European Chemicals Agency

2 December 2009

Substance name: **Coal tar pitch, high temperature**
EC number: **266-028-2**
CAS number: **65996-93-2**

MEMBER STATE COMMITTEE SUPPORT DOCUMENT FOR IDENTIFICATION OF COAL TAR PITCH, HIGH TEMPERATURE AS A SUBSTANCE OF VERY HIGH CONCERN BECAUSE OF ITS PBT AND CMR PROPERTIES

Adopted on 2 December 2009

CONTENTS

TABLES

FIGURES

Substance Name: Coal tar pitch, high temperature

EC Number: 266-028-2

CAS number: 65996-93-2

- *The substance is identified as a CMR (Carc. cat. 2) according to Article 57 (a) of Regulation (EC) 1907/2006 (REACH).*
- *The substance is identified as a PBT according to Article 57 (d) of Regulation (EC) 1907/2006 (REACH).*
- *The substance is identified as a vPvB according to Article 57 (e) of Regulation (EC) 1907/2006 (REACH).*

Summary of how the substance meets the CMR (Cat 1 or 2), PBT or vPvB criteria, or is considered to be a substance giving rise to an equivalent level of concern

The PBT assessment of CTPHT focused on the assessment of its PAH-constituents having been identified in concentrations above or equal to 0.1 % (indicator PAH-constituents). For 10 of these 12 indicator PAH-constituents assessed in total, half-lives in soil have been reported to be in the range of 5.7 to 9.1 years under field conditions. As these half-lives observed in soil exceed the P- and vP-criteria (half lives of 120, respectively 180 days), it is concluded that the vP criterion is fulfilled by all 10 PAH-constituents. Experimentally obtained BCF values higher than 5,000 are reported in fish, mollusks, or crustaceans for 9 indicator PAH-constituents of CTPHT. As these BCF values exceed the B- and vB criteria (measured BCF values in aquatic species > 2000, respectively > 5000), it is concluded that the vB-criterion is fulfilled by the respective 9 substances. BCF values > 2000 have been reported for anthracene, which is a further indicator PAH-constituent of CTPHT and thus fulfils the B-criterion. Long-term data for marine or freshwater species showing no effect concentrations ($NOEC/EC_{10}$) < 0.01 mg/l are available for 9 of the indicator PAH-constituents of CTPHT. Furthermore, 6 of the indicator PAHs found in CTPHT are classified as carcinogen, mutagen or as toxic to reproduction in Annex VI of Regulation (EC) No 1272/2008 (CLP Regulation). Based on the available experimental aquatic toxicity data and the data on classification, it is concluded that 11 of the 12 indicator PAH-constituents for the assessment of CTPHT fulfil the T-criteria of Annex XIII of the REACH Regulation.
On the basis of the available data, it is concluded that 7 of the 12 indicator PAH-constituents identified in CTPHT in concentrations equal to or above 0.1 % are to be considered as both vPvB and PBT substances (fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(a)pyrene, benzo(k)fluoranthene, and benzo(ghi)perylene), one (phenanthrene) as vPvB, and one (anthracene) as PBT. For coal tar pitch, high temperature (CTPHT), the above conclusion on the PBT/vPvB properties of its indicator PAH-constituents has the consequence that this substance needs as well be considered as a substance meeting both the criteria of Article 57(d) and of Article 57(e) of the REACH Regulation.

As, in addition, CTPHT is classified as carcinogen (Carc. Cat.2; R45) (May cause cancer) according to Annex VI, part 3, Table 3.2 (the list of harmonised classification and labelling of hazardous

substances from Annex I to Directive 67/548/EEC) of Regulation (EC) No 1272/2008[1], CTPHT is as well a substance meeting the criteria of Article 57 (a) of the REACH Regulation.

Registration number(s) of the substance or of substances containing a given constituent/impurity or leading to the same transformation or degradation products:

No registration dossier for the substance was submitted to ECHA by the date of agreement on this support document.

[1] This corresponds to a classification Carc. 1B; H350 (May cause cancer) in Annex VI, part 3, Table 3.1 of Regulation (EC) No 1272/2008 (list of harmonised classification and labelling of hazardous substances).

JUSTIFICATION

1 IDENTITY OF THE SUBSTANCE AND PHYSICAL AND CHEMICAL PROPERTIES

1.1 Name and other identifiers of the substance

EC number:	266-028-2
EC name:	Pitch, coal tar, high-temp.
CAS number (in the EC inventory):	65996-93-2
CAS number:	65996-93-2
CAS name:	Pitch, coal tar, high-temp.
IUPAC name:	not applicable
Synonyms:	anode pitch, binder pitch, clay pigeon binder, electrode pitch, hard pitch, impregnating pitch, soft pitch, vacuum pitch
Index number in Annex VI of the CLP Regulation	648-055-00-5
Molecular formula:	not applicable
Molecular weight range:	not applicable
Structural formula:	not applicable

Coal tar pitch, high temperature (CTPHT) is the residue from the distillation of high temperature coal tar (CAS no. 65996-89-6)[2] under vacuum in closed systems. The EINECS description is as follows: "*The residue from the distillation of high temperature coal tar. A black solid with an approximate softening point from 30°C to 180°C. Composed primarily of a complex mixture of three or more membered condensed ring aromatic hydrocarbons*". The composition of CTPHT includes a large variety of polynuclear aromatic constituents, including heterocyclic derivatives.

1.2 Composition of the substance

CTPHT is a complex hydrocarbon mix consisting of three- to seven-membered condensed ring aromatic hydrocarbons, high molecular weight compounds, heterocyclic compounds and benzocarbazoles (The Netherlands, 2008b). Among its constituents also (poly)methylated derivatives of PAHs are found (Steinhauser, 1997, cited in The Netherlands, 2008).

In general, coal tars and coal tar pitches have variable compositions due to variation in source materials and in manufacturing processes. CTPHT is an UVCB substance characterised by a

[2] Coal tars are produced as a by-product of the carbonisation of coal, by cooling and condensing the gases evolved in this process. Coal tars are composed of a complex mix of hydrocarbons and may contain as many as 10,000 constituents, of which approximately 400 have been identified (Franck, 1963). The composition of coal tars may vary greatly, depending on the type of coking coal employed, the coking process and the distillation process used.

variable and high content of polycyclic aromatic hydrocarbons (PAHs) and heterocyclic compounds. Its exact composition varies due to its variable and complex nature, as well as due to variations in the distillation temperature. CTPHTs of different composition may be named with different synonyms hinting to their intended use, e.g. binder pitch or impregnating pitch. Differences in the composition of these two CTPHTs are shown in Table 1.1.

In the Annex XV Transitional Dossier on CTPHT (The Netherlands, 2008), the EPA 16 homocyclic PAHs (structural formulae in Figure 1) are regarded as being representative for the PAH emissions from CTPHT and the risk assessment is based on exposure and effect data available for these PAHs (addressed as 'indicator PAHs' in the following).

Information on the content of the 16 indicator PAHs and other organic constituents in CTPHT is available for CTPHT either used for impregnating or for binding (Table 1.1). As the main use of CTPHT is as binder pitch for the production of anodes and electrodes (see Part II of this support document and The Netherlands, 2008), the data on composition available for binder pitch is therefore chosen as reference for the content of PAHs in the substance.

The present support document focuses on indicator PAH-constituents that are considered relevant for the PBT assessment of CTPHT, i.e. those 12 PAHs confirmed to be contained in the substance in concentrations equal to or higher than 0.1 %. In total, those 12 PAHs represent approx. 10% of the matter of CTPHT. According to the information on binder pitch shown in Table 1.1 this includes the following 12 PAHs: anthracene, phenanthrene, fluoranthene, pyrene, benz(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. It should be noted that the selection of indicator PAHs for PBT assessment would be almost identical on the basis of composition data of impregnating pitch and the 0.1 % threshold (it would differ only with respect to anthracene, with a concentration of 0.074% in impregnating pitch).

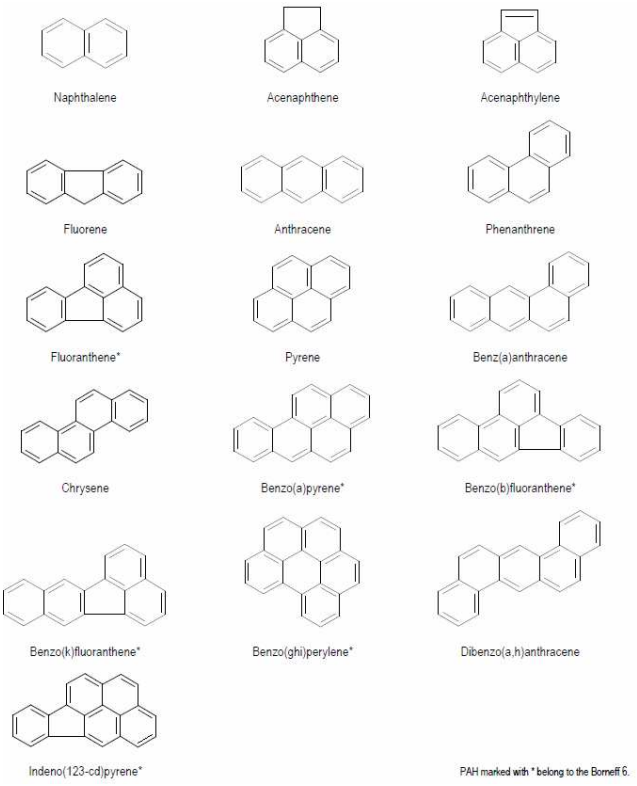

Figure 1: Structural formulae of the 16 PAHs listed in Table 1.1

Table 1.1: Indicative data on composition of CTPHT (The Netherlands, 2008)								
Chemical name	**EINECS Number**	**CAS Number**	**Molecular Formula**	**Molecular Weight**	**Concentration in Impregnating pitch**		**Concentration in Binder pitch**	
					(mg/kg)	**% ***	(mg/kg)	**% ***
Polycyclic Aromatic Hydrocarbons (PAHs)[3]								
Naphthalene	202-049-5	91-20-3	$C_{10}H_8$	128.17	n.d.	**n.d.**	n.d.	**n.d.**
Acenaphthylene	205-917-1	208-96-8	$C_{12}H_8$	152.20	n.d.	**n.d.**	n.d.	**n.d.**
Acenaphthene	201-469-6	83-32-9	$C_{12}H_{10}$	154.21	390	**0.039**	432	**0.043**
Fluorene	201-695-5	86-73-7	$C_{13}H_{10}$	166.22	144	**0.014**	472	**0.047**
Phenanthrene	201-581-5	85-01-8	$C_{14}H_{10}$	178.23	3874	**0.387**	6299	**0.630**
Anthracene	204-371-1	120-12-7	$C_{14}H_{10}$	178.23	737	**0.074**	1311	**0.131**
Fluoranthene	205-912-4	206-44-0	$C_{16}H_{10}$	202.25	17389	**1.739**	10789	**1.079**
Pyrene	204-927-3	129-00-0	$C_{16}H_{10}$	202.25	14849	**1.485**	9449	**0.945**
Benz(a)anthracene **	200-280-6	56-55-3	$C_{18}H_{12}$	228.29	15008	**1.501**	7715	**0.772**
Chrysene	205-923-4	218-01-9	$C_{18}H_{12}$	228.29	14041	**1.404**	8053	**0.805**
Benzo(b)fluoranthene **	205-911-9	205-99-2	$C_{20}H_{12}$	252.31	17408	**1.741**	12131	**1.213**
Benzo(k)fluoranthene **	205-916-6	207-08-9	$C_{20}H_{12}$	252.31	8704	**0.870**	6065	**0.607**
Benzo(a)pyrene **	200-028-5	50-32-8	$C_{20}H_{12}$	252.31	12924	**1.292**	10021	**1.002**
Dibenzo(a,h)anthracene **	200-181-8	53-70-3	$C_{22}H_{14}$	278.35	2209	**0.221**	1749	**0.175**
Benzo(ghi)perylene	205-883-8	191-24-2	$C_{22}H_{12}$	276.33	9945	**0.995**	8664	**0.866**
Indeno(1,2,3cd)pyrene **	205-893-2	193-39-5	$C_{22}H_{12}$	276.33	11106	**1.111**	9061	**0.906**
Other Aromatic Hydrocarbons								
1-Methylfluorene	217-048-5	1730-37-6	$C_{14}H_{12}$	180.26	n.d	**n.d.**	61	**0.006**
2-Methylfluorene	215-853-6	1430-97-3	$C_{14}H_{12}$	180.26	50	**0.005**	112	**0.011**
Cyclopenta(def)phenanthrene **	205-905-6	203-64-5	$C_{15}H_{10}$	190.25	918	**0.092**	821	**0.082**

[3] The 16 PAHs regarded as being representative for the emissions of CTPHT in the Annex XV Transitional Dossier (The Netherlands, 2008).

Table 1.1: Indicative data on composition of CTPHT (The Netherlands, 2008)

Chemical name	EINECS Number	CAS Number	Molecular Formula	Molecular Weight	Concentration in Impregnating pitch		Concentration in Binder pitch	
					(mg/kg)	% *	(mg/kg)	% *
Acephenanthrylene **	205-911-9	205-99-2	$C_{20}H_{12}$	252.32	828	**0.083**	386	**0.039**
Benzo(a)fluorene **	205-944-9	238-84-6	$C_{17}H_{12}$	216.29	4509	**0.451**	1974	**0.197**
Benzo(b)fluorene **	205-952-2	243-17-4	$C_{17}H_{12}$	216.29	4306	**0.431**	2456	**0.246**
Benzo(e)pyrene **	205-892-7	192-97-2	$C_{20}H_{12}$	252.32	11891	**1.189**	8976	**0.898**
Perylene	205-900-9	198-55-0	$C_{20}H_{12}$	252.32	5014	**0.501**	3167	**0.317**
Anthantrene	205-884-3	191-26-4	$C_{22}H_{12}$	276.34	4581	**0.458**	3464	**0.346**
Tar Bases / Nitrogen-containing Heterocycles								
Acridine	205-971-6	260-94-6	$C_{13}H_9N$	179.21	242	**0.024**	264	**0.026**
Carbazole	201-696-0	86-74-8	$C_{12}H_9N$	167.2	1556	**0.156**	1664	**0.166**
Sulfur-containing Heterocycles								
Dibenzothiophene	205-072-9	132-65-0	$C_{12}H_8S$	184.26	269	**0.027**	438	**0.044**
Oxygen-containing Heterocycles / Furans								
Dibenzofuran	205-071-3	132-64-9	$C_{12}H_8O$	168.19	n.d	**n.d.**	215	**0.022**

* n.d. = not detected (detection limit 50 mg/kg)

** EC names reported in EINECS: for Benz(a)anthracene → Benz[a]amthracene; for Benzo(b)fluoranthene → Benzo[e]acephenanthrylene; for Benzo(k)→ Benzo[k]fluoranthene; for Benzo(a)pyrene → Benzo[def]chrysene; for Dibenzo(ah)anthracene → Dibenzo[ah]anthracene; for Benzo(ghi)perylene → Benzo[ghi]perylene; for Indeno(1,2,3cd)pyrene → Indeno[1,2,3-cd]pyrene; for Cyclopenta(def)phenanthrene → 4H-Cyclopenta[def]phenanthrene; for Acephenanthrylene → Benzo[e]acetophenanthrylene; for Benzo(a)fluorene → Benzo[a]fluorene; for Benzo(b)fluorene → Benzo[b]fluorine; for Benzo(e)pyrene → Benzo[e]fluorene

1.3 Physico-chemical properties

Table 1.2: Summary of physico-chemical properties of CTPHT (The Netherlands, 2008)			
REACH ref Annex, §	**Property**	**Value**	**Comment/reference**
VII, 7.1	Physical state at 20°C and 101.3 kPa	Black solid	
VII, 7.2	Melting/freezing point	65 - 150 °C	Softening range; CCSG 2006[4]
VII, 7.3	Boiling point	>360 °C	At 1013 hPa
VII, 7.5	Vapour pressure (Pa)	< 10 < 1000	At 20 °C; At 200 °C; OECD 104; CCSG 2006[2]
VII, 7.7	Water solubility (mg/l)	~0.040	16 EPA PAHs, at a loading of 10 g/L at 22 ^{o}C; RÜTGERS VFT 1999
VII, 7.8	Partition coefficient n-octanol/water (log value)		Not applicable
	Density (g/m^3)	1.15 – 1.40	At 20 °C; ASTM D 71; CCSG 2006[2]
VII, 7.9	Flash point (°C)	>250	ISO 2719; CCSG 2006[2]
VII, 7.12	Auto flammability (°C)	>450	Ignition point at 101.3 kPa; DIN 51794 ; CCSG 2006[2]
VII, 7.11	Explosive properties	Not explosive	CCSG 2006[2]
VII, 7.13	Oxidizing properties	Not oxidizing	CCSG 2006[2]

4 CCSG 2006: Internal communication, Coal Chemicals Sector Group/CEFIC 2006 (The Netherlands, 2008)

1.3.1 Physico-chemical properties of indicator constituents of CTPHT relevant for PBT/vPvB assessment

Table 1.3: Physico-chemical Properties of the 12 PAHs present in CTPHT in concentrations above or equivalent to 0.1% (The Netherlands, 2008)

Substance	CAS no	Molecular formula	Molecular weight ($g.mol^{-1}$)	Melting point (°C)	Boiling point (°C)	Water solubility ($\mu g.l^{-1}$)	Log Kow (-)	Vapour pressure (Pa at 25 °C)	Density ($kg.l^{-1}$)	Henry's constant (Pa m^3/mol at 25 °C)
Anthracene	120-12-7	$C_{14}H_{10}$	178.2	216.4	342[e]	47[a]	4.68[d]	9.4×10^{-4}[i]	1.283	4.3[l]
Phenanthrene	85-01-8	$C_{14}H_{10}$	178.2	100.5	340	974[a]	4.57[d]	2.6×10^{-2}[i]	0.980	3.7[l]
Fluoranthene	206-44-0	$C_{16}H_{10}$	202.3	108.8	375	200[a]	5.20[d]	1.2×10^{-3}[h]	1.252	1.1[o]
Pyrene	129-00-0	$C_{16}H_{10}$	202.3	156	360	125[a]	4.98[e]	1.0×10^{-3}[i]	1.271	1.4[n]
Benz(a)anthracene	56-55-3	$C_{18}H_{12}$	228.3	160.7	435	10.2[a]	5.91[d]	7.6×10^{-6}[i]	1.226	0.81[p]
Chrysene	218-01-9	$C_{18}H_{12}$	228.3	253.8	448	1.65[a]	5.81[d]	5.7×10^{-7}[j]	1.274	0.079[q]
Benzo(a)pyrene	50-32-8	$C_{20}H_{12}$	252.3	175	496	1.54[a]	6.13[d]	7.3×10^{-7}[j]	1.35	0.034[o(20 °C)]
Benzo(b)fluoranthene	205-99-2	$C_{20}H_{12}$	252.3	168.3	481	1.28[a]	6.12[f]	3.3×10^{-6}[k]	-	0.051[o(20 °C)]
Benzo(k)fluoranthene	207-08-9	$C_{20}H_{12}$	252.3	217	480	0.93[a]	6.11[d]	1.3×10^{-7}[k]	-	0.043[o(20 °C)]
Benzo(ghi)perylene	191-24-2	$C_{22}H_{12}$	276.3	277	545[i]	0.14[a]	6.22[d]	1.4×10^{-8} [j]	1.329	0.027[o(20 °C)]
Dibenzo(a,h)anthracene	53-70-3	$C_{22}H_{14}$	278.4	266.6	524	0.82[b]	6.50[e]	3.7×10^{-10}[j]	1.282	$1.3.10^{-4}$[q]
Indeno(1,2,3-cd)pyrene	193-39-5	$C_{22}H_{12}$	276.3	163.6	536	0.1[c]	6.58[f]	1.7×10^{-8}[k]	-	0.046[q]

The data presented above were taken form Mackay *et al.* (1992). The selected values for water solubility were preferably based on generated column methods (a) and if absent, on shake-flask methods (b) using geometric means ((c) for indeno(1,2,3-cd)pyrene, no data were available, a default value of 0.1 µg/l was used). The selected values for log Kow were preferably based on slow-stirring/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/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).

2 CLASSIFICATION AND LABELLING

2.1 Classification in Annex VI of Regulation (EC) No 1272/2008

CTPHT has index number 648-055-00-5 in Annex VI, part 3, Tables 3.1 and 3.2 of Regulation (EC) No 1272/2008.

CTPHT is classified as carcinogen (Carc. Cat.2 ; R45) according to Annex VI, part 3, Table 3.2 (the list of harmonised classification and labelling of hazardous substances from Annex I to Directive 67/548/EEC) of Regulation (EC) No 1272/2008. According to the same Regulation, some of the indicator PAH-constituents relevant for the PBT/vPvB assessment of CTPHT are classified as carcinogen, mutagen or as toxic to reproduction. The full classification of CTPHT and its indicator PAH-constituents according to Annex VI, part 3, Table 3.2 of Regulation (EC) No 1272/2008) is provided in Table 2.1.

Table 2.1: Classification and labelling of CTPHT and its 12 PAH-constituents according to Regulation (EC) No 1272/2008 (Annex VI, part 3, Table 3.2)

Substance	CAS no	Index Number	Classification [concentration limits]
CTPHT	65996-93-2	648-055-00-5	Carc. Cat. 2;R45
Anthracene	120-12-7	*, **	*, **
Phenanthrene	85-01-8	*	*
Fluoranthene	206-44-0	*	*
Pyrene	129-00-0	*	*
Benz(a)anthracene	56-55-3	601-033-00-9	Carc. Cat. 2; R45 N; R50-53
Chrysene	218-01-9	601-048-00-0	Carc. Cat. 2; R45 Muta. Cat. 3; R68 N; R50-53
Benzo(a)pyrene	50-32-8	601-032-00-3	Carc. Cat. 2; R45 [C ≥ 0.01%] Muta. Cat. 2; R46 Repr. Cat. 2; R60-61 R43 N; R50-53
Benzo(b)fluoranthene	205-99-2	601-034-00-4	Carc. Cat. 2; R45 N; R50-53
Benzo(k)fluoranthene	207-08-9	601-036-00-5	Carc. Cat. 2; R45 N; R50-53
Benzo(ghi)perylene	191-24-2	*	*
Dibenzo(a,h)anthracene	53-70-3	601-041-00-2	Carc. Cat. 2; R45 [C ≥ 0.01%] N; R50-53
Indeno(1,2,3-cd)pyrene	193-39-5	*	*

Key:
*: No classification in the context of Regulation (EC) No. 1272/2008
**: Xi; R38 N;R50-53 (in the context of Directive 67/548/EEC) proposed in the draft risk assessment report on anthracene (Greece, 2008)
Carc.: carcinogenic; Muta: mutagenic; Repr.: toxic for reproduction
R43: May cause sensitisation by skin contact
R45: May cause cancer
R46: May cause heritable genetic damage
R50: Very toxic to aquatic organisms, and
R53: May cause long-term adverse effects in the aquatic environment
R60: May impair fertility
R61: May cause harm to the unborn child
R68: Possible risk of irreversible effects.
N: Dangerous for environment

Table 2.2: Classification and labelling of CTPHT and its 12 PAH-constituents according to Regulation (EC) No 1272/2008 (Annex VI, part 3, Table 3.1)

Substance	CAS no [Index No]	Classification		Labelling	
		Hazard Class and Category Code(s) [specific concentration limits]	Hazard statement Code(s)	Pictogram, Signal Word Code(S)	Hazard statement Code(s)
CTPHT	65996-93-2 [648-055-00-5]	Carc. 1B	H350	GHS08 Dgr	H350
Anthracene	120-12-7	*,**	*,**	*,**	*,**
Phenanthrene	85-01-8	*	*	*	*
Fluoranthene	206-44-0	*	*	*	*
Pyrene	129-00-0	*	*	*	*
Benz(a)anthracene	56-55-3 [601-033-00-9]	Carc. 1B Aquatic Acute 1 AquaticChronic 1	H350 H400 H410	GHS08 GHS09 Dgr	H350 H410
Chrysene	218-01-9 [601-048-00-0]	Carc. 1B Muta. 2 Aquatic Acute 1 Aquatic Chronic 1	H350 H341 H400 H410	GHS08 GHS09 Dgr	H350 H341 H410
Benzo(a)pyrene	50-32-8 [601-032-00-3]	Carc. 1B [C ≥ 0.01%] Muta. 1B Repr. 1B Skin Sens. 1 Aquatic Acute 1 Aquatic Chronic 1	H350 H340 H360-FD H317 H400 H410	GHS08 GHS07 GHS09 Dgr	H350 H340 H360FD H317 H410
Benzo(b)fluoranthene	205-99-2 [601-034-00-4]	Carc. 1B Aquatic Acute 1 Aquatic Chronic 1	H350 H400 H410	GHS08 GHS09 Dgr	H350 H410
Benzo(k)fluoranthene	207-08-9 [601-036-00-5]	Carc. 1B Aquatic Acute 1 Aquatic Chronic 1	H350 H400 H410	GHS08 GHS09 Dgr	H350 H410
Benzo(ghi)perylene	191-24-2	*	*	*	*
Dibenzo(a,h)anthracene	53-70-3 [601-041-00-2]	Carc. 1B [C ≥ 0.01%] Aquatic Acute 1 Aquatic Chronic 1	H350 H400 H410	GHS08 GHS09 Dgr	H350 H410
Indeno(1,2,3-cd)pyrene	193-39-5	*	*	*	*

Key:
*: No classification in the context of Regulation (EC) No. 1272/2008
**: Xi; R38 N;R50-53 (in the context of Directive 67/548/EEC) proposed in the draft risk assessment report on anthracene (Greece, 2008) [translated according to Table 1.1 of Annex VII of Regulation (EC) No. 1272/2008 into: Skin Irrit. 2; Aquatic Acute 1; Aquatic Chronic 1]
N: Dangerous for environment; R50-53: Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment.
Carc.1B: Carcinogen; Muta 2, 1B: Germ cell mutagen; Repr.1B: Toxic to reproduction
Aquatic acute 1, Aquatic chronic 1: Hazardous to the aquatic environment
Skin Sens.1: Skin sensitizing
H317: May cause an allergic skin reaction; H341: Suspected of causing genetic defects
H350: May cause cancer; H360-FD: May damage fertility. May damage the unborn child
H400: Very toxic to aquatic life; H410: Very toxic to aquatic life with long lasting effects.
GHS07: exclamation mark; GHS08: health hazard; GHS09: environment; Dgr: Danger

The harmonised classification and labelling as hazardous substances according to Regulation (EC) No 1272/2008 (Annex VI, part 3, Table 3.1 (list of harmonised classification and labelling of hazardous substances)) for CTPHT and its 12 indicator PAH-constituents relevant for the PBT/vPvB assessment is presented in Table 2.2.

3 ENVIRONMENTAL FATE PROPERTIES

3.1 Overview

The data presented here were retrieved from the Annex XV Transitional Dossier on coal tar pitch, high temperature (CTPHT) (The Netherlands, 2008).

According to the approach followed herein (see Section 1.2), the evaluation of the fate properties is based on available data for the 12 indicator PAHs considered relevant for the PBT/vPvB assessment of CTPHT. No information on the environmental fate of CTPHT itself was found.

3.2 Degradation

3.2.1 Abiotic degradation

3.2.1.1 Hydrolysis

In general, PAHs are hydrolytically stable in aqueous systems. Under environmental conditions, therefore, hydrolysis does not contribute to the degradation of PAHs (Howard *et al.* (1991) cited in The Netherlands, 2008).

3.2.1.2 Atmospheric degradation

In the atmosphere, the PAHs are either gas phase or particle-associated. It