditions. In the table below the derived PNECs for the different compartments are presented.

# Aquatic compartment (incl. sediment)

Compound	PNEC	AF	Species	PNEC	AF	species	
	fresh			marine			
	water			water			
	(µg/l)			(µg/l)			
Naphthalene	2	10	Oncorhynchus mykiss	2	10	O. mykiss	
Anthracene	0.1	10	Daphnia pulex acute	0.1	10	D. pulex acute	
Phenanthrene	1.3	10	Ceriodaphnia dubia	1.3	10	C. dubia	
Fluoranthene	0.01	10	Pleuronectes	0.01	10	P. americanus	
			americanus acute			acute	
Pyrene	0.023	10	Mulinea lateralis acute	0.023	10	M. lateralis acute	
9H-Fluorene	2.5	10	C. dubia	0.25	100	C. dubia	
Acenaphthylene	1.3	50	C. dubia	0.13	500	C. dubia	
Acenaphthene	3.8	10	Pseudokirchneriella	0.38	100	P. subcapitata	
			subcapitata				
Chrysene	0.07	10	D. magna acute	0.007	100	D. magna acute	
Benzo(a)anthracene	0.012	100	P. subcapitata	0.0012	1000	P. subcapitata	
Benzo(b)fluoranthene	0.017	*	Brachydanio rerio	0.0017	100	B. rerio	
Benzo(ghi)perylene	0.0082	10	C. dubia	0.00082	100	C. dubia	
Benzo(k)fluoranthene	0.017	10	Brachydanio rerio	0.0017	100	B. rerio	
Benzo(a)pyrene	0.022	10	Crassostrea gigas	0.022	10	C. gigas	
Dibenzo(a,h)anthracene	0.0014	100	P. subcapitata	0.00014	1000	P. subcapitata	
Indeno[123cd]pyrene	0.0027	100	C. dubia	0.00027	1000	C. dubia	

Table 3.19. The PNEC for the various PAHs for fresh and marine water o	rganisms
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\* For benzo(b)fluoranthene the PNEC is the same as for benzo(k)fluoranthene after read-across with this compound

Compound	PNEC fresh	AF	Species	PNEC	AF	species
	water			marine		
	sediment			sediment		
	(mg/kg <sub>dw</sub> )			(mg/kg <sub>dw</sub> )		
Naphthalene	2.9	1000	R. abronius	0.29	10000 vs.	R. abronius
		vs. EqP			EqP	
Anthracene	0.14	100	C. riparius	0.014	1000	C. riparius
Phenanthrene	5	10	H. azteca/	5	10	H. azteca/
			C. riparius			C. riparius
Fluoranthene	0.96	10	C. riparius	0.96	10	C. riparius
Pyrene	2.8	50	R. abronius	1.4	100	R. abronius
9H-Fluorene	2,56	EqP		0.26	EqP	
Acenaphthylene	0.34	EqP		0.03	EqP	
Acenaphthene	1.6	100	R. abronius	0.16	1000	R. abronius
Chrysene	2.79	EqP		0.28	EqP	
Benzo(a)anthracene	0.60	EqP		0.06	EqP	
Benzo(b)fluoranthene	1.38	EqP		0.14	EqP	
Benzo(ghi)perylene	0.84	EqP		0.084	EqP	
Benzo(k)fluoranthene	1.38	EqP		0.14	EqP	
Benzo(a)pyrene	1.83	EqP		1.83	EqP	
Dibenzo(a,h)anthracene	0.27	EqP		0.027	EqP	
Indeno[123cd]pyrene	0.63	EqP		0.063	EqP	

Table 3.20. The PNEC for the various	PAHs for fresh and	d marine sediment organisms
	17th of the hour and	a marine ocament organieme

# Terrestrial compartment

Compound	PNEC soil	AF	species	
	(mg/kg <sub>dw</sub> )			
Naphthalene	1.0	10	Folsomia candida	
Anthracene	0.13	50	F. fimetaria	
Phenanthrene	1.8	10	F. fimetaria	
Fluoranthene	1.5	10	Nitrification	
Pyrene	1.0	10	F. candida	
9H-Fluorene	1.0	10	F. fimetaria	
Acenaphthylene	0.29	100	F. fimetaria	
Acenaphthene	0.038	50	Lactuca sativa	
Chrysene	0.55	EqP		
Benzo(a)anthracene	0.079	10	Oniscus asellus	
Benzo(b)fluoranthene	0.28	EqP		
Benzo(ghi)perylene	0.17	EqP		
Benzo(k)fluoranthene	0.27	EqP		
Benzo(a)pyrene	0.053	10	Porcellio scaber	
Dibenzo(a,h)anthracene	0.054	EqP		
Indeno[123cd]pyrene	0.13	EqP		

Table 3.21. The PNEC for the various PAHs for soil organisms

# Atmosphere

No data available and no PNEC<sub>air</sub> can be derived.

## Sewage treatment plant

The toxicity of CTPHT (electrode binder BX 90) to *Pseudomonas putida* has been tested in a cell multiplication inhibition test according to a draft guideline DIN 38412; 1989 (Hillman, 1991). Over the whole test range (625 to 10000 mg CTPHT /l ) no inhibition was observed. In an addition test in the same study, CTPHT (24 mg) was dissolved in the highest permissible concentration of a solubilizer toluol (0.1 g/l). From this solution 5 test concentrations from 1.5 to 20 mg/l were prepared. Within this test range no inhibition was observed. No analysis of the test solution was performed.

Although this study is sufficient for the base set of CTPHT, it does not provide data to derive exact  $PNEC_{microorganisms}$  values for the individual PAHs in a STP. Based on the solubility data given in section 1.2, it can however be assumed that the PNEC values will be in the range of  $\mu g/l$  or higher.

An additional study is available in which creosote was tested for toxicity towards activated sludge according to OECD 209 (Lebertz, 1984). The EC50 was determined at 670 mg/l, which suggest that the EC50 values for the individual PAHs are not below the  $\mu$ g/l range. Although toxicity data on *Vibrio fischeri* cannot be used for the risk assessment of a STP, supporting evidence for the last conclusion is found in toxicity studies with this species for the different PAHs (Loibner et al., 2004). The EC10 values for the two and three ring PAHs range from 0.13 mg/l for phenanthrene to 0.39 mg/l for naphthalene. For PAHs with four rings or more no toxicity is observed up to the saturated aqueous solution. It was argued that the toxicity of PAHs towards V. *fischeri* seems therefore to be related to the maximum water solubility rather than the toxicity of the individual PAH.

#### Secondary poisoning

Based on the available information PNEC oral values for the individual PAHs can not be derived.

## 3.3 RISK CHARACTERISATION

Considering that a range of PAHs are emitted simultaneously, it is obvious to assess the risk for the mixture of PAHs and not for the PAHs individually. A common method to determine the toxicity of a mixture is the toxic unit concept. A toxic unit (TU) is defined as the ratio of the concentration in a medium to the effect concentration in that medium. The toxicity of the mixture is the sum of the individuals TUs. Use of the toxic unit concept requires that the dose-response relationships of the individual compounds have similar shapes, which in general holds for compounds with the same mode of action. The additivity of the toxicity of narcotic chemicals has been demonstrated by a number of investigators and is also considered applicable for PAHs (DiToro *et al.*, 2000; DiToro & McGrath, 2000). As shown in section 3.2, the most sensitive endpoints were not for all PAHs based on the same mode of action. For a limited number of PAHs (anthracene, fluoranthene, pyrene and chrysene) the lowest toxicity is based on phototoxicity and not non-polar narcosis. However, the difference in toxicity is overall small and limited to the aquatic compartment. Therefore, the TU approach is considered feasible for the sum of the 16 EPA PAHs.

For the risk assessment of CTPHT the TU is expressed as a ratio of the Clocal to the PNEC for each PAH. The toxicity of the combination of PAHs is assessed by adding all the risk quotients (Clocal/PNEC) together. The exposure to the mixture is considered as a risk in case the sum is higher than 1.

Since many unintentional sources contribute to the total emission of PAHs into the environment (see section 3.1.2.), which by extension are not related to production and use of CTPHT, the risk characterisation will only be focussed on the PAHs emitted by producers and downstream users of CTPHT on a local scale. To put the risk ratio's derived for the local scale into perspective risk ratio's for the regional background are calculated using monitoring data available for fresh water environment (COMMPS database), the marine environment (OSPAR BRCs) and soil (peer review of Wilcke) and the PNEC determined for the 16 EPA PAHs. No formal conclusions are derived for the regional background.

## **3.3.1** Aquatic compartment (incl. sediment)

In Table 3.22 and Table 3.23 the risk characterisation (RC) for surface water and sediment is presented for the CTPHT production. For the industrial use the RC is listed in Table 3.24, Table 3.25 and Table 3.26.

In accordance to the EU TGD, for all PAHs with a log Kow > 5 an additional factor of 10 is applied to the PNEC<sub>sediment</sub> in case no experimental data are available and therefore the equilibrium partitioning approach is used.

# 3.3.1.1 Production

Substance/Site	1	3*	4	5	6	7	8	9
Naphthalene	0.0	0.0	0.0	0.001	0.0	0.0	0.0	0.0
Acenaphthene	0.0	0.0	0.0	0.000	0.0	0.0	0.0	0.0
Acenaphthylene	n.d.	0.0	0.0	0.003	0.0	0.0	0.0	0.0
Fluorene	0.0	0.0	0.0	0.000	0.0	0.0	0.0	0.0
Anthracene	0.0	0.0	0.0	0.008	0.0	0.0	0.0	0.0
Phenanthrene	0.0	0.0	0.0	0.000	0.0	0.0	0.0	0.0
Fluoranthene	0.0	0.0	0.5	0.025	0.0	0.0	0.0	0.0
Pyrene	0.0	0.0	0.2	0.010	0.0	0.0	0.0	0.0
Benzo(a)anthracene	0.0	0.0	0.22	0.002	0.0	0.0	0.0	0.0
Chrysene	0.0	0.0	0.0	0.000	0.0	0.0	0.0	0.0
Benzo(a)pyrene	0.0	0.0	0.3	0.000	0.0	0.0	0.0	0.0
Benzo(b)fluoranthene	0.0	0.0	0.7	0.000	0.0	0.0	0.0	0.0
Benzo(k)fluoranthene	0.0	0.0	0.2	0.000	0.0	0.0	0.0	0.0
Benzo(ghi)perylene	0.0	0.0	0.5	0.000	0.0	0.0	0.0	0.1
Dibenzo[a.h]anthracene	0.0	0.0	0.5	0.001	0.0	0.0	0.0	0.4
Indeno[1.2.3-cd]pyrene	0.0	0.0	1.0	0.000	0.0	0.0	0.0	0.2
Sum PAH	0.0	0.0	4	0.05	0.1	0.01	0.1	0.9

Table 3.22 Clocal/PNEC for surface water and marine water (\*) for the different CTPHT production sites.

Table 3.23 Clocal/PNEC for sediment for the different C	TPHT production sites.
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Substance/Site	1	3	4	5	6	7	8	9
Naphthalene	0.0	0.0	0.0	0.00	0.0	0.00	0.0	0.0
Acenaphthene	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.0
Acenaphthylene	0.0	0.0	0.0	0.01	0.0	0.00	0.0	0.0
Fluorene	0.0	0.0	0.0	0.00	0.0	0.00	0.0	0.0
Anthracene	0.0	0.1	0.0	0.05	0.0	0.00	0.0	0.0
Phenanthrene	0.0	0.0	0.0	0.00	0.0	0.00	0.0	0.0
Fluoranthene	0.0	0.0	0.1	0.01	0.0	0.00	0.0	0.0
Pyrene	0.0	0.0	0.0	0.00	0.0	0.00	0.0	0.0
Benzo(a)anthracene	0.0	0.0	2.5	0.06	0.0	0.00	0.1	0.5
Chrysene	0.0	0.0	0.4	0.00	0.0	0.00	0.0	0.1
Benzo(a)pyrene	0.0	0.0	4.0	0.00	0.0	0.00	0.0	0.4
Benzo(b)fluoranthene	0.0	0.0	8.0	0.00	0.0	0.00	0.0	0.3
Benzo(k)fluoranthene	0.0	0.0	2.5	0.00	0.0	0.00	0.0	0.3

Substance/Site	1	3	4	5	6	7	8	9
Benzo(ghi)perylene	0.0	0.0	6.0	0.01	0.0	0.00	0.0	1.0
Dibenzo[a.h]anthracene	0.0	0.0	6.1	0.02	0.1	0.00	0.1	3.7
Indeno[1.2.3-cd]pyrene	0.0	0.0	10.9	0.01	0.0	0.01	0.0	1.7
Sum PAH	0.0	0.0	41	0.2	0.3	0.02	0.3	8

3.3.1.2

# Industrial use/processing

Table 3.24 Clocal/PNEC for	water and sediment for the ferro-alloy industry.
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Substance	Sea water	Marine sediment
Naphthalene	0.00028	0.00025
Acenaphthene	0.0072	0.010
Acenaphthylene	0.0084	0.0084
Fluorene	0.0064	0.0065
Anthracene	0.033	0.71
Phenanthrene	0.014	0.0084
Fluoranthene	2.8	0.28
Pyrene	0.75	0.077
Benzo(a)anthracene	2.3	23
Chrysene	0.85	8.5
Benzo(a)pyrene	0.043	0.43
Benzo(b)fluoranthene	1.1	11
Benzo(k)fluoranthene	NA	NA
Benzo(ghi)perylene	0.49	4.9
Dibenzo(a,h)anthracene	0.81	8.1
Indeno(1,2,3-cd)pyrene	0.85	8.4
Sum of PAH	10	69

Ferro-alloy: Ferro-alloy production (including paste preparation)

Use cat.	Site	Naphthalene	Acenaphthene	Acenaphthylene	Fluorene	Anthracene	Phenanthrene	Fluoranthene	Pyrene	Benz(a)anthracene	Chrysene	Benzo(a)pyrene	Benzo(b)fluoranthene	Benzo(ghi)perylene	Dibenzo(a,h)anthracene	Indeno(1,2,3-cd)pyrene	Total Clocal/PNEC
VSS II	S1	2.9E-03	6.4E-02	4.4E-02	6.2E-02	2.1E-01	1.4E-01	2.6E+01	7.1E+00	2.3E+01	7.7E+00	3.9E-01	1.5E+01	4.6E+00	7.3E+00	8.1E+00	100
VSS II	S3	8.5E-04	1.9E-02	1.3E-02	1.8E-02	6.0E-02	4.2E-02	7.6E+00	2.1E+00	6.8E+00	2.2E+00	1.1E-01	4.5E+00	1.4E+00	2.1E+00	2.4E+00	29
VSS II	S4	8.8E-02	2.0E+00	1.4E+00	1.9E+00	6.2E+00	4.4E+00	7.8E+02	2.2E+02	7.1E+02	2.3E+02	1.2E+01	4.6E+02	1.4E+02	2.2E+02	2.5E+02	3038
VSS I	S5				NE	NE	NE	NE	NE	10010	11001		NE	NE	NE		NE
VSS I	S6		-		NE	NE	1010013		NE	NE	and the second se	- · ·	NE	NE			NE
Anode I	PA1 <sup>1)</sup>	5.1E-03	1.1E-01	7.9E-02	1.1E-01	3.3E+00	9.4E-01	6.9E+01	2.3E+01	6.8E+01	1.0E+01	6.9E-01	1.9E+01	4.9E+00	2.5E+01	1.1E+01	234
Anode I	PA2	8.1E-03	1.8E-01	1.2E-01	1.7E-01	5.3E+00	1.5E+00	1.1E+02	3.6E+01	1.1E+02	1.6E+01	1.1E+00	3.0E+01	7.7E+00	3.9E+01	1.7E+01	369
Anode I	PA3				NE	NE	NE	NE	NE	NE		NE	NE	NE			NE
Anode I	PA4		=			NE	NE			NE		NE	NE	NE			NE
Anode I	PA5			A construction of the local sector	lootootootootootootootootootootootootoot		COROCHY		Another the second second second						1.6E+01		
Anode I	PA6	NE	NE	NE	NE	NE	NE	NE	NE	NE	NE	NE	NE	NE	NE	NE	NE
Anode I	PA7														1.1E+01		
Anode I	PA8								NE				NE	NE			NE
Anode I	PA9				NE	NE			NE			NE	NE	NE			NE
Anode I	PA10			ki oo loo loo loo loo loo l											2.6E+00		25
Anode I	PA11					A DESCRIPTION DESCRIPTION AND A DESCRIPTION AND									9.7E-01		9
Anode I	PA12 <sup>1)</sup>			and a second sec											7.5E-02		3
Anode I	PA13				Also iso iso iso iso i	And the food of									6.5E+00		295
Anode I	PA14														5.9E+01		2659
Anode I	PA15	4.0E-06	8.8E-05	6.2E-05	8.4E-05	2.6E-03	7.4E-04	5.5E-02	1.8E-02	5.3E-02	7.9E-03	5.4E-04	1.5E-02	3.9E-03	1.9E-02	8.7E-03	0.2
Anode I	A1 <sup>1)</sup>	1.6E-01	3.4E-01	2.4E-01	3.2E-01	1.0E+02	2.9E+01	2.1E+03	7.0E+02	2.1E+02	3.0E+01	2.1E+01	5.7E+01	1.5E+01	7.5E+01	3.4E+01	3386

#### Table 3.25 CLocal/PNEC in water (marine and fresh) for primary aluminium production and anode baking.

NE: no emission to water; <sup>1)</sup> emission to fresh water

Use cat.	Site	Naphthalene	Acenaphthene	Acenaphthylene	Fluorene	Anthracene	Phenanthrene	Fluoranthene	Pyrene	Benz(a)anthracene	Chrysene	Benzo(a)pyrene	Benzo(b)fluoranthene	Benzo(ghi)perylene	Dibenzo(a,h)anthracene	Indeno(1,2,3-cd)pyrene	Total Clocal/PNEC
VSS II	S1	2.8E-03	9.5E-02	4.6E-02	6.1E-02	4.3E+00	8.5E-02	2.6E+00	6.9E-01	2.3E+01	7.7E+00	3.9E+00	1.5E+02	4.6E+01	7.3E+01	8.1E+01	395
VSS II	S3	8.1E-04	2.8E-02	1.3E-02	1.8E-02	1.3E+00	2.5E-02	7.7E-01	2.0E-01	6.8E+00	2.2E+00	1.1E+00	4.5E+01	1.3E+01	2.2E+01	2.4E+01	116
VSS II	S4		2.9E+00	1.4E+00			2.6E+00	8.0E+01	2.1E+01				4.6E+03	1.4E+03	2.2E+03	2.5E+03	12019
VSS I	S5	NE	NE	NE	NE	NE	NE	NE	NE	NE	NE	NE	NE	NE	NE	NE	NE
VSS I	S6	NE	NE	NE	NE	NE	NE	NE	NE	NE	NE	NE	NE	NE	NE	NE	NE
Anode I	PA1 <sup>1)</sup>	4.9E-03	1.6E-01	8.1E-02	1.0E-01	7.1E+01	5.6E-01	7.0E+00	2.2E+00	6.8E+01	9.9E+00	6.9E+00	1.9E+02	4.9E+01	2.5E+02	1.1E+02	761
Anode I	PA2	7.7E-03	2.6E-01		1.6E-01	1.1E+02	8.8E-01	1.1E+01	3.5E+00	1.1E+02	1.6E+01	1.1E+01	3.0E+02	7.7E+01	3.9E+02	1.7E+02	1198
Anode I	PA3	NE	NE				NE	NE	NE		=	-	NE	NE	NE		NE
Anode I	PA4	NE	NE	NE	NE	NE	NE	NE	NE	NE	NE	NE	NE	NE	NE	NE	NE
Anode I	PA5	3.2E-03		5.3E-02													591
Anode I	PA6	NE	NE						NE					NE		NE	NE
Anode I	PA7	2.2E-03		3.6E-02		100											337
Anode I	PA8		NE	Con 100 00 00 000		Internet in the second		NE	1103				NE	NE			NE
Anode I	PA9	NE	NE	100100100100		100100		NE				-		NE			NE
Anode I	PA10	5.3E-04		8.8E-03	Internet Internet												82
Anode I	PA11		Zielen	3.2E-03	internet Antoniosis	Down Receipt		techoological techool									30
Anode I	PA12 <sup>1)</sup>			2.5E-04		/											3
Anode I	PA13	Lange and Lange		2.2E-02													240
Anode I	PA14		and the second se	1.9E-01													2155
Anode I	PA15	100		6.4E-05			tootootooto										0.6
Anode I	A1 <sup>1)</sup>	1.5E-02	5.0E-01	2.5E-01	3.2E-01	2.2E+02	1.7E+01	2.1E+02	3.4E+01	2.1E+02	3.0E+01	2.1E+02	5.7E+02	1.5E+02	7.6E+02	3.4E+02	2745

Table 3.26 CLocal/PNEC for sediment	(marine and fresh) at p	rimary aluminium productio	n and anode baking sites.
	(		

NE: no emission to water; <sup>1)</sup> emission to fresh water

# 3.3.1.3 Regional background in fresh and marine surface water (including sediment)

Not for all 16 EPA PAHs EU fresh water monitoring data are available. The available data result in risk ratio's > 1 for fresh water and fresh water sediment. (see Table 3.27).

With respect to the marine environment OSPAR data gives information on 4 PAHs. Based on these monitoring data the risk quotients for water well below 1. However, the concentrations for benzo (b+k) fluoranthene and fluoranthene, result in risk ratio's > 1 for marine sediment organisms (see Table 3.28).

	Surfac	e water	Sedi	iment
Compound	Median	90- percentile	Median	90- percentile
Naphthalene	0.03	0.84	0.05	0.67
Acenaphthene	0.00	0.11	0.03	0.42
Acenaphthylene			0.34	3.33
Fluorene			0.09	0.29
Anthracene	0.04	0.83	1.24	3.35
Phenanthrene			0.12	0.68
Fluoranthene	1.60	8.23	6.0	26.7
Pyrene			0.20	1.13
Benzo(a)anthracene	1.76	6.93	5.0	22.7
Chrysene			1.8	14.7
Benzo(a)pyrene	0.32	1.24	1.7	5.3
Benzo(b)fluoranthene	0.52	2.85	2.5	10.0
Benzo(k)fluoranthene	0.26	1.46	1.4	4.8
Benzo(ghi)perylene	0.98	5.73	3.5	11.9
Indeno(1,2,3- cd)pyrene	12.41	34.67	4.9	20.6
Total	17.9	62.9	28.9	126.6

Table 3.27 Ratio between the COMMPS monitoring data and PNEC for surfacewater and sediment organisms

РАН		North Sea/ gerrak	southern	North Sea	Arctic Ocean/ Iceland Sea			
	water	sediment	water	sediment	water	sediment		
Benzo(a)pyrene	0.00	0.05 - 0.61	0.00	0.00 - 0.28	0.00	0.01 - 0.03		
Fluoranthene	0.03	0.10 - 1.7	0.03	0.00 - 1.0	0.01	0.02 - 0.08		
Benzo(b+k)fluoranthene	0.01	3.2 - 31	0.01	0.08 - 10.1	0.00	0.52 - 2.1		
Pyrene	0.00	0.01- 0.09	0.00	0.00 - 0.06	0.00	0.00		

Table 3.28 Ratio between the OSPAR monitoring data and PNEC for marine water and sediment organisms.

#### **3.3.2** Sewage treatment plant

There are insufficient data available to obtain  $PNEC_{micro-organism}$  values for the individual PAHs in a STP. However, based on the assumption that the PNECs have to be in the  $\mu g/l$  range or higher, it is not expected the calculated concentrations for the CTPHT production sites (see table 3.67) will pose a risk for micro-organisms in a STP (conclusion ii).

The down stream users of CTPHT do not emit waste water to a STP

#### **3.3.3** Terrestrial compartment

In Table 3.29 the RC for agricultural soil is presented for the production. For the industrial use the RC is listed inTable 3.30 and Table 3.31. In accordance to the EU TGD, for all PAHs with a log Kow > 5 an additional factor of 10 is applied to the PNEC<sub>soil</sub> in case no experimental data are available and by extension the equilibrium partitioning approach is used. The risk assessment is based on the local concentration for terrestrial compartment without taking the regional background concentration into account.

#### 3.3.3.1 Production

Substance/Site	1	3	4	5	6	7	8	9
Naphthalene	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Acenaphthene	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Acenaphthylene	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Fluorene	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Anthracene	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Phenanthrene	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Fluoranthene	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Pyrene	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

Table 3.29 Clocal/PNEC for agricultural soil for the different CTPHT production sites.

Substance/Site	1	3	4	5	6	7	8	9
Benzo(a)anthracene	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Chrysene	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Benzo(a)pyrene	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Benzo(b)fluoranthene	0.3	0.2	0.1	0.0	0.1	0.1	0.2	0.2
Benzo(k)fluoranthene	0.1	0.1	0.0	0.1	0.1	0.0	0.1	0.0
Benzo(ghi)perylene	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Dibenzo(a,h)anthracene	0.4	0.3	0.1	0.2	0.2	0.1	0.3	0.3
Indeno(1,2,3-cd)pyrene	0.1	0.1	0.0	0.1	0.0	0.0	0.1	0.1
Sum PAH	0.95	0.69	0.2	0.5	0.5	0.2	0.7	0.5

#### 3.3.3.2

# Industrial use/processing

Table 3.30 Clocal/PNEC for agricultural soil and grassland for the ferro-alloy and graphite industry.

	agricult	tural soil
Substance/Scenario	Ferro-Alloy	Graphite
Naphthalene	0.0	0.0
Acenaphthene	0.0	0.0
Acenaphthylene	0.0	0.0
Fluorene	0.0	0.0
Anthracene	0.0	0.0
Phenanthrene	0.0	0.0
Fluoranthene	0.0	0.0
Pyrene	0.0	0.0
Benzo(a)anthracene	0.1	0.1
Chrysene	0.2	0.4
Benzo(a)pyrene	0.2	0.0
Benzo(b)fluoranthene	0.7	0.5
Benzo(k)fluoranthene	-	-
Benzo(ghi)perylene	0.3	0.2
Dibenzo(a,h)anthracene	0.5	0.3
Indeno(1,2,3-cd)pyrene	0.5	0.3
Sum of PAH	2.6	1.7

See for a description of the other scenarios table 3.73. graphite: production of graphite electrodes (including paste preparation using a wet process for cooling)

Use cat.	Site	Naphthalene	Acenaphthene	Acenaphthylene	Fluorene	Anthracene	Phenanthrene	Fluoranthene	Pyrene	Benz(a)anthracene	Chrysene	Benzo(a)pyrene	Benzo(b)fluoranthene	Benzo(k)fluoranthene	Benzo(ghi)perylene	Dibenzo(a,h)anthracene	Indeno(1,2,3-cd)pyrene	Total Clocal/PNEC
VSS II	S1	6.7E-04	3.6E-03	1.1E-03	1.3E-03	3.2E-03	2.0E-03	3.8E-03	3.3E-03	4.3E-02	1.4E-01	1.4E-01	5.2E-01		2.7E-01	3.7E-01	3.8E-01	1.9
VSS II	S3	1.7E-03	9.3E-03	2.9E-03	3.4E-03	8.2E-03	5.2E-03	9.8E-03	8.4E-03	1.1E-01	3.7E-01	3.7E-01	1.3E+00		7.0E-01	9.6E-01	9.9E-01	4.9
VSS II	S4	1.8E-03		3.1E-03						P location of control of					7.5E-01	1.0E+00	1.1E+00	5.2
VSS I	S5	1.9E-03	1.0E-02	3.2E-03	3.7E-03	6.4E-03	2.4E-03	4.1E-03	5.3E-03	1.1E-01	3.8E-01	4.1E-01	2.0E+00		9.3E-01	5.4E-01	1.1E+00	5.5
VSS I	S6	1.8E-03	1.0E-02	3.1E-03	3.5E-03	6.1E-03	2.3E-03	4.0E-03	5.1E-03	1.1E-01	3.7E-01	4.0E-01	1.9E+00		9.0E-01	5.2E-01	1.1E+00	5.3
Anode I	PA1	7.0E-04	3.4E-03	2.1E-05	7.9E-04	5.5E-03	2.3E-03	4.0E-03	3.8E-03	7.8E-02	2.6E-01	1.1E-01	9.3E-01		3.2E-01	1.1E+00	4.5E-01	3.2
Anode I	PA2	3.0E-04	1.4E-03	8.9E-06	3.4E-04	2.3E-03	9.7E-04	1.7E-03	1.6E-03	3.3E-02	1.1E-01	4.5E-02	3.9E-01		1.4E-01	4.6E-01	1.9E-01	1.4
Anode I	PA3	2.7E-07	1.3E-06	8.0E-09	3.1E-07	2.1E-06	8.8E-07	1.5E-06	1.5E-06	3.0E-05	1.0E-04	4.1E-05	3.6E-04		1.2E-04	4.2E-04	1.7E-04	0.001
Anode I	PA4	3.1E-05	1.5E-04	9.2E-07	3.5E-05	2.4E-04	1.0E-04	1.8E-04	1.7E-04	3.4E-03	1.2E-02	4.7E-03	4.1E-02		1.4E-02	4.8E-02	2.0E-02	0.14
Anode I	PA5	1.9E-04	9.2E-04	5.6E-06	2.1E-04	1.5E-03	6.1E-04	1.1E-03	1.0E-03	2.1E-02	7.1E-02	2.9E-02	2.5E-01		8.7E-02	2.9E-01	1.2E-01	0.9
Anode I	PA6	6,7E-04	3,3E-03	2,0E-05	7,6E-04	5,3E-03	2,2E-03	3,8E-03	3,6E-03	7,4E-02	2,5E-01	1,0E-01	8,9E-01		3,1E-01	1,0E+00	4,3E-01	3,1E+00
Anode I	PA6	1.8E-03	8.8E-03	5.4E-05	2.1E-03	1.4E-02	5.9E-03	1.0E-02	9.8E-03	2.0E-01	6.8E-01	2.8E-01	2.4E+00		8.4E-01	2.8E+00	1.2E+00	8.4
Anode I	PA7	2.8E-05	1.3E-04	8.3E-07	3.1E-05	2.2E-04	9.0E-05	1.6E-04	1.5E-04	3.1E-03	1.0E-02	4.2E-03	3.7E-02		1.3E-02	4.3E-02	1.8E-02	0.1
Anode I	PA8	6.7E-06	3.3E-05	2.0E-07	7.6E-06	5.3E-05	2.2E-05	3.8E-05	3.6E-05	7.5E-04	2.5E-03	1.0E-03	8.9E-03		3.1E-03	1.0E-02	4.3E-03	0.031
Anode I	PA9	1.6E-02	7.7E-02	4.7E-04	1.8E-02	1.2E-01	5.1E-02	9.0E-02	8.5E-02	1.7E+00	5.9E+00	2.4E+00	2.1E+01		7.3E+00	2.4E+01	1.0E+01	73
Anode I	PA10	1.7E-04	8.5E-04	5.2E-06	2.0E-04	1.4E-03	5.7E-04	1.0E-03	9.5E-04	1.9E-02	6.6E-02	2.7E-02	2.3E-01		8.1E-02	2.7E-01	1.1E-01	0.8
Anode I	PA11	6.7E-04	3.3E-03	2.0E-05	7.6E-04	5.3E-03	2.2E-03	3.8E-03	3.6E-03	7.4E-02	2.5E-01	1.0E-01	8.9E-01		3.1E-01	1.0E+00	4.3E-01	3.1
Anode I	PA12 <sup>1)</sup>	1.9E-05	9.2E-05	5.6E-07	2.1E-05	1.5E-04	6.1E-05	1.1E-04	1.0E-04	2.1E-03	7.1E-03	2.9E-03	2.5E-02		8.7E-03	2.9E-02	1.2E-02	0.09
Anode I	PA13	2.4E-03	1.2E-02	7.2E-05	2.7E-03	1.9E-02	7.9E-03	1.4E-02	1.3E-02	2.7E-01	9.1E-01	3.7E-01	3.2E+00		1.1E+00	3.7E+00	1.6E+00	11
Anode I	PA14	1.8E-03	8.8E-03	5.4E-05	2.1E-03	1.4E-02	5.9E-03	1.0E-02	9.8E-03	2.0E-01	6.8E-01	2.8E-01	2.4E+00		8.4E-01	2.8E+00	1.2E+00	8.4
Anode I	PA15	8.1E-07	3.9E-06	2.4E-08	9.2E-07	6.4E-06	2.6E-06	4.6E-06	4.4E-06	9.0E-05	3.0E-04	1.2E-04	1.1E-03		3.7E-04	1.2E-03	5.2E-04	0.004
Anode I	A1 <sup>1)</sup>	9.9E-03	4.8E-02	3.0E-04	1.1E-02	7.8E-02	3.2E-02	5.6E-02	5.3E-02	1.1E+00	3.7E+00	1.5E+00	1.3E+01		4.5E+00	1.5E+01	6.3E+00	45.8

#### Table 3.31 CLocal/PNEC agricultural soil at primary aluminium production and anode baking sites.

## 3.3.3.3 Regional background in soil

Based on the mean values for arable land, grassland, forest and urban soil there is a potential risk for soil organism (see Table 3.32).

land	grassland	Forest soil	Urban soil
0.01	0.00	0.03	0.04
0.06	0.01	0.01	0.06
0.25	0.58	0.05	1.50
0.00	0.00	0.01	0.02
0.01	0.01	0.03	0.11
0.02	0.01	0.07	0.45
0.04	0.03	0.08	0.54
0.04	0.03	0.07	0.59
0.49	0.33	0.54	5.53
0.40	0.38	2.13	5.05
0.12	0.12	0.56	1.63
0.04	0.07	0.69	0.87
0.34	0.36	0.74	6.60
0.12	0.11	0.63	2.98
0.20	0.19	0.28	1.02
0.11	0.16	0.36	2.18
1.89	2.05	4.37	24.61
	0.06           0.25           0.00           0.01           0.02           0.04           0.04           0.49           0.40           0.12           0.04           0.34           0.12           0.20           0.11	0.06         0.01           0.25         0.58           0.00         0.00           0.01         0.01           0.02         0.01           0.02         0.01           0.04         0.03           0.49         0.33           0.40         0.38           0.12         0.12           0.04         0.07           0.34         0.36           0.12         0.11           0.20         0.19           0.11         0.16	$\begin{array}{ c c c c c c c c c c c c c c c c c c c$

Table 3.32 Ratio between the background concentration in different soils presented by Wilcke (2000) PNEC for soil organism

## 3.3.4 Atmosphere

Due to the lack of data, no PNEC has been established for the atmospheric compartment. In the risk assessment for man indirectly exposed to the environment the exposure to air concentrations in the vicinity of the different plants is considered. It is to be expected that any precautions necessary to limit that risk will also be protective for wild life.

#### 3.3.5 Secondary poisoning

In the absence of sufficient toxicity data, a PNECoral for none of the PAHs can be derived. The risk assessment is also hampered by the lack of sufficient information on the bioaccumulation potential in fish. Therefore, a realistic quantitative risk assessment for secondary poisoning for the PAHs can not be made.

CTPHT has been indentified as PBT and vPvB, as several PAHs, like B(a)P, are identified as PBT and/or vPvB substances. Therefore it is also not considered necessary to perform a full risk assessment for secondary poisoning, as companies already have to take the most effective measures to minimise the emission of PAHs to the environment with automatically will reduce the risk for secondary poisoning.

To illustrate the potential risk the following preliminary assessment for B(a)P is made:

All BCF values for fish were not considered reliable, although a value of 600 could be used as an upper limit. For mussels reliable BCF values are available which are on average around 100,000. Based on this value as a worst case estimate for mussel-eating birds and mammals, a concentration in the water phase of > 14 ng/l will lead to concentrations in mussels that exceed the preliminary PNEC oral of 1.4 mg/kg food, which is the case for some of the uses of CTPHT.

It should be noted that the PNEC for aquatic compartment is 22 ng B(a)P/l, indicating that it might also be protective for secondary poisoning.

#### **3.3.6 PBT** assessment

Based on the following information CTPHT meets the P, vP, B, vB and T criteria and hence is considered as a PBT and vPvB substance.

- Most of the PAHs in CTPHT have a  $DT_{50}$  value both in soil and sediment > 125 days.
- The BCF values for fluorene, anthracene, phenanthrene, fluoranthene and pyrene were measured > 2000. For anthracene, phenanthrene and fluoranthene the BCF values were > 5000.
- The aquatic NOEC of all EPA 16 PAHs are < 0.01 mg/l
- Most of the (higher molecular) PAHs are present in CTPHT in more than 0.1%.

## 3.3.7 Areas of uncertainty in the environmental risk assessment

#### Adsorption and bioavailability

Uncertainties exist towards the sorption and bioavailability of PAHs. As highlighted in section 3.1.4.2.1, PAHs can be sorbed to amorphous organic matter (traditionally referred to as organic carbon), to black carbon BC and other carbonaceous geosorbents (CG), which have differential adsorption properties. Consequently, the Koc value can show a high degree of variation. Hence, the fate and behaviour of PAHs will depend on how PAHs are emitted (gas or particle bound), the characteristics of particles to which the PAHs are bound and the characteristics of the soil or sediment. In addition, sorption of PAHs will also depend on the concentration. The results of the research on the particle affinity of PAHs associated with coal tar pitch (Naes and Ruus, 2007) suggests that the Koc values in sediment in the vicinity of aluminium smelters are higher than those used in the present risk assessment. However, no clear relationship could be found between the characteristics of the sediment and Koc values measured and no difference with clean sediment was demonstrated, which hamper the implementation of these results in a generic approach.

In addition, the effect of the sorption on carbonaceous materials on uptake of PAHs by biota is still unclear. Where some studies show that uptake of PAHs is significantly decreased in the presence of carbonaceous materials, others show that this effect is not present or negligible.

It should be noted that in the present risk assessment, the impact of a change in Koc values will be limited as for most high molecular PAHs both the PEC and the PNEC are derived by using equilibrium partitioning. Consequently, by taking a different Koc value both values will change in the same extent and in concomitant the PEC : PNEC ratio will remain the same. It should also be noted that most of the high molecular PAHs are emitted particle-bound and as such contaminate sediment via direct deposition without dissolving first and partitioning to sediment, successively.

Therefore, for a refinement of the risk assessment monitoring data for all relevant sites are needed together with information on the composition of the organic material present. In addition, it is also crucial to obtain toxicity data for sediment and soil dwelling organism for the high molecular PAHs preferable in relation to the binding to various organic carbon material present.

#### Ageing

The bioavailability may also depend on the age of the particles. Several studies indicate that bioavailability decreases with increasing residence time. The extent of aging seems to be dependent on the organic carbon content. As no ageing effect were found at an organic carbon content of standard soil (2%) and the fact that this phenomenon is not sufficiently quantified, aging is as yet not considered in the risk assessment.

#### Information on the release of the individual PAHs

Another factor of uncertainty is the emission estimated for the individual PAHs. In most cases the emissions are reported as B(a)P only or total PAHs and not specified for the individual PAHs. As been described in section 3.1.3.3 for each process one general emission profile is used to estimate the emission of the single PAHs. Consequently, the actual emission of the PAHs could deviate.

#### Prediction air concentration

The measured data shows that the modelled air concentration can be considered as a conservative prediction. A more accurate measure of air concentration is difficult to make with the generic tools available and can only be obtained by local measurements taking into account the site-specific conditions.





4

# 5 **RESULTS**

# 5.1 ENVIRONMENT

#### Aquatic compartment (incl. sediment)

Based on the risk characterisation ratios derived above it can be concluded that a risk to water and sediment could exist for some CTPHT production sites and at sites using CTPHT for anode, electrode baking and in Søderberg anodes.

## CTPHT production:

**Conclusion (i) on hold** applies for production site 9 as the sum of the PEC/PNEC for all PAHs is > 1 for sediment.

To refine the PNEC<sub>sediment</sub> there is need for information on the toxicity for sediment dwelling organisms of benzo(a)anthracene, chrysene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(ghi)perylene, dibenzo(a,h)anthracene and indeno(1,2,3-cd)pyrene. (production site 9).

#### **Conclusion (ii)** applies to production site 1, 3, 5, 6, 7 and 8.

**Conclusion (iii)** applies for production site 4. For site 4 there is a need for limiting the risk beside the risk reduction measures which are already being applied, as for this site the Clocal/PNEC<sub>water</sub> ratios are higher than 1 based on PAHs for which the PNEC<sub>water</sub> is derived from a complete data set and the local concentrations were based on site specific emission data.

#### industrial use/processing:

**Conclusion** (i) applies to industry using CTPHT for the production of binder for coal briquetting, clay pigeons and heavy duty corrosion protection (see section 2.2.3). Industry is requested to provide information on the release of PAHs from production and use of these types of use.

**Conclusion (ii)** applies to the following primary aluminium plants: plants S5 and S6 (using Søderberg anodes) and plants PA3, PA4, PA6, PA8 and PA9 (using prebakes anodes with an anode production on-site), as they do not emit to water. Conclusion (ii) also applies to site PA15 where the PEC/PNEC ratio is below 1 for water and sediment. Furthermore conclusion (ii) applies for all primary aluminium plants using prebaked anodes without an anode plant on site and the graphite industry as the emission of PAHs is negligible. No further information is considered necessary.

**Conclusion (iii)** applies to the primary aluminium plants S1, S3, S4, PA1, PA2, PA5, PA7, PA10, PA11, PA12, PA13, PA14, and anode production site A1 with respect to surface water and sediment, as here the Clocal/PNEC ratios are higher than 1, even based on PAHs for which a complete data set is available and the calculated local concentrations are based on measured emission data. More information on the chronic toxicity of the PAHs mentioned above could be considered for further refinement of the PNECs to determine the extent in which the emission to water have to be reduced to exclude a risk for the aquatic environment. There are also indications that PAH in sediments around aluminium smelters might be less

bioavailable than the extent calculated by the methods used. More research is needed to elucidate this aspect.

**Conclusion** (iii) applies to the ferro alloy industry. This use category has been assessed using emission rates to water obtained from literature and emission profiles based on those used for VSS. Using the available information to estimate the emission to water Clocal/PNEC ratios are higher than 1 for PAHs for which a complete data set is available for water (fluoranthene) and sediment (benzo(a)anthracene).Terrestrial compartment

## STP

**Conclusion (i)** applies to industry using CTPHT for the production of binder for coal briquetting, clay pigeons and heavy duty corrosion protection (see section 2.2.3). Industry is requested to provide information on the release of PAHs from production and use of these types of use.

**Conclusion (ii)** applies to all CTPHT production sites and the main downstream users assessed in the RAR.

Terrestrial compartment

## CTPHT production

Conclusion (ii) applies to all CTPHT production sites.

#### Industrial use/processing:

**Conclusion (i) on hold** applies to the ferro-alloy industry, graphite industry, anode production industry (including prebake primary aluminium industry with on-site anode production plant) and primary aluminium industry using Søderberg technology others than mentioned above as the sum of Clocal/PNEC is higher than 1 mainly based on PNECs which were determined with equilibrium partitioning or where additional toxicity data could refine the PNEC. Further testing is needed to elucidate the chronic toxicity for soil organisms of benz(a)anthracene<sup>2</sup> chrysene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, dibenzo(a,h)anthracene and indeno(1,2,3-cd)pyrene, benzo(ghi)perylene.

For site PA2, S3 and S4 measured B(a)P concentrations in air were more than a factor of 10 lower than the predicted concentrations. As the contamination of soil at these sites is determined by atmospheric deposition, this would mean that the PAH concentrations in soil will deviate in the same extent, provided that the measurements are reliable and representative. The PEC/PNEC ratio for both sites is < 10. Consequently, the risk for soil organisms might also be low.

**Conclusion** (i) also applies to industry using CTPHT for the production of binder for coal briquetting, clay pigeons and heavy duty corrosion protection (see section 2.2.3). Industry is requested to provide information on the release of PAHs from production and use of these types of use.

 $<sup>^{2}</sup>$  The PNEC for benz(a)anthracene is based on an high extrapolation factor to normalise it from 90 to 2% o.c. This might be overconservative

**Conclusion** (ii) applies to the primary aluminium plant PA3, PA4, PA5 PA7, PA8, PA10, PA12 and PA15. Conclusion (ii) also applies to all primary aluminium plants using prebaked anodes without an anode plant on site as the emission of PAHs is negligible.

#### Atmosphere

Due to the lack of data, no PNEC has been established for the atmospheric compartment. In the risk assessment for man indirectly exposed to the environment the exposure to air concentrations in the vicinity of the different plants is considered. It is to be expected that any precautions necessary to limit that risk will also be protective for wild life.

#### Secondary poisoning

In the absence of sufficient toxicity data, a PNECoral for none of the PAHs can be derived. The risk assessment is also hampered by the lack of sufficient information on the bioaccumulation potential in fish. Therefore, a realistic quantitative risk assessment for secondary poisoning for the PAHs can not be made.

CTPHT has been indentified as PBT and vPvB, as several PAHs, like B(a)P, are identified as PBT and/or vPvB substances. Therefore it is also not considered necessary to perform a full risk assessment for secondary poisoning, as companies already have to take the most effective measures to minimise the emission of PAHs to the environment which automatically will reduce the risk for secondary poisoning.

**HUMAN HEALTH** 

5.2

RAPPORTEUR[NETHERLANDS]

# COAL TAR PITCH, HIGH TEMPERATURE

CAS No: 65996-93-2

EINECS No: 266-028-2

## SUMMARY RISK ASSESSMENT REPORT

Final report, April 2008

The Netherlands

Rapporteur for the risk assessment of Coal Tar Pitch high temperature is the Ministry of Housing, Spatial Planning and the Environment (VROM) and the Ministry of Social Affairs and Employment (SZW), in consultation with the Ministry of Public Health, Welfare and Sport (VWS). Responsible for the risk evaluation and subsequently for the contents of this report is the rapporteur.

The scientific work on this report has been prepared by the Netherlands Organization for Applied Scientific Research (TNO) and the National Institute of Public Health and Environment (RIVM), by order of the rapporteur.

Contact point: Chemical Substances Bureau P.O. Box 1 3720 BA Bilthoven The Netherlands Date of Last Literature Search: Review of report by MS Technical Experts finalised: Final report:

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# PREFACE

The report provides the comprehensive risk assessment of the substance coal tar pitch, high temperature (CTP(ht)). It has been prepared by the Netherlands in the frame of Council Regulation (EEC) No. 793/93 on the evaluation and control of the risks of existing substances. For detailed information on the risk assessment principles and procedures followed, the underlying data and the literature references, the reader is referred to the original risk assessment report that can be obtained from European Chemicals Bureau<sup>1</sup>. The present summary report should preferably not be used for citation purposes.



<sup>&</sup>lt;sup>1</sup> European chemicals Bureau – Existing Chemicals - http://ecb.ei.jrc.it

# CONTENTS

1	GEN	NERAL SUBSTANCE INFORMATION	2
2	GEN	NERAL INFORMATION ON EXPOSURE	6
3	ENV	VIRONMENT	7
4	HUI	MAN HEALTH	8
	4.1	EXPOSURE	8 11
	4.2	EFFECTS ASSESSEMENT	
	4.3	RISK CHARACTERISATION         4.3.1 Workplace         4.3.2 Consumers         4.3.3 Man indirectly exposed via the environment	17 29
	4.4	HUMAN HEALTH (PHYSICO-CHEMICAL PROPERTIES)	32
5	OVI	ERALL RESULTS OF THE RISK ASSESSMENT	33
	5.1	ENVIRONMENT	33
	5.2	HUMAN HEALTH	33
G	LOSS	SARY	35

# **1 GENERAL SUBSTANCE INFORMATION**

#### Identification of the substance

This RAR concerns only Pitch, coal tar, high temperature (CTP(ht)) with CAS # 65996-93-2. Coal tar pitch high temperature (CTP(ht)) is the solid fraction produced during the distillation of coal tars. Coal tars are condensation products obtained during the production of coke an/or natural gas through the destructive distillation of coal, called carbonisation or coking. The composition and properties of a coal tar (and coal tar pitch derived thereof) depend mainly on the temperature of carbonisation and, to a lesser extent, on the nature of the coal used as feedstock. High-temperature coal tars (CAS # 65996-89-6) is defined in EC (1976) as 'the condensation product obtained by cooling, to approximately ambient temperature, of the gas evolved in the high temperature (greater than 700 °C (1292 °F)) destructive distillation of coal. A black viscous liquid denser than water. Composed primarily of a complex mixture of condensed ring aromatic hydrocarbons. May contain minor amounts of phenolic compounds and aromatic nitrogen bases'. The distillation of high-temperature coal tars results in tar oils (including naphthalene oil, creosote oil, anthracene oil, and creosote) and a solid fraction (coal tar pitch high temperature). When CTP(ht) is heated, Coal tar pitch volatiles (CTPV(ht)) are released. However, the term CTPV is not only used for volatiles released when coal tar pitch (CTP) is heated, but also for volatiles released when coal tar or it's products are heated.

CTP and related substances like CTPV, creosotes and tars are complex and have variable compositions. CTP is a complex hydrocarbon mixture consisting of three- to seven-membered condensed aromatic hydrocarbons and of high molecular weight compounds. It is a shiny, dark brown to black solid produced during the distillation of coal tars. Coal tars are the condensation products obtained by cooling of the gas evolved in the carbonisation of coal. The relative proportions of the components in the mixture of CTP are complex and variable and dependent on whether low temperature or high temperature processes were involved in the production of the tar. Over 400 compounds have been identified in coal tars, and probably as many as 10 000 are actually present. The number of compounds present in most coal tar pitches is estimated in the thousands. Because of variation in source materials and manufacturing processes, including different temperatures and times of carbonization, no two coal tars or pitches are chemically identical. In general, however, approximately 80% of the total carbon present in coal tars exists in aromatic form. Volatile fumes, designated CTPV, are released when coal tar, CTP, or their products, are heated.

Because of the complexity and variability of CTP(ht), great difficulties have been encountered in assessing exposure in the epidemiological studies. Generally, the presence of coal tars and derived products is detected by the presence of their specific constituents, especially CTPV and Polycyclic Aromatic Hydrocarbons (PAHs), in the air. Since PAHs are among the major components of CTP(ht), and some individual PAHs are proven animal carcinogens, PAH levels are considered as a measure of exposure to CTP(ht). Existing exposure information suggested that the airborne concentration of BaP correlates well with the concentration of total PAHs for most workplaces. Based on these findings and the availability of exposure data, the Working group on Assessment of Toxic Chemicals (WATCH) from the HSE has pinpointed BaP as the most suitable marker for assessing exposure to PAHs<sup>2</sup> for Coal Tar Pitch Volatile (CTPV) industries. As such, in conducting this exposure assessment to CTP(ht), exposure to BaP has been adopted as the primary indicator.

 $<sup>^2</sup>$  These are 11 PAHs identified by HSE as having the greatest carcinogenic potential of the PAH family of compounds.

The database on possible health hazards induced by CTP(ht) is rather limited, and it is, therefore, hardly possible to perform a full risk assessment for all the required endpoints. There is, though, quite some information from epidemiological studies on workers in specific industrial processes where CTP(ht) is produced and/or used, that indicate that carcinogenicity is a striking hazard associated with CTP(ht). This is attributed to the presence of the PAHs in CTP(ht), as indicated above. Given the uncertainties with respect to the effects of other chemical constituents of CTP(ht) (and related substances), it is not completely sure that carcinogenicity is the only relevant effect of CTP(ht). However, as it is also noted that the carcinogenic potencies of these PAHs are quite high, limitation of the risks for cancer will automatically reduce the risk for any other possible effect, quite possibly even to zero. Therefore, in spite of the limited database, it is decided that the focus will be on the carcinogenic and mutagenic properties, using the best-studied PAH BaP as a guidance substance.

CAS Number:	65996-93-2 <sup>3</sup>
EINECS Number:	266-028-2
IUPAC Name:	not applicable
Molecular formula:	not applicable; coal tar pitch is a complex hydrocarbon mixture
	consisting of three- to seven-membered condensed ring aromatic
	hydrocarbons (90%) and of high molecular weight compounds. Besides
	these polycyclic aromatic hydrocarbons and their (poly)methylated
	derivatives, it contains heterocyclic compounds and benzocarbazoles.
Structural formula:	not applicable
Molecular weight:	not applicable
Synonyms:	anode pitch, binder pitch, clay pidgeon binder, electrode pitch, hard
	pitch, impregnating pitch, pitch, soft pitch, vacuum pitch

#### **Purity/impurities, additives**

Purity:	not applicable
Impurity:	not applicable
Additives:	not applicable

#### **Physico-chemical properties**

The physico-chemical properties of high-temperature coal tar pitch are listed in Table 1.1.

<sup>&</sup>lt;sup>3</sup> The rapporteur notices that the CAS registry number is not used by CAS. The effect may be that the registry number may have been applied to records that deal with (coal) tar pitches in a more general sense in files like TOXLINE and NIOSHTIC, whereas relevant records in files like MEDLINE and CA will not be retrieved due to absence of the registry number in indexing. Therefore additional searches on "coal tar pitch" and "coal-tar pitch" were performed in MEDLINE, TOXLINE and CURRENT CONTENTS. However, it is still possible some relevant data are not found with these searches and therefore not discussed in this RAR

Property	Value	Comment / Reference
Physical state	black solid	
Melting point	65-150°C	softening range; CCSG (2006a)
Boiling point	>360°C	at 1013 hPa
Density	1.15-1.4 g/cm <sup>3</sup>	at 20°C; ASTM D 71; CCSG (2006a)
Vapour pressure	<0.1 Pa	at 20°C
	<10 Pa	at 200°C ; OECD 104; CCSG (2006a)
Water solubility	<1 mg/L at 20°C	No test reports were available. Data are from data sheets (ACCCI, 1992; van den Bosch, 1997) (see also HEDSET).
Partition coefficient	-	not applicable
n-octanol/water (log value)		
Flash point	>250°C	ISO 2719; CCSG (2006a)
Flammability	non flammable	No test reports were available. Data are from data sheets (ACCCI, 1992; van den Bosch, 1997) (see also HEDSET).
Auto ignition temperature	>450°C	at 1013 hPa; DIN 51794; CCSG (2006a)
Explosive properties	not explosive	CCSG (2006a)
Oxidizing properties	not oxidising	CCSG (2006a)

 Table 1.1 Summary of physico-chemical properties of CTP(ht)

## Conclusion

All relevant physico-chemical data were available. None of them are substantiated with test reports. However, the data are considered as sufficiently reliable to fulfil the Annex VIIA requirements.

## **Classification and labelling**

Current Classification according to Annex I:

Classification	:	Carc. Cat. 2
Symbol	:	Т
R-phrases	:	45
S-phrases	:	53-45
Notes	:	H (pitch)

Proposed classification

Decisions by the Technical Committee on Classification and Labelling (TC-C&L) in October 2006 for physical and human health endpoints.

Classification	:	Mut. Cat 2; Carc. Cat. 1; Repro. Cat. 2.
Symbol	:	T; Xi
R-phrases	:	41, 43, 45, 46, 60-61
S-phrases	:	53 - 45
Notes	:	H (pitch)

There are insufficient data available on the sensitising properties, mutagenicity and toxicity for reproduction of CTP(ht) itself. However, it is proposed to classify CTP(ht) as a skin sensitiser, a category 2 mutagen, and as toxic to reproduction (category 2), because CTP(ht) contains substances which are classified as such (see 1.7.2.1 of Annex VI of Directive 67/548).



# 2 GENERAL INFORMATION ON EXPOSURE



# **3 ENVIRONMENT**



# 4 HUMAN HEALTH

## 4.1 EXPOSURE

#### 4.1.1 Occupational exposure

CTP(ht) (Coal Tar Pitch high temperature) is a complex hydrocarbon produced during distillation of coal tars. To assess exposure to CTP(ht), benzo(a)pyrene (BaP) is used as the primary marker. The estimated proportion of BaP in CTP(ht) is 1%. Occupational exposure assessment has been conducted for the production of CTP(ht) in a coal tar distillation facility (most prevalent source of exposure), use as a binder and impregnation of electrodes, use as a binder in the asphalt industry and in refractories. Additionally, exposure assessment has been conducted, if possible, for the following exposure scenarios which represent a small part of the overall use of CTP(ht): use as a binder for active carbon, heavy duty corrosion protection, coal briquetting and clay pigeons.

Operators, cleaners, drivers and quality control annalists may be exposed to CTP(ht) in coal tar distillation plants during all activities of production. Based on measured inhalation data "handling of solid pitch" and "tar processing and handling of liquid pitch" are identified as two high exposure sub-scenarios for both inhalation and dermal exposure assessment. Dermal exposure during "tar processing and handling of liquid pitch" is estimated to be negligible due to the high temperature of the liquid pitch.

CTP(ht) is used as a binding agent for electrodes in the aluminium industry. In many different tasks such as stud-pulling, rack-raising, mounting of flaints and adding of anode paste, the exposure can be considerable. However, exposure concentrations are dependent on the technology used and the age of the plant. Therefore, four sub-scenarios have been identified: Søderberg potrooms (not modernised and modernised), anode bake plants and paste plants, for which inhalation and dermal exposure estimates have been assessed. If only (hot) liquid pitch is used dermal exposure is estimated to be negligible.

There is potential for inhalation and dermal exposure to CTP(ht) particulates and vapour at electrode paste plants where CTP(ht) is used as a binding agent during impregnation of electrodes with liquid pitch. Inhalation exposures are estimated for the higher exposed group: workers in mixing/grinding, baking and impregnation and maintenance and repair staff. Daily dermal exposure due to handling of hot CTP(ht) is estimated to be negligible. Workers in other areas will have lower exposures.

Workers in the road construction industry carry out road paving and recycling/resurfacing activities. These individuals can be exposed, via the skin and via inhalation, to CTPV (Coal tar pitch volatiles), when CTP(ht) is used as a binder. It should be noted that the estimate for inhalation exposure is based on one source only and the data to estimate current exposure is outdated. The extraction of data from a graph includes some degree of uncertainty.

During the laying down of a new roof or the repair of a roof with patches hot CTP(ht) is used. Volatile matter emanates from the heated asphalt resulting in possible inhalation and dermal exposure to CTP(ht) or CTPV. Removal of an old roof using hand tools may also result in inhalation and dermal exposure.

Refractories are materials that are found in use in many industries for lining boilers, kilns and furnaces of all kinds, but the largest percentage are used in manufacture of metals. Inhalation exposure and dermal exposure to CTP(ht) in refractories may occur during production and use. There is one source of inhalation exposure data for the use of CTP(ht) as a binding agent for refractories. Due to the high temperatures in the use of refractories, dermal exposure is expected not to occur repeatedly in this part of the scenario.

No measured information is available on the use of CTP(ht) as a binding agent for active carbon. At present, there is insufficient information with regard to process details and proportion of CTP(ht) used in the binder to allow for the derivation of exposure estimates using EASE modelling.

Hot-applied coal tar enamel coatings are used in heavy-duty corrosion protection. Coal tar enamels are formulated from refined CTP(ht). Inhalation exposure to CTPV(ht) is expected with the coating operator, paper latcher, breakout man, holiday patcher, end finisher and the kettle tender. Dermal exposure is expected to be low due to the high operating temperature of the process. Where the coal tar enamel may have spilled dermal exposure is expected to be incidental. Based on measured data coating operators and other workers are defined as two distinctive exposure groups for which exposure values are assessed.

During coal briquetting fine coal is compressed to form a 'patent fuel' or briquette where CTP(ht) is used as a binder. During the whole process there is potential for inhalation and dermal exposure. Based on measured data exposure values are assessed for two groups of workers namely cleaners and other workers.

In an artificial shooting target factory, targets (clay pigeons) are made of chalk (70-75%) and a basic binder (23-30%) like CTP(ht). There is potential for dermal and inhalation exposure during packing where packers may handle nude targets or painted targets without gloves, maintenance of presses and conveyor belts and during tasks performed by the foreman. Indications show that this scenario is a minor market.

The estimated exposure levels for CTP(ht) are presented in **Table 4.1**.

## Table 4.1 Summary of occupational exposure to CTP(ht); exposure expresses using BaP as primary indicator

Scenario/sub scenario	Estimated inhalation exposure level (µg/m)							Skin exposure (mg/day)	
	Full-shift (8 hour time weighted average)				Short term		Full-Shift		
	Typical	Method	RWC	Method	RWC	Method	RWC	Method	
1. Production of Coal Tar Pitch (ht) in tar distillation plants									
a. Tar processing and handling of liquid pitch	0.1	measured	0.4	measured	0.8	measured	negligible	modelled	
b. Handling of solid pitch	2.6	measured	3.6	measured	7.2	measured	0.5	modelled	
2. Use – Binder for electrodes									
i. aluminium industry									
a. Søderberg potrooms (not modernised)	1	measured	8	measured	17	measured	0.5	modelled	
b. Søderberg potrooms (modernised)	0.20	measured	0.35	measured	0.75	measured	0.5	modelled	
c. Anode bake plants	0.15	measured	0.40	measured	1.40	measured	0.5	modelled	
d. Paste plants	0.08	measured	0.15	measured	0.30	measured	0.5	modelled	
ii. Graphite electrode paste plants									
a. Mixing and grinding; Baking; Maintenance	2	measured	7.5	measured	16	measured	negligible	modelled	
<ol><li>Use – Binder in the Asphalt Industry</li></ol>									
i Road construction	0.55	measured	1.2	measured	5	measured	100	modelled	
ii. Roofing	35	measured	60	measured	120	expert judg.	100	modelled	
4. Use – Binder for refractories									
a. Production of refractories	0.17	measured	3.5	measured	7	expert judg.	na	-	
b. Use of refractories	0.63	measured	23	measured	64	expert judg.	na		
5. Use - Binder for active carbon	na		na		na		na	-	
<ol><li>Use – Heavy duty corrosion protection</li></ol>									
a. Coating operators	23	measured	90	measured	120	measured	0.4	modelled	
b. other workers	6	measured	30	measured	50	measured	0.4	modelled	
7. Use – Binder in coal briquetting									
a Production	670	measured	1760	measured	2200	measured	10	modelled	
b. Cleaning	14	measured	40	measured	80	measured	0.6	modelled	
<ol><li>Use – Binder for clay pigeons operators/packers; foremen</li></ol>	1	measured	3	measured	6	measured	1	measured	

Notes to summary table:

The eight different occupational scenarios upon which exposure assessments were done are labelled 1, 2, 3 etc., the sub-scenarios are numbered

i, ii, etc., and the different workgroups under the scenarios or sub-scenarios, which have different levels of exposure are listed a, b etc.

RWC - reasonable worst case.

expert judg. - expert judgement



#### 4.1.2 Consumer exposure

Consumer use was not identified by industry, not in literature nor on the Internet. Therefore the exposure to consumers to CTP(ht) can be considered negligible.

#### 4.1.3 Man exposed indirectly via the environment

Like in the environmental risk assessment, the exposure to humans exposed via the environment will focus on the emission of PAHs on a local scale for production of coal tar pitch and the main applications (e.g. anode, aluminium, graphite electrode and ferro-alloy production), primarily because lower emissions for the other sources are expected. The emission of PAHs at coke ovens are not considered because coal tar is produced at this process. In Western Europe the use of coal tar pitch as use of a binder in road construction and in roofing will be discontinued. Milling of old road surfaces may still result in exposure to coal tar containing material.

Coal tar pitch (CTP) is a complex mixture of constituents of variable and partly unknown composition. The different constituents of CTP will show a different behaviour (fate) in the environment resulting in exposure of man through the environment to several constituents of CTP in a ratio which may be different from the ratio of these constituents in CTP itself.

The environmental exposure assessment was limited to 16 selected PAHs. In view of their differences in physical-chemical parameters, especially log Kow, the distribution of these different PAHs from the point sources will be different. The exposure to the different PAHs for humans exposed via the environment will thus occur via different routes, meaning that in principle the risk characterisation should be based on the effects of each individual component. However, as the composition of CTP is variable and unknown and the human health effects of the known individual components are mostly unknown, this is practically impossible. Therefore, as a practical solution benzo(a)pyrene (B(a)P) is chosen as the 'leading' PAH in establishing exposure for humans via the environment, because for this compound the largest amount of effects data is available and B(a)P can be considered one of the most toxic PAHs. For this reason the risk assessment will be focussed on the exposure to B(a)P. In case a risk is identified already for this one PAH, the other 15 PAHs will not be considered further.

The estimated concentrations of B(a)P in air and food and the resulting estimated human daily intake are given in **Table 4.2** and **Table 4.3**, respectively.

source	Air (ng/m <sup>3</sup> )	Root crops (µg/kg)	Leaf crops (µg/kg)	Meat (µg/kg)	Milk (µg/kg)	Drinking water (ng/L)
Production site	s					
1	7.7	0.81	19	43	14	0.09
3	5.5	0.58	13	31	9.7	0.06
4	2.0	0.21	4.8	11	3.5	1.9
5	4.9	0.52	12	27	8.6	0.06
6	4.1	0.43	9.9	23	7.2	0.05

Table 4.2 Estimated concentrations of Benzo(a)pyrene in air and food for humans

7	1.6	0.17	3.9	8.9	2.8	0.02
8	6.1	0.64	15	34	11	0.07
9	4.6	0.49	11	26	8.1	0.23
Downstream	users					
Ferro-alloy	56	5.9	140	310	99	0.65
Graphite	13	1.4	31	72	23	0.15
Primary alum	inium produ	uction and and	de baking fa	cilities		
S1	36	3.8	87	200	63	0.42
S3	92	9.7	220	510	160	1.1
S4	98	10	240	540	170	1.1
P7	2.9	0.31	7.0	16	5.1	0.0
S5	100	11	240	560	180	1.2
S6	98	10	240	540	170	1.1
PA1+S2	27	2.9	65	150	48	0.31
PA2	11	1.2	27	61	19	0.13
PA3	0.01	0.0	0.0	0.1	0.0	0.0
PA4	1.2	0.1	2.9	6.7	2.1	0.01
PA5	7.3	0.8	18	41	13	0.08
PA6	70	7.4	170	390	120	0.8
PA7	1.1	0.1	2.7	6.1	1.9	0.01
PA8	0.26	0.0	0.6	1.4	0.5	0.00
PA9	610	64	1500	3400	1100	7.0
PA10	6.8	0.7	16	38	12	0.08
PA11	26	2.7	63	140	46	0.30
PA12	0.73	0.1	1.8	4.1	1.3	0.12
PA13	94	9.9	230	520	170	10
PA14	70	7.4	170	390	120	0.81
PA15	0.031	0.0	0.1	0.2	0.1	0.0
A1	380	40	920	2100	670	115

Table 4.3 Esti	mated l	human	daily intake <sup>1</sup>	of Benzo(a)pyrene via environmental routes in
ng/kg bw/d				

Source	Air	Root crops	Leaf crops	Meat	Milk	Drinking water	Total
Production site	es			•			
1	2.2	4.5	320	180	110	0.00	620
3	1.6	3.2	230	130	77	0.02	440
4	0.6	1.2	83	48	28	2.2	160
5	1.4	2.8	200	120	69	0.02	390
6	1.2	2.4	170	98	58	0.01	330
7	0.5	0.9	66	38	22	0.01	130
8	1.7	3.5	250	150	86	0.02	490
9	1.3	2.7	190	110	65	0.26	370
Downstream u	isers						
Ferro-alloy	16	32	2300	1300	790	0.18	4500
Graphite	3.7	7.5	540	310	180	0.04	1000
Primary alumi	nium produ	ction and an	ode baking faci	lities			
S1	10	21	1500	860	510	0.12	2900
S3	26	53	3800	2200	1300	0.30	7400
S4	28	57	4000	2300	1400	0.32	7900
P7	0.8	1.7	120	69	41	0.01	230
S5	29	58	4100	2400	1400	0.33	8000
S6	28	57	400	2300	1400	0.32	7900
PA1+S2	7.7	16	1100	650	380	0.09	2200
PA2	3.1	6.4	450	260	150	0.04	880

PA3	0.00	0.01	0.41	0.24	0.14	0.00	0.80
PA4	0.34	0.70	50	29	17	0.00	96
PA5	2.1	4.2	300	170	100	0.02	590
PA6	20	41	2900	1700	980	0.23	5600
PA7	0.31	0.64	45	26	15	0.00	88
PA8	0.07	0.15	11	6.2	3.6	0.00	21
PA9	170	350	25000	15000	8600	2.01	49000
PA10	1.9	3.9	280	160	95	0.02	550
PA11	7.4	15	1100	620	370	0.09	2100
PA12	0.21	0.42	30	17	10	0.13	589
PA13	27	55	3900	2200	1300	11	7500
PA14	20	41	2900	1700	980	0.23	5600
PA15	0.01	0.02	1.3	0.74	0.43	0.00	2.5
A1	110	220	16000	9100	5300	130	31000

Regional exposure via the environment

Since many unintentional sources contribute to the total emission of PAHs into the environment, which by extension are not related to production and use of CTP(ht), the risk characterisation will only be focussed on the PAHs emitted by producers and downstream users of CTP(ht) on a local scale. To put this risk characterisation into perspective, the daily dose is also calculated for the regional background using monitoring data available for air and fresh water environment. No formal conclusions will be derived for the regional background.

## 4.2 EFFECTS ASSESSEMENT

The database on possible health hazards induced by CTP(ht) is rather limited, implicating that a full hazard assessment for all the required endpoints is not possible. There is, though, quite some information from epidemiological studies on workers in specific industrial processes where CTP(ht) is produced and/or used, that indicate that carcinogenicity is a striking hazard associated with CTP(ht). This is attributed to the presence of the PAHs in CTP(ht). Given the uncertainties with respect to the effects of other chemical constituents of CTP(ht) and related substances also exposed to, it is not completely sure that carcinogenicity is the only relevant effect of CTP(ht). However, as it is also noted that the carcinogenic potencies of these PAHs are quite high, limitation of the risks for cancer will automatically reduce the risk for any other possible effect, quite possibly even to zero. Therefore, in spite of the limited available data on non-carcinogenic properties of CTP(ht), it is decided that in this risk characterisation for CTP(ht) conclusions on risks and further testing for some endpoints will be subordinated to conclusions on risks based on carcinogenic and mutagenic properties, using the beststudied PAH BaP as a guidance substance.

In the data set animal as well as human studies are available. Some of the studies were not performed according to current standards, and were in some cases not suitable to be used in risk assessment.

There were no data available on the toxicokinetics of CTP(ht). Some information on the toxicokinetics of selected homocyclic polycyclic aromatic hydrocarbons was available. From these data, it was concluded that PAHs are lipophilic compounds that can be absorbed through the respiratory and gastrointestinal tract and the skin. After absorption, PAHs are widely distributed throughout the organism to almost all organs, especially the lipid-rich ones. They can cross the placenta and reach foetal tissues. The metabolism of PAHs can take place in the liver, respiratory tract, and the skin, and appears very complex leading to a variety of metabolites from a limited number of reaction types. Only a few metabolites are

toxicologically relevant. Most metabolic processes result in detoxification products that are excreted in urine and faeces. However, some pathways yield reactive compounds capable of binding to DNA and initiating tumour formation. Generally, the metabolism appears to be qualitatively similar with respect to cell or tissue type. However, large quantitative variations may occur between different cell types, tissues, and species caused by the inducibility and availability of enzyme systems, leading to differences in the susceptibility for the carcinogenic action of PAHs. Based on the calculated dermal absorption of ten different PAHs from dermally applied coal tar to pig-ears a dermal absorption of PAHs from CTP(ht) of 30% is taken forward to risk assessment. Since no data were available to allow a quantitative estimation of absorption after inhalation and oral exposure, for CTP(ht) default values of (in this case) 100% may be used for absorption of critical components via inhalation and oral exposure. It is emphasised though that these absorption rates are not used for consumer risk assessment, because of the absent of relevant identified exposures, and not for worker risk assessment, because both hazard- and exposure assessment are based on similar worker scenarios, i.e. include the combined specific inhalation and dermal exposure conditions.

From acute oral and dermal toxicity studies in experimental animals conducted according to EU guidelines, it is concluded that the substance does not need classification and labelling according to EC criteria (EC-Directive 2001/59/EC) for these exposure routes. No inhalation studies in animals were available. No human data were available on the acute toxicity.

Skin effects were observed in animals and humans after repeated exposure to CTP(V) or combined exposure to CTP(V) and sunlight. However, from the available animal and human data it is not possible to conclude whether the observed dermal effects are caused by irritation or/and sensitisation (photosensitisation or sensitisation after repeated exposure), therefore classification of CTP(ht) for skin irritation is not possible. In view of the human data on occupation exposure to CTP (fumes, volatiles and dust, not further specified) which show eye irritation and, after repeated exposure, chemosis of the conjunctiva, ulceration and infiltration of the cornea, deep staining of the cornea, and conjunctival discolouration and irritation, classification as 'irritant' with 'risk of serious damage to eyes (Xi, R41) is proposed. Sunlight aggravated irritating effects of CTP(V) on the eyes and skin.

No experimental data on the potential corrosivity and sensitising properties of CTP(ht) required as specified in Annex VIIA of Directive 67/548/EEC were available. Taking the available human and animal data into account, there are no indications that CTP has corrosive properties. According to section 1.7.2.1 of Annex VI of Directive 67/548, complex substances containing more than 1% of a skin sensitising substance need to be classified as a skin sensitiser. Since CTP(ht) may contain up to 1.5% BaP (a skin sensitiser) it is proposed to classify CTP(ht) as a skin sensitiser(Xi;R43).

With regard to repeated dose toxicity, apart from one oral study of limited significance in pigs, no repeated dose toxicity animal studies with CTP(ht) addressing effects other than carcinogenicity were available to the rapporteur. Therefore, the available data set does not meet the basic requirements as specified in Annex VIIA of Directive 67/548/EEC and no NOAEL for non-carcinogenic effects could be derived from these studies.

In humans no statistical significant effects on lung function parameters were found in a group of phosphorus rock refinery workers exposed at the time of study to about  $0.1 \text{ mg/m}^3 \text{ CTPV}$ 

in addition to other substances (including phosphorus pentoxide (about 2.2 mg/m<sup>3</sup>) and fluorides (about  $4.2 \text{ mg/m}^3$ ).

In addition, animal data was available on high-boiling coal liquid (LOAEC of 30 mg/m<sup>3</sup> in rats regarding semichronic inhalation exposure), and Manufactured Gas Plant (MGP) residue (a coal-tar like material) (NOAEL of 462 mg/kg/day (male mice; oral exposure) and 344 mg/kg/day (female mice; oral exposure). These, however, are not considered representative for establishing a NOAEL value for risk characterisation of CTP(ht).

The data set available on the mutagenicity/genotoxicity of CTP(ht) does not meet the basis requirements as specified in Annex VIIA of Directive 67/548/EEC. From mutagenicity testing in *Salmonella typhimurium* conducted according to EU guidelines, it is concluded that CTP is a bacterial mutagen. Results from *in vitro* genotoxicity testing in mammalian cells are somewhat inconsistent, but mostly positive. Human body fluids are generally not mutagenic in bacterial gene mutation tests, except for urine samples of heavily exposed psoriasis patients (to coal-tar applications), and coke oven, and carbon plant workers.

There were no data on *in vivo* genotoxicity testing of CTP(ht) in experimental animals. Results on genotoxic endpoints in human blood cells after occupational exposure to CTP(V) are inconsistent, but in heavily PAH-exposed people increased DNA-adduct levels have been reported.

In addition, numerous genotoxicity studies with coal tar, coal tar waste, coal tar products, and individual PAHs demonstrated the genotoxicity of these substances (ATSDR, 2002, WHO, 1998).

According to section 1.7.2.1 of Annex VI of Directive 67/548, complex substances containing more than 0.1% of a category 1 or 2 mutagen need to be classified as a category 1 or 2 mutagen. CTP(ht) may contain a variable amount of mutagenic PAHs. The mutagenic effect of these individual PAHs may be considered at least additive. Since CTP(ht) may at least contain up to 1.5% BaP (a category 2 mutagen), the amount of category 2 mutagens in CTP(ht) is estimated to be more than 0.1% in nearly if not all circumstances.

Based on the amount of category 2 mutagens in CTP(ht) and the available genotoxicity data on CTP(ht), CTPV(ht), coal tar, coal tar waste, coal tar products, and individual PAHs, classification of CTP(ht) as a category 2 mutagen is proposed (T; R46).

There were no data available on the potential carcinogenicity of CTP(ht) after oral exposure in experimental animals. However, studies with coal tar resulted in increased tumour incidences in various organs. After oral exposure in mice main target organs appeared to be liver, lung, and forestomach. Studies with BaP resulted in increased tumour incidences in amongst others the liver, forestomach, and auditory canal in rats and forestomach and upper GI tract in mice.

Inhalation of CTP(ht) caused lung tumours in rats and mice, while dermal exposure to CTP(ht) caused skin tumours in mice. Although most of the available experimental animal studies were not conducted according to EC or OECD guidelines, they clearly indicate that CTP(ht) is carcinogenic following inhalation and dermal exposure.

Already in the 19<sup>th</sup> century, reports on the induction of cancer in persons occupationally exposed to combustion products containing PAHs have been published. Studies on possible carcinogenic effects due to exposure to CTPV have been reviewed by several working groups of the International Agency for Research on Cancer and by the UK Health and Safety Executive (HSE). The IARC concluded that there is sufficient evidence that coal-tar pitches are carcinogenic in humans already in 1985. Several additional studies have been published since including some attempting to derive quantitative cancer risk estimates. A recent meta-

analysis by Armstrong et al.  $(2003; 2004)^4$  showed statistically increased overall relative risks for lung and bladder cancer for all CTPV exposure scenarios, and an industry-specific increased relative risk for workers exposed in aluminium smelters. These meta-analyses estimates are considered the best estimates of the risk on lung and bladder cancer risk due to exposure of CTP(ht). Therefore, the relative risk value (URR) found for lung cancer in this meta-analysis is forwarded to the risk characterisation: an overall relative risk estimate (URR) of 1.20 (95% confidence interval (CI): 1.11-1.29) per *unit* of 100 µg/m<sup>3</sup>.year cumulative BaP exposure<sup>5</sup>. Furthermore, for aluminium smelters, the only industry exposed to CTPV(ht) for which rather precise estimates could be established in the meta-analysis, the combined URR estimate was 1.16 (95% confidence interval: 1.05-1.28) for lung cancer. This value will be taken forward to the risk characterisation for aluminium smelters.

Regarding bladder cancer, for which the association with PAH exposure was less robust than the PAH-lung cancer association, the overall relative risk estimate (URR) of 1.33 (95% confidence interval: 1.17-1.51) per unit of 100  $\mu$ g/m<sup>3</sup>.year cumulative BaP exposure is forwarded to the risk characterisation. Furthermore, for aluminium smelters, the only industry exposed to CTPV(ht) for which rather precise estimates could be established in the metaanalysis, the combined URR estimate was 1.42 (95% confidence interval: 1.23-1.65) per unit of 100  $\mu$ g/m<sup>3</sup>.year cumulative BaP exposure for bladder cancer. This value will be taken forward to the risk characterisation for aluminium smelters.

Based on the available experimental and epidemiological data on the carcinogenicity of CTP(ht) and CTPV(ht) and the evaluation of these data by the IARC, CTP(ht) and CTPV(ht) will be classified as a category 1 carcinogen (T; R45).

Based on the genotoxic and carcinogenic properties of CTP(ht), for risk characterisation a non-threshold approach will be adopted.

No valid experimental animal studies were available which addressed the potential reproduction toxicity of CTP(ht). Data was available on high-boiling coal liquid, coal tar derived products and creosote (inhalation, oral and dermal route).

High-boiling coal liquid had effects on fertility in a repeated dose inhalation toxicity study (13 weeks): statistically significant increased testis weights were observed in rats from a concentration of 140 mg/m<sup>3</sup> (NOAEC: 30 mg/m<sup>3</sup>). At the highest tested concentration (690 mg/m<sup>3</sup>) also decreased ovary weights and loss of luteal tissue were observed.

Coal tar derived products and coal tar creosote had no effects on fertility in mouse studies (with NOAELs of 344 mg/kg bw/day and 100 mg/kg, respectively). In a summary of a multigeneration study it is reported that creosote had effects on fertility in rats (at a dose level of 25 mg/kg bw/day) below maternal toxic doses (75 mg/kg bw/day).

<sup>&</sup>lt;sup>4</sup> Armstrong B, Hutchinson,E Fletcher T. (2003) Cancer risk following exposure to polycyclic aromatic hydrocarbons (PAHs): a meta-analysis. Rep No 068. Sudbury, UKL Health and safely Executive.

Armstrong B, Hutchchinson E, Unwin J, Fletcher T. (2004) Lung Cancer Risk after Exposure to Polycyclic Aromatic Hydrocarbons: A Review and Meta-Analysis. *Envinron Helath Perspect* 112 (9): 970-978.

<sup>&</sup>lt;sup>5</sup> The indicator function of BaP is rather scenario-specific: i.e. the amount of total PAHs may correlate well with the airborne concentration of BaP (in  $\mu g/m^3$ ) in most workplaces, while the PAH profile (the relative distribution of the individual PAHs) may be different for the different workplaces. In addition, the workers studied in the available epidemiological studies are exposed not only to CTP(ht) and CTPV(ht), but also to coal tar and/or other chemicals, which makes it difficult to determine which components of these mixed exposures are the most important causal agents of the observed carcinogenic effects. Ideally, therefore, industry- and scenario-specific hazard estimates should be used. However, industry-specific data were only available for the aluminium smelter industry.

Although developmental effects were observed in the available studies, it is not clear whether they were directly induced by high-boiling coal liquid, coal tar derived products, and creosote. In most of the studies, the observed foetal deformities appeared to be related to maternal toxicity except for one study, which showed an increase in foetal mortality in pigs without apparent maternal toxicity.

In humans no adverse effects on sperm characteristics, including differences in sperm count and sperm morphology were observed in workers exposed to CTPV in an aluminium reduction plant. In a small retrospective study among psoriasis or dermatitis patients, dermal exposure to coal tar did not induce a significant increase in spontaneous abortion.

According to section 1.7.2.1 of Annex VI of Directive 67/548, complex substances containing more than 0.5% of a substance classified as toxic for reproduction fertility and development need to be classified as a toxic for reproduction fertility and development. Since CTP(ht) may contain up to 1.5% BaP, which is classified for effects on reproduction (category 2; T, R.60/61), it is proposed to classify CTP(ht) as toxic to reproduction(T; R60/61).

## 4.3 RISK CHARACTERISATION

## 4.3.1 Workplace

An overview of the occupational exposure to CTP(ht) is given in Table 4.1.

Assuming that oral exposure is prevented by personal hygienic measures, the risk characterisation for workers is limited to the dermal and inhalation routes of exposure.

#### Acute toxicity

Given the low toxicity observed in the acute oral and dermal toxicity studies and the anticipated occupational exposure levels it is concluded that CTP(ht) is of no concern for workers with regard to acute systemic effects (**conclusion ii**).

#### Irritation and corrosivity

#### Skin

Skin effects were observed in animals and humans after repeated exposure to CTP(V) or combined exposure to CTP(V) and sunlight. However, from the available animal and human data it is not possible to conclude if the observed dermal effects are caused by irritation or sensitisation (photosensitisation or sensitisation after repeated exposure), therefore the data do not allow a conclusive statement on the skin irritating properties of CTP(ht).

However, since it is concluded that the carcinogenic activity of CTP(ht) is the critical effect, the need for more information on local skin effects of CTP(ht) will be revised in the light of the risk reduction strategy due to its carcinogenic properties (**conclusion i on hold**).

Eye

Given the effects observed in humans exposed to CTP (fumes, volatiles and dust, not further specified), it is proposed to classify CTP(ht) as irritant with risk of serious damage to eyes (Xi, R41). Although the data are insufficient for quantitative risk characterisation, it is concluded that CTP(ht) is of concern for workers. However, if the required protection is strictly adhered to, exposure will occur only incidentally, so **conclusion ii** is justifiable.

## Corrosivity

No experimental data on the potential corrosivity of CTP(ht) are available, however taking the available human and animal data into account, there are no indications that CTP(ht) has corrosive properties, so **conclusion ii** is justifiable.

### Sensitisation

No experimental data on the sensitisation potential of CTP(ht) are available. However, since CTP(ht) may contain up to 1.5% BaP, which is classified for skin sensitisation, it is proposed to classify CTP(ht) as a skin sensitiser (R43). The available data are insufficient for a quantitative risk characterisation. However, as sensitisation is considered a non-threshold effect, it is concluded that CTP(ht) is of concern for workers (conclusion iii).

### Repeated dose toxicity

No valid experimental animal studies addressing the potential non-carcinogenic effects of CTP(ht) were available to the rapporteur. In humans no statistically significant effects on lung function parameters were found in a group of phosphorus rock refinery workers exposed at the time of study to about 0.1 mg/m<sup>3</sup> CTPV in addition to other substances (including phosphorus pentoxide (about 2.2 mg/m<sup>3</sup>) and fluorides (about 4.2 mg/m<sup>3</sup>)). However, exposure was as well to phosphorus pentoxide (about 2.2 mg/m<sup>3</sup>) and fluorides (about 4.2 mg/m<sup>3</sup>), after adjustment for smoking.

However, since it is concluded that the carcinogenic activity of CTP(ht) is the critical effect, the need for more information on non-carcinogenic effects of CTP(ht) after repeated exposure will be revised in the light of the risk reduction strategy due to its carcinogenic properties (conclusion i on hold).

### Mutagenicity

Based on the proposal to classify CTP(ht) as a category 2 mutagen, it is concluded that exposure to CTP(ht) is associated with a mutagenic risk: **conclusion iii**.

## **Carcinogenicity**

Based on the available experimental and epidemiological data and the evaluation of these data by the IARC, it is concluded that CTP(ht) and CTPV(ht) should be classified as category 1 carcinogens. Human data are mainly available on lung and bladder cancer risk in occupationally CTPV(ht)-exposed cohorts. Although a considerable number of epidemiological studies on CTPV(ht) exposure and risk of cancer is available, many of them have little statistical power (are imprecise), they vary with respect to type of industry and workplace, and in more than half of them no information on exposure is presented. Although it is likely that the composition (PAH profile) and therefore the carcinogenic potential of the exposures is not exactly similar across industries, deriving a precise risk estimate based on all PAH-exposed cohorts is still considered superior to deriving industry-specific but very uncertain estimates. Although a few larger studies, mainly in the aluminium industry, are available, a better (i.e. precise and more realistic) risk estimate can be obtained using a weight-of-the-evidence approach, such as a meta-analysis. Recently, a meta-analysis on lung and bladder cancer risk after exposure to PAHs has been published by Armstrong et al. (2003; 2004). As exposure to BaP has been adopted as the primary indicator of exposure to CTPV(ht) at the workplace and is also used as indicator of exposure in the meta-analysis, the results of this meta-analysis provide currently the best option for deriving a quantitative risk estimate for exposure to CTPV(ht).

In this meta-analysis, unit relative risks (URRs) for lung and bladder cancer were estimated by fitting a log-linear model to the data. An overall URR per unit of 100  $\mu$ g/m<sup>3</sup>.year cumulative BaP exposure of 1.20 (95% confidence interval: 1.11-1.29) for lung cancer and 1.33 (95% confidence interval: 1.17-1.51) for bladder cancer was calculated. The combined URR estimates in aluminium smelters, the only industry exposed to CTPV(ht) for which rather precise estimates could be established, were 1.16 (95% confidence interval: 1.05-1.28) and 1.42 (95% confidence interval: 1.23-1.65) per unit of 100  $\mu$ g/m<sup>3</sup>.year cumulative BaP exposure, for lung and bladder cancer, respectively.

Although a log-linear model is the most logical model to fit relative risks, it is not the best model per se for deriving quantitative risk estimates. In particular when benchmark exposures or exposure scenarios outside the range of data observed in the underlying study or studies are compared with the fitted model, unrealistic estimates may be the result. A linear relative risk model (RR = 1 + bx) is often better suited for risk assessment, but there are statistical limitations in conducting a meta-analysis fitting a linear model and results should be viewed more cautiously. In the meta-analysis also a linear model was fitted, resulting in an overall URR of 1.19 for lung cancer, very similar to the overall estimate from the log-linear model, although estimates for the major industries differed more. For bladder cancer, no results on the linear model were reported. Comparison between industry-specific URRs derived from the two models revealed that studies in industries with relatively low exposure, for example tar distillation, had very high URRs in the log-linear model, but lower URRs in the linear model. The explanation is that the benchmark exposure of  $100 \,\mu g/m^3$  year cumulative BaP is much higher than that in the highest exposure category of industries with relatively low exposures (e.g., the benchmark of 100  $\mu$ g/m<sup>3</sup>.year is ten times higher than the exposure in the highest exposure category in tar distilleries) and therefore these industry-specific URRs are overestimated using the results from the log-linear model due to extrapolation. See figure 1 for an illustration with a hypothetical example. Therefore industry-specific URRs estimated with the log-linear model should not be used for industries for which the benchmark exposure  $(100 \,\mu g/m^3.year \text{ cumulative BaP})$  is far higher than the observed exposure range.

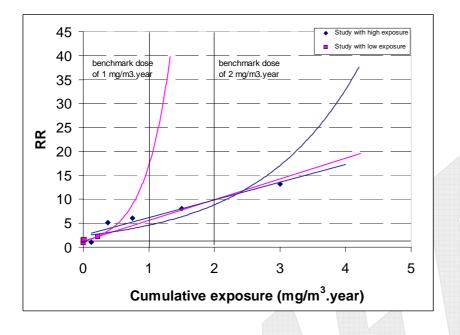


Figure 1. Influence of the choice of a benchmark dose on predicted relative risk: a hypothetical example of fitting log-linear and linear slopes to exposure-risk data points from studies with relatively low exposure (below 1 mg/m<sup>3</sup>.yr, red) to studies with relatively high exposure 0-3  $mg/m^3$ .yr, blue). In the log-linear case, using a benchmark dose above the range of exposure data for which the curve was fitted, in (severe) results overestimation of the relative risk.

Considering the results and arguments presented in the meta-analyses by Armstrong et al. (2004), the following decisions were taken in deriving risk estimates for each of the exposure scenarios addressed in this report.

- 1. The overall URRs of 1.20 for lung cancer and 1.33 for bladder cancer, estimated from the log-linear model, are the best estimates for all relevant industry/workplace combinations. Due to lack of statistical precision and extrapolation problems in studies with low exposures, industry-specific estimates do not provide the best estimate. An exception may be the aluminium smelters, as the statistical precision is sufficient and the benchmark exposure is comprised in the observed exposure range. The URRs for aluminium smelters were 1.16 (95% confidence interval: 1.05-1.28) for lung cancer and 1.42 (95% confidence interval: 1.23-1.65) for bladder cancer.
- 2. Exposure scenarios resulting in exposures (much) higher than the benchmark exposure  $(100 \ \mu g/m^3.year$  cumulative BaP exposure) should not be compared with the URR from the log-linear model, but with that from the linear model instead. This URR was 1.19 for lung cancer (no confidence interval and no URR for bladder cancer were presented). At exposures within the range of the data from which the URRs were estimated, the log-linear and linear models will give similar estimates.

Excess lifetime risk (ELR) was calculated from the RR at the reasonable worst case (RWC) exposure estimated for the specified exposure scenarios (see **Table 4.1**) with the formula: ELR = RR\*P - P, in which P denotes the background risk in the exposed target population (i.e., the population figuring in the exposure scenario) (see **Table 4.4** and **Table 4.5**).

As typical exposure levels may be substantially lower than the reasonable-worst-case exposure levels and it is unlikely that a worker is exposed to worst-case exposure during the whole working life, they might be valuable input to the risk management process (note: both types of exposure levels need to be well-defined in terms of technical and organisational conditions of exposure (TGD Human Health Risk Characterisation, 2005)): for this reason typical exposure values are included as well.

The RR at the exposure level specified in the exposure scenario, was calculated from the URR at 100  $\mu$ g/m<sup>3</sup>.year cumulative BaP derived from the log-linear model as follows: RR<sub>x</sub> = URR <sup>x/100</sup> and from the linear model as follows: RRx = 1+ (URR - 1) x/100. Background lifetime

risks were chosen as 0.08 for lung cancer and 0.018 for bladder cancer, being the 1997 figures for British males, also used in the papers by Armstrong et al.

For comparison: in Europe in the mid-nineties, the background lifetime risks for male lung cancer up to age 74 varied between 0.10 (Eastern Europe) and 0.03 (Sweden), while bladder cancer risk varied between 0.05 (Italy) and 0.02 (Sweden). As several uncertainties are inherently associated with the data and approach used, presentation of a calculated exact figure would be misleading. Therefore, the calculated ELRs (point estimates) were rounded to the nearest order of magnitude.

Because only data on airborne concentrations are available from the epidemiological studies, the (8-hour Time Weighted Average of the) airborne concentration of BaP (in  $\mu$ g/m<sup>3</sup>) is used for risk assessment. It is assumed that in the epidemiological studies, the effects of combined exposure (inhalation and dermal) were studied. Assuming a constant (linear) relation between the airborne concentration and the inhalation as well as the dermal exposure, the airborne concentration can be used for risk assessment of combined exposure.



Exposure scenario	Cancer type	Estimated RWC exposure (TWA <sup>1</sup> of airborne concentration) (µg/m <sup>3</sup> BaP)	Estimated RWC cumulative exposure <sup>2</sup> (µg/m <sup>3</sup> BaP.year)	Estimated unit relative risk (URR) (per 100 µg/m³ BaP.year)	Model	Calculated relative risk at the estimated cumulative exposure level	Order of magnitude of estimated excess lifetime risk (ELR)	Conclusion
1 a. Tar distillation plants - Tar	lung	0.4	16	1.20 (CI: 1.11-1.29)	log-linear	1.03 (CI: 1.02-1.04)	10 <sup>-3</sup>	iii
processing and handling of liquid pitch	bladder	0.4	16	1.33 (Cl: 1.17-1.51)	log-linear	1.05 (CI: 1.03-1.07)	10-3	iii
1 b. Tar distillation plants - Handling	lung	3.6	144	1.20 (CI: 1.11-1.29)	log-linear	1.30 (CI: 1.16-1.44)	10-2	iii
of solid pitch	bladder	3.6	144	1.33 (CI: 1.17-1.51)	log-linear	1.51 (CI: 1.25-1.81)	10-2	iii
2 i a. Søderberg potroom	lung	8	320	1.16 (CI): 1.05-1.28)	log-linear	1.61 (CI: 1.17-2.20)	10-2	iii
Not modernised	bladder	8	320	1.42 (CI: 1.23-1.65)	log-linear	3.07 (CI: 1.94-4.97)	10-2	iii
2 i b. Søderberg potroom	lung	0.35	14	1.16 (CI): 1.05-1.28)	log-linear	1.02 (CI: 1.01-1.04)	10 <sup>-3</sup>	iii
Modernised	bladder	0.35	14	1.42 (CI: 1.23-1.65)	log-linear	1.05 (CI: 1.03-1.07)	10 <sup>-3</sup>	iii
2 i c. Anode bake plants	lung	0.40	16	1.16 (CI): 1.05-1.28)	log-linear	1.02 (CI: 1.01-1.04)	10 <sup>-3</sup>	iii
	bladder	0.40	16	1.42 (Cl: 1.23-1.65)	log-linear	1.06 (CI: 1.03-1.08)	10 <sup>-3</sup>	iii
2 i d. Paste plants	lung	0.15	6	1.16 (CI): 1.05-1.28)	log-linear	1.01 (CI : 1.0-1.01)	10 <sup>-3</sup>	iii
	bladder	0.15	6	1.42 (CI: 1.23-1.65)	log-linear	1.02 (CI : 1.01-1.03)	10-4	iii
2 ii Graphite electode past plants	lung	7.5	300	1.20 (CI): 1.11-1.29)	log-linear	1.73 (Cl: 1.37-2.15)	<b>10</b> -1	iii
	bladder	7.5	300	1.33 (CI: 1.17-1.51)	log-linear	2.35 (CI: 1.60-3.44)	10-2	iii
3 i. Road construction	lung	1.2	48	1.20 (CI): 1.11-1.29)	log-linear	1.09 (CI: 1.05-1.13)	10-2	iii
	bladder	1.2	48	1.33 (Cl: 1.17-1.51)	log-linear	1.15 (CI: 1.08-1.22)	10 <sup>-3</sup>	iii
3 ii. Roofing	lung	60	2400	1.19	linear	5.56	10 <sup>-1</sup>	iii
	bladder	60	2400	Linear estimate	n.a. <sup>3</sup>		10-2	iii
4 a. Production of refractories	lung	3.5	140	1.20 (CI): 1.11-1.29)	log-linear	1.29 (CI: 1.16-1.43)	10-2	iii

## Table 4.4 Occupational lung and bladder cancer risk characterisation workers using RWC exposure values

Exposure scenario	Cancer type	Estimated RWC exposure (TWA <sup>1</sup> of airborne concentration) (µg/m <sup>3</sup> BaP)	Estimated RWC cumulative exposure <sup>2</sup> (µg/m³ BaP.year)	Estimated unit relative risk (URR) (per 100 µg/m³ BaP.year)	Model	Calculated relative risk at the estimated cumulative exposure level	Order of magnitude of estimated excess lifetime risk (ELR)	Conclusion
	bladder	3.5	140	1.33 (CI: 1.17-1.51)	log-linear	1.49 (CI: 1.25-1.78)	10-2	iii
4 b. Use of refractories	lung	23	920	1.19	linear	2.75	10 <sup>-1</sup>	iii
	bladder	23	920	Linear estimate n.a. <sup>3</sup>			10-2	iii
6 a. Use - Heavy duty corrosion protection – coating operators	lung	90	3600	1.19	linear	7.84	>10-1	iii
	bladder	90	3600	Linear estimate n.a. 3			10-2	iii
6 b. Use - Heavy duty corrosion	lung	30	1200	1.19	linear	3.28	<b>10</b> -1	iii
protection – other workers	bladder	30	1200	Linear estimate n.a. <sup>3</sup>			10-2	iii
7 a. Use – Binder in coal briquetting -	lung	1760	70400	1.19	linear	135	<b>&gt;10</b> -1	iii
Production	bladder	1760	70400	Linear estimate	n.a. <sup>3</sup>		10-2	iii
7 b. Use - Binder in coal briquetting - Cleaning	lung	40	1600	1.19	linear	4.04	<b>10</b> -1	iii
	bladder	40	1600	Linear estimate	n.a. <sup>3</sup>		10-2	iii
8. Binder for clay pigeons	lung	3	120	1.20 (CI: 1.11-1.29)	log-linear	1.24 (CI: 1.13-1.36)	10-2	iii
	bladder	3	120	1.33 (CI: 1.17-1.51)	log-linear	1.41 (CI: 1.21-1.64)	10-2	iii

<sup>1</sup>TWA: Time Weighted Average over 8 hours;

<sup>2</sup> TWA x 40 year;

<sup>3</sup> Linear URR estimates were not available for bladder cancer (indicated by n.a). In these cases, the ELR for bladder cancer was assumed to be approximately one third of that for lung cancer as the ELR values for bladder cancer are about one third of the ELR value for lung cancer for each scenario for which the log-linear method was used.

4 4 104 104 40 40 40 8 8 8 8 6 6 6	1.20 (CI: 1.11-1.29) 1.33 (CI: 1.17-1.51) 1.20 (CI: 1.11-1.29) 1.33 (CI: 1.17-1.51) 1.33 (CI: 1.17-1.51) 1.16 (CI): 1.05-1.28) 1.42 (CI: 1.23-1.65) 1.16 (CI): 1.05-1.28) 1.42 (CI: 1.23-1.65) 1.16 (CI): 1.05-1.28)	log-linear log-linear log-linear log-linear log-linear log-linear log-linear log-linear	1.01 (CI : 1.0-1.01)           1.01 (CI : 1.01-1.02)           1.21 (CI: 1.11-1.30)           1.35 (CI: 1.18-1.54)           1.06 (CI: 1.02-1.10)           1.15 (CI: 1.09-1.22)           1.01 (CI: 1.0-1.02)           1.03 (CI: 1.02-1.04)           1.01 (CI: 1.0-1.01)	10 <sup>-3</sup> 10 <sup>-4</sup> 10 <sup>-2</sup> 10 <sup>-2</sup> 10 <sup>-2</sup> 10 <sup>-3</sup> 10 <sup>-3</sup> 10 <sup>-3</sup> 10 <sup>-3</sup>	
4 104 104 40 40 8 8 8 6	1.33 (CI: 1.17-1.51) 1.20 (CI: 1.11-1.29) 1.33 (CI: 1.17-1.51) 1.16 (CI): 1.05-1.28) 1.42 (CI: 1.23-1.65) 1.16 (CI): 1.05-1.28) 1.42 (CI: 1.23-1.65) 1.16 (CI): 1.05-1.28)	log-linear log-linear log-linear log-linear log-linear log-linear log-linear	1.01 (CI : 1.01-1.02)         1.21 (CI: 1.11-1.30)         1.35 (CI: 1.18-1.54)         1.06 (CI: 1.02-1.10)         1.15 (CI: 1.09-1.22)         1.01 (CI: 1.0-1.02)         1.03 (CI: 1.02-1.04)	10 <sup>-4</sup> 10 <sup>-2</sup> 10 <sup>-2</sup> 10 <sup>-2</sup> 10 <sup>-3</sup> 10 <sup>-3</sup> 10 <sup>-3</sup>	
104 104 40 40 8 8 8 8 6	1.20 (CI: 1.11-1.29)           1.33 (CI: 1.17-1.51)           1.16 (CI): 1.05-1.28)           1.42 (CI: 1.23-1.65)           1.16 (CI): 1.05-1.28)           1.42 (CI: 1.23-1.65)           1.42 (CI: 1.23-1.65)           1.42 (CI: 1.23-1.65)           1.42 (CI: 1.23-1.65)	log-linear log-linear log-linear log-linear log-linear log-linear	1.21 (CI: 1.11-1.30) 1.35 (CI: 1.18-1.54) 1.06 (CI: 1.02-1.10) 1.15 (CI: 1.09-1.22) 1.01 (CI: 1.0-1.02) 1.03 (CI: 1.02-1.04)	10 <sup>-2</sup> 10 <sup>-2</sup> 10 <sup>-2</sup> 10 <sup>-3</sup> 10 <sup>-3</sup>	
104 40 40 8 8 8 6	1.33 (CI: 1.17-1.51) 1.16 (CI): 1.05-1.28) 1.42 (CI: 1.23-1.65) 1.16 (CI): 1.05-1.28) 1.42 (CI: 1.23-1.65) 1.42 (CI: 1.23-1.65) 1.16 (CI): 1.05-1.28)	log-linear log-linear log-linear log-linear log-linear	1.35 (CI: 1.18-1.54) 1.06 (CI: 1.02-1.10) 1.15 (CI: 1.09-1.22) 1.01 (CI: 1.0-1.02) 1.03 (CI: 1.02-1.04)	10 <sup>-2</sup> 10 <sup>-2</sup> 10 <sup>-3</sup> 10 <sup>-3</sup> 10 <sup>-3</sup>	
40 40 8 8 8 6	1.16 (Cl): 1.05-1.28) 1.42 (Cl: 1.23-1.65) 1.16 (Cl): 1.05-1.28) 1.42 (Cl: 1.23-1.65) 1.16 (Cl): 1.05-1.28)	log-linear log-linear log-linear log-linear	1.06 (CI: 1.02-1.10) 1.15 (CI: 1.09-1.22) 1.01 (CI: 1.0-1.02) 1.03 (CI: 1.02-1.04)	10 <sup>-2</sup> 10 <sup>-3</sup> 10 <sup>-3</sup> 10 <sup>-3</sup>	iii iii iii
40 8 8 6	1.42 (CI: 1.23-1.65) 1.16 (CI): 1.05-1.28) 1.42 (CI: 1.23-1.65) 1.16 (CI): 1.05-1.28)	log-linear log-linear log-linear	1.15 (CI: 1.09-1.22) 1.01 (CI: 1.0-1.02) 1.03 (CI: 1.02-1.04)	10 <sup>-3</sup> 10 <sup>-3</sup> 10 <sup>-3</sup>	
8 8 6	1.16 (Cl): 1.05-1.28) 1.42 (Cl: 1.23-1.65) 1.16 (Cl): 1.05-1.28)	log-linear log-linear	1.01 (CI: 1.0-1.02) 1.03 (CI: 1.02-1.04)	10 <sup>-3</sup> 10 <sup>-3</sup>	iii iii
8	1.42 (Cl: 1.23-1.65) 1.16 (Cl): 1.05-1.28)	log-linear	1.03 (CI: 1.02-1.04)	10-3	iii
6	1.16 (CI): 1.05-1.28)				
		log-linear	1.01 (CI: 1.0-1.01)	10-3	
6				10-5	iii
	1.42 (CI: 1.23-1.65)	log-linear	1.02 (CI: 1.01-1.03)	10-4	iii
3.2	1.16 (CI): 1.05-1.28)	log-linear	1.0 (CI : 1.0-1.01)	10-4	iii
3.2	1.42 (CI: 1.23-1.65)	log-linear	1.01 (CI : 1.01-1.02)	10-4	iii
80	1.20 (CI): 1.11-1.29)	log-linear	1.16 (CI : 1.09-1.23)	10-2	iii
80	1.33 (Cl: 1.17-1.51)	log-linear	1.26 (CI: 1.13-1.39)	10-2	iii
22	1.20 (CI): 1.11-1.29)	log-linear	1.04 (CI: 1.02-1.06)	10 <sup>-3</sup>	iii
22	1.33 (Cl: 1.17-1.51)	log-linear	1.06 (CI: 1.04-1.09)	10 <sup>-3</sup>	iii
1400	1.19	linear	3.66	<b>10</b> -1	iii
1400	Linear estimate	n.a. <sup>3</sup>		10 <sup>-2</sup>	iii
6.8	1.20 (CI): 1.11-1.29)	log-linear	1.01 (CI : 1.01-1.02)	10 <sup>-3</sup>	iii
	80       80       22       22       1400       1400       6.8	80         1.20 (CI): 1.11-1.29)           80         1.33 (CI: 1.17-1.51)           22         1.20 (CI): 1.11-1.29)           22         1.33 (CI: 1.17-1.51)           1400         1.19           1400         Linear estimate	80         1.20 (CI): 1.11-1.29)         log-linear           80         1.33 (CI: 1.17-1.51)         log-linear           22         1.20 (CI): 1.11-1.29)         log-linear           22         1.33 (CI: 1.17-1.51)         log-linear           22         1.33 (CI: 1.17-1.51)         log-linear           1400         1.19         linear           1400         Linear estimate n.a. <sup>3</sup> 6.8	3.2         1.42 (CI: 1.23-1.65)         log-linear         1.01 (CI : 1.01-1.02)           80         1.20 (CI): 1.11-1.29)         log-linear         1.16 (CI : 1.09-1.23)           80         1.33 (CI: 1.17-1.51)         log-linear         1.26 (CI: 1.13-1.39)           22         1.20 (CI): 1.11-1.29)         log-linear         1.04 (CI: 1.02-1.06)           22         1.33 (CI: 1.17-1.51)         log-linear         1.04 (CI: 1.02-1.06)           22         1.33 (CI: 1.17-1.51)         log-linear         1.06 (CI: 1.04-1.09)           1400         1.19         linear         3.66           1400         Linear estimate n.a. <sup>3</sup> 1.01 (CI : 1.01-1.02)	3.2         1.42 (Cl: 1.23-1.65)         log-linear         1.01 (Cl: 1.01-1.02)         10 <sup>4</sup> 80         1.20 (Cl): 1.11-1.29)         log-linear         1.16 (Cl: 1.09-1.23)         10 <sup>-2</sup> 80         1.33 (Cl: 1.17-1.51)         log-linear         1.26 (Cl: 1.13-1.39)         10 <sup>-2</sup> 22         1.20 (Cl): 1.11-1.29)         log-linear         1.04 (Cl: 1.02-1.06)         10 <sup>-3</sup> 22         1.33 (Cl: 1.17-1.51)         log-linear         1.06 (Cl: 1.04-1.09)         10 <sup>-3</sup> 22         1.33 (Cl: 1.17-1.51)         log-linear         1.06 (Cl: 1.04-1.09)         10 <sup>-3</sup> 1400         1.19         linear         3.66         10 <sup>-1</sup> 1400         Linear estimate n.a. <sup>3</sup> 10 <sup>-2</sup> 10 <sup>-3</sup> 6.8         1.20 (Cl): 1.11-1.29)         log-linear         1.01 (Cl : 1.01-1.02)         10 <sup>-3</sup>

## Table 4.5 Occupational lung and bladder cancer risk characterisation workers using typical exposure values

Exposure scenario	Cancer type	Estimated RWC exposure (TWA <sup>1</sup> of airborne concentration) (µg/m <sup>3</sup> BaP)	Estimated RWC cumulative exposure <sup>2</sup> (µg/m <sup>3</sup> BaP.year)	Estimated unit relative risk (URR) (per 100 µg/m³ BaP.year)	Model	Calculated relative risk at the estimated cumulative exposure level	Order of magnitude of estimated excess lifetime risk (ELR)	Conclusion
	bladder	0.17	6.8	1.33 (CI: 1.17-1.51)	log-linear	1.02 (CI : 1.01-1.03)	10-4	iii
4 b. Use of refractories	lung	0.63	25.2	1.20 (CI): 1.11-1.29)	log-linear	1.05 (CI: 1.03-1.07)	10 <sup>-3</sup>	iii
	bladder	0.63	25.2	1.33 (CI: 1.17-1.51)	log-linear	1.07 (CI: 1.04-1.11)	10 <sup>-3</sup>	iii
6 a. Use - Heavy duty corrosion protection – coating operators	lung	23	920	1.19	linear	2.75	<b>10</b> -1	iii
	bladder	23	920	Linear estimate n.a. 3			10-2	iii
6 b. Use - Heavy duty corrosion	lung	6	240	1.20 (CI): 1.11-1.29)	log-linear	1.55 (CI: 1.28-1.84)	10 <sup>-2</sup>	iii
protection – other workers	bladder	6	240	1.33 (CI: 1.17-1.51)	log-linear	1.98 (CI: 1.46-2.69)	10 <sup>-2</sup>	iii
7 a. Use – Binder in coal briquetting -	lung	670	26800	1.19	linear	52	>10-1	iii
Production	bladder	670	26800	Linear estimate	n.a. <sup>3</sup>		10 <sup>-2</sup>	iii
7 b. Use - Binder in coal briquetting -	lung	14	560	1.19	linear	2.06	<b>&gt;10</b> -1	iii
Cleaning	bladder	14	560	Linear estimate	n.a. <sup>3</sup>		10-2	iii
8. Binder for clay pigeons	lung	1	40	1.20 (CI: 1.11-1.29)	log-linear	1.08 (CI: 1.04-1.11)	10-2	iii
	bladder	1	40	1.33 (CI: 1.17-1.51)	log-linear	1.12 (CI : 1.06-1.18)	10 <sup>-3</sup>	iii

<sup>1</sup> TWA: Time Weighted Average over 8 hours;

<sup>2</sup> TWA x 40 year;

<sup>3</sup> Linear URR estimates were not available for bladder cancer (indicated by n.a). In these cases, the ELR for bladder cancer was assumed to be approximately one third of that for lung cancer as the ELR values for bladder cancer are about one third of the ELR value for lung cancer for each scenario for which the log-linear method was used.

Table 4.6 Comparison of occupational lung and bladder cancer risk characterisation for workers using RWC and typical exposure values

Exposure scenario	Cancer type	Estimated <b>RWC</b> cumulative exposure (µg/m³ BaP.year)	Order of magnitude of estimated excess lifetime risk (ELR)	Conclusion	Estimated <b>typical</b> cumulative exposure (µg/m³ BaP.year)	Order of magnitude of estimated excess lifetime risk (ELR)	Conclusion
1 a. Tar distillation plants - Tar I	lung	16	10-3	iii	4	10 <sup>-3</sup>	iii
processing and handling of liquid bitch	bladder	16	10-3	iii	4	10-4	iii
1 b. Tar distillation plants - Handling I	lung	144	10-2	iii	104	10-2	iii
of solid pitch	bladder	144	10-2	iii	104	10-2	iii
2 i a. Søderberg potroom	lung	320	10-2	iii	40	10 <sup>-2</sup>	iii
Not modernised	bladder	320	10-2	iii	40	10 <sup>-3</sup>	iii
2 i ab. Søderberg potroom	lung	14	10-3	iii	8	10 <sup>-3</sup>	iii
Modernised	bladder	14	10-2	iii	8	10 <sup>-3</sup>	iii
2 i bc. Anode bake and past plants	lung	16	10-3	iii	6	10 <sup>-3</sup>	iii
t	bladder	16	10-3	iii	6	10-4	iii
2 i d. Paste plants	lung	6	10-3	iii	3.2	10-4	iii
ł	bladder	6	10-4	iii	3.2	10-4	iii
2 ii Graphite electode past plants	lung	300	10 <sup>-1</sup>	iii	80	10-2	iii
ł	bladder	300	10-2	iii	80	10-2	iii
3 i. Road construction	lung	48	10-2	iii	22	10 <sup>-3</sup>	iii
t	bladder	48	10 <sup>-3</sup>	iii	22	10 <sup>-3</sup>	iii
3 ii. Roofing	lung	2400	10 <sup>-1</sup>	iii	1400	10 <sup>-1</sup>	iii
	bladder	2400	10-2	iii	1400	10-2	iii
4 a. Production of refractories	lung	140	10 <sup>-2</sup>	iii	6.8	10 <sup>-3</sup>	iii

### EU RISK ASSESSMENT – COAL TAR PITCH, HIGH TEMPERATURE CAS 65996-93-2

Exposure scenario	Cancer type	Estimated <b>RWC</b> cumulative exposure (µg/m <sup>3</sup> BaP.year)	Order of magnitude of estimated excess lifetime risk (ELR)	Conclusion	Estimated <b>typical</b> cumulative exposure (µg/m³ BaP.year)	Order of magnitude of estimated excess lifetime risk (ELR)	Conclusion
	bladder	140	10-2	:=	6.8	10-4	
4 b. Use of refractories	lung	920	10-1	:	25.2	10 <sup>-3</sup>	iii
	bladder	920	10-2	:=	25.2	10 <sup>-3</sup>	
6 a. Use - Heavy duty corrosion protection – coating operators	lung	3600	>10-1	:=	920	10 <sup>-1</sup>	ij
	bladder	3600	10-2		920	10-2	iii
6 b. Use - Heavy duty corrosion protection – other workers	lung	1200	10-1	iii	240	10 <sup>-2</sup>	iii
	bladder	1200	10-2		240	10 <sup>-2</sup>	iii
7 a. Use – Binder in coal briquetting - Production	lung	70400	>10-1	:=	26800	>10 <sup>-1</sup>	ij
	bladder	70400	10-2	:=	26800	10 <sup>-2</sup>	
7 b. Use - Binder in coal briquetting -	lung	1600	10-1	:=	560	<b>&gt;10</b> -1	ij
Cleaning	bladder	1600	10-2	iii	560	10 <sup>-2</sup>	iii
8. Binder for clay pigeons	lung	120	10-2	iii	40	10-2	
	bladder	120	10-2		40	10 <sup>-3</sup>	iii



All ELR values listed in **Table 4.4** and **Table 4.5** are equal or higher than an additional risk level of  $1 \times 10^{-4}$  (see also **Table 4.6**). Therefore, not only the reasonable worst case exposure estimates but also the typical exposure estimates for the specified exposure scenarios lead to unacceptable high risks for lung as well as bladder cancer, respectively. Application of other background lifetime risks of lung and bladder cancer as prevailing in Europe (with a maximum threefold variation across the countries), does not alter these conclusions: therefore, **conclusion iii** is drawn.

There is insufficient information with regard to exposure scenario 5 for the derivation of exposure estimates. However, based on the proposal to classify CTP(ht) and CTPV(ht) as category 1 carcinogens and a category 2 mutagen, and the quantitative risk assessment for the other exposure scenarios, **conclusion iii** is also applicable for scenario 5.

#### Toxicity for reproduction

No valid experimental animal studies were available which addressed the potential reproduction toxicity of CTP(ht). However, animal studies have shown that exposure to highboiling coal liquid, coal tar derived products, and creosote cause effects on fertility in mice and rats. Although some developmental effects were also observed in these studies, it is not clear that they were directly induced by high-boiling coal liquid, coal tar derived products, or creosote. In humans no adverse effects on sperm characteristics were observed in workers exposed to CTPV in an aluminium reduction plant. In a small retrospective study among psoriasis or dermatitis patients, dermal exposure of to coal tar did not induce a significant increase in spontaneous abortion.

Since CTP(ht) may contain up to 1.5% BaP (classified as toxic for effects on reproduction (category 2)) it is proposed to classify CTP(ht) as toxic to reproduction (category 2). Although the data are insufficient for quantitative risk characterisation, it is concluded that CTP(ht) is of concern for workers. However, since it is concluded that the carcinogenic activity of CTP(ht) is the critical effect, the need for more information on the reproductive toxicity of CTP(ht) will be revised in the light of the risk reducing strategy due to its carcinogenic properties (**conclusion i on hold**).

## 4.3.2 Consumers

Since there is no consumer exposure, no risk characterisation is performed.

### 4.3.3 Man indirectly exposed via the environment

In view of the differences in physical-chemical parameters, the exposure to the different PAHs for humans exposed via the environment will occur via different routes. In principle, this would mean that the risk characterisation should be based on the effects of each individual component. However, as the composition of CTP is variable and unknown and the effects of the known individual components are mostly unknown, this is practically impossible.

From the available database it appears that carcinogenicity is a striking hazard associated with CTP(ht), attributable to the presence of PAHs in CTP(ht), and that B(a)P is the best-studied PAH and one of the most toxic ones. Therefore, as a practical solution B(a)P is chosen as the 'leading' PAH on which the risk characterisation will focuss. Although carcinogenicity may not be the only relevant effect of CTP(ht), given the quite high carcinogenic potencies of the PAHs it is likely that limitation of the risk for cancer will automatically reduce the risk for any other possible effect, quite possibly even to zero.

#### Repeated dose toxicity

No valid experimental animal studies or human data addressing the potential noncarcinogenic effects of CTP(ht) were available to the rapporteur. However, since it is concluded that the carcinogenic activity of CTP(ht) is the critical effect, the need for more information on non-carcinogenic effects of CTP(ht) after repeated exposure will be revised in the light of the risk reduction strategy due to its carcinogenic properties (conclusion **i on hold**).

#### **Mutagenicity**

Based on the classification of CTP(ht) as a category 2 mutagen, it is concluded that exposure to CTP(ht) is associated with a mutagenic risk: conclusion **iii**.

#### Carcinogenicity

CTP(ht) and CTPV(ht) are classified as category 1 carcinogens. For quantitative risk assessment, valid human data (mainly in occupationally CTPV(ht)-exposed cohorts) and experimental animal data are available for inhalation and oral exposure, respectively.

#### Exposure via air - Local

For the inhalatory route, the risks for humans exposed via the environment to CTP(ht) can be determined using B(a)P as a marker for total PAHs in the same way as for workers because of the low volatility of the carcinogenic PAHs (the more volatile PAHs are less carcinogenic). Aerosol particles with a fixed ratio of PAHs are formed during the different processes described and will either be released from the factory or be removed from the air. It is assumed that the ratio of the carcinogenic PAHs in the released aerosols will be the same as for the worker.

In conformity with the risk characterisation for workers, starting points for the risk characterisation for humans exposed inhalatory via the environment are the airborne concentrations of B(a)P from table 4.2 and the unit relative risks (URRs) for lung and bladder

cancer as estimated by Armstrong et al. (2003; 2004) in a recent meta-analysis on lung and bladder cancer risk after occupational exposure to PAHs, using B(a)P as indicator of exposure. For lung cancer, the overall URR per unit of 100  $\mu$ g/m<sup>3</sup>.year cumulative B(a)P exposure was 1.20 (95% confidence interval: 1.11-1.29), for bladder cancer this was 1.33 (95% confidence interval: 1.17-1.51).

First, the exposure estimates for the different sites were multiplied by 70, to account for lifetime (70 years) exposure. Then, the RRs at the (cumulative) exposure level were calculated from the URRs at 100  $\mu$ g/m<sup>3</sup>.year cumulative B(a)P as follows: RR<sub>x</sub> = URR<sup>x/100</sup>. Subsequently, excess lifetime risks (ELR) were calculated from the RRs with the formula: ELR = RR\*P –P, in which P is the background lifetime risk in the exposed target population (i.e., the population figuring in the exposure scenario). Background lifetime risks were chosen as 0.08 for lung cancer and 0.018 for bladder cancer, being the 1997 figures for British males, also used by Armstrong et al. (2003; 2004). As several uncertainties are inherently associated with the data and approach used, presentation of a calculated exact figure would be misleading. Therefore, the calculated ELRs (point estimates) were rounded to the nearest order of magnitude.

With a few exceptions (sites PA3 and PA15), all ELR values were equal to or higher than an additional risk level of  $1 \times 10^{-6}$ . Therefore, the inhalatory exposure estimates for all but 2 sites lead to unacceptable high risks for lung as well as bladder cancer. Therefore, a conclusion **iii** is drawn for these sites. For sites PA3 and PA15 also a **conclusion iii** is drawn, but for these two scenarios the level of concern is low.

#### Exposure via food and water - Local

For the oral route, the risks for humans exposed via the environment to CTP(ht) should be determined for the 16 individual PAHs because the ratio of the PAHs in the human intake media will be different. However, as a practical approach in first instance the carcinogenic risk due to B(a)P will be determined. If already for this one PAH a risk is identified, the other 15 PAHs will not be considered further, nor the combination of these PAHs.

Starting points for the risk characterisation for humans exposed orally via the environment are the intake estimates for B(a)P from table 4.3 and the overall dose descriptor T25 derived for B(a)P from the oral carcinogenicity studies in mice and rats.

The lowest, overall T25 of 1 mg/kg bw/d is used for the risk characterisation. From this T25 a human T25 (HT25) of 0.14 mg/kg bw/d is calculated by applying an overall assessment factor of 7 to the T25. The overall assessment factor of 7 only covers for the allometric scaling part of interspecies differences, which is 7 when extrapolating from mice to humans. Other factors (e.g. for intraspecies differences) can be set to 1, because according to the final draft TGD on human health risk characterisation the linear model used for high to low dose extrapolation is considered sufficiently conservative to cover also for these factors.

The estimated lifetime risks for the exposures in the different scenarios were calculated from the HT25 using the formula: eLR = exposure/(HT25/0.25). The calculated eLRs (point estimates) were rounded to the nearest order of magnitude.

All eLR values were equal to or higher than an additional risk level of  $1 \ge 10^{-6}$ . Therefore, for all sites the total oral exposure estimates lead to unacceptable high risks for cancer. Therefore, a conclusion **iii** is drawn for all sites.

Since already exposure to this one PAH shows a considerable risk for cancer, the carcinogenic risks of the 15 other PAHs will not be determined, nor the carcinogenic risk for the combined PAHs. It is to be noted, though, that if there are carcinogens among these PAHs with higher potency than B(a)P, the estimated lifetime risk could be even higher, depending on the exposure estimates for these higher potency PAHs. As to combined exposure to all 16 PAHs, this could also result in even higher lifetime risks than for B(a)P alone.

### Exposure via air and food and water - Regional

As indicated in section 4.1.3, no formal conclusions will be derived for the regional background exposure because of the many unintentional sources contributing to the total emission of PAHs into the environment. For illustrative purposes, however, the lifetime risks have been calculated for the lowest and highest regional B(a)P concentrations found in air (0.02 and 39 ng/m<sup>3</sup>, respectively) and for the resulting lowest and highest total daily B(a)P intake (1.6 and 3100 ng/kg bw/d, respectively), in the same way as described above for the local exposures. The results are presented in **Table 4.7**.

Table 4.7 Cancer risk characterisation for humans exposed via the environment – regional

Regional	ELR	eLR	Conclusion
Air concentration of E	B(a)P		
0.02 ng/m <sup>3</sup>	10 <sup>-7</sup> (lung)		jija
	10 <sup>-7</sup> (bladder)		iiia
39 ng/m <sup>3</sup>	10 <sup>-4</sup> (lung)		
	10 <sup>-4</sup> (bladder)		ii
Total daily intake of E	B(a)P		-
1.6 ng/kg bw/d		10-6	iii
3100 ng/kg bw/d		10-2	iii

<sup>a</sup> Low concern

## Toxicity for reproduction

No valid experimental animal studies were available which addressed the potential reproduction toxicity of CTP(ht). However, animal studies have shown that exposure to high-boiling coal liquid, coal tar derived products, and creosote cause effects on fertility in mice and rats. Although some developmental effects were also observed in these studies, it is not clear that they were directly induced by high-boiling coal liquid, coal tar derived products, or creosote. In humans no adverse effects on sperm characteristics were observed in workers exposed to CTPV in an aluminium reduction plant. In a small retrospective study among psoriasis or dermatitis patients, dermal exposure of to coal tar did not induce a significant increase in spontaneous abortion.

Since CTP(ht) may contain up to 1.5% BaP (classified as toxic for effects on reproduction (category 2)), CTP(ht) is classified as toxic to reproduction (category 2). Although the data are insufficient for quantitative risk characterisation, it is concluded that CTP(ht) is of concern for humans exposed indirectly via the environment. However, since it is concluded that the carcinogenic activity of CTP(ht) is the critical effect, the need for more information on the

reproductive toxicity of CTP(ht) will be revised in the light of the risk reduction strategy due to its carcinogenic properties (conclusion **i on hold**).

## 4.4 HUMAN HEALTH (PHYSICO-CHEMICAL PROPERTIES)

Based on the available information, CTP(ht) is not flammable, not explosive and not oxidising. Therefore, CTP(ht) is expected to be of no concern for human health regarding physico-chemical properties (**conclusion ii**).



# **5** OVERALL RESULTS OF THE RISK ASSESSMENT

### 5.1 ENVIRONMENT

## 5.2 HUMAN HEALTH

#### 5.2.1 Human health (toxicity)

#### Workers

Conclusion (i)	There is a need for further information and/or testing.
Conclusion (ii)	There is at present no need for further information and/or testing and no
	need for risk reduction measures beyond those which are being applied already.
Conclusion (iii)	There is a need for limiting the risks; risk reduction measures which are already being applied shall be taken into account.

Conclusion (i) applies to skin irritation, systemic toxicity after repeated exposure, and effects on reproduction. The conclusion can be put 'on hold' and the necessity for further testing be revisited after a risk reduction strategy.

Conclusion (ii) applies to acute toxicity, eye irritation, and corrosivity.

Conclusion (iii) applies to:

- skin sensitisation, the substance is considered a skin sensitiser and occupational dermal exposure cannot be excluded in several scenarios;

- mutagenicity and carcinogenicity, effects that cannot be excluded for exposure (inhalation and dermal) arising from production and use as an intermediate.

#### Consumers

Not applicable, since there is no consumer exposure.

#### Humans exposed via the environment

- **Conclusion** (i) There is a need for further information and/or testing.
- **Conclusion (iii)** There is a need for limiting the risks; risk reduction measures which are already being applied shall be taken into account.

Conclusion (i) applies to systemic toxicity after repeated exposure and effects on reproduction. The conclusion can be put 'on hold' and the necessity for further testing be revisited after a risk reduction strategy.

Conclusion (iii) applies to mutagenicity and carcinogenicity, effects that cannot be excluded for exposure (inhalation and oral) via the environment.

## 5.2.2 Human health (risks from physico-chemical properties)

**Conclusion (ii)** There is at present no need for further information and/or testing and no need for risk reduction measures beyond those which are being applied already.



# GLOSSARY

Standard term Abbreviation	Explanation/Remarks and Alternative Abbreviation(s)
Ann.	Annex
AF	assessment factor
BCF	bioconcentration factor
bw	body weight / Bw, b.w.
°C	degrees Celsius (centigrade)
CAS	Chemical Abstract System
CEC	Commission of the European Communities
CEN	European Committee for Normalisation
СЕРЕ	European Council of the Paint, Printing Ink and Artists' Colours Industry
d	day(s)
d.wt	dry weight / dw
DG	Directorate General
DT <sub>50</sub>	period required for 50 percent dissipation (define method of estimation)
DT <sub>50lab</sub>	period required for 50 percent dissipation under laboratory conditions (define method of estimation)
DT <sub>90</sub>	period required for 90 percent dissipation (define method of estimation)
DT <sub>90field</sub>	period required for 90 percent dissipation under field conditions (define method of estimation)
EC	European Communities
EC	European Commission
EC <sub>50</sub>	median effective concentration
EEC	European Economic Community
EINECS	European Inventory of Existing Commercial Chemical Substances
EU	European Union
EUSES	European Union System for the Evaluation of Substances
$f_{oc}$	Fraction of organic carbon
G	gram(s)

PNEC(s)	Predicted No Effect Concentration(s)
PNEC <sub>water</sub>	Predicted No Effect Concentration in Water
(Q)SAR	Quantitative Structure Activity Relationship
STP	Sewage Treatment Plant
TGD	Technical Guidance Document <sup>6</sup>
UV	Ultraviolet Region of Spectrum
UVCB	Unknown or Variable composition, Complex reaction products or Biological material
v/v	volume per volume ratio
w/w	weight per weight ratio
W	gram weight
GLP	Good Laboratory Practice
h	hour(s)
ha	Hectares / h
HPLC	High Pressure Liquid Chromatography
IARC	International Agency for Research on Cancer
C <sub>50</sub>	median immobilisation concentration or median inhibitory concentration 1 / <i>explained by a footnote if necessary</i>
ISO	International Standards Organisation
IUPAC	International Union for Pure Applied Chemistry
kg	kilogram(s)
kPa	kilo Pascals
K <sub>oc</sub>	organic carbon adsorption coefficient
K <sub>ow</sub>	octanol-water partition coefficient
Кр	Solids water partition coefficient
1	litre(s)
log	logarithm to the basis 10
L(E)C <sub>50</sub>	Lethal Concentration, Median
LEV	Local Exhaust Ventilation
m	Meter

<sup>&</sup>lt;sup>6</sup> Commission of the European Communities, 1996. Technical Guidance Documents in Support of the Commission Directive 93/67/EEC on risk assessment for new substances and the Commission Regulation (EC) No 1488/94 on risk assessment for existing substances. Commission of the European Communities, Brussels, Belgium. ISBN 92-827-801[1234]

μg	microgram(s)
mg	milligram(s)
MAC	Maximum Accessibility Concentration
MOS	Margins Of Safety
NOAEL	No Observed Adverse Effect Level
NOEC	No Observed Effect Concentration
NOEL	No Observed Effect Level
OEL	Occupational Exposure Limit
OECD	Organisation for Economic Co-operation and Development
OJ	Official Journal
рН	potential hydrogen <i>-logarithm</i> (to the base 10) of the hydrogen ion concentration $\{H^+\}$
рКа	-logarithm (to the base 10) of the acid dissociation constant
рКb	-logarithm (to the base 10) of the base dissociation constant
Pa	Pascal unit(s)
PEC	Predicted Environmental Concentration
STP	Sewage Treatment Plant
WWTP	Waste Water Treatment Plant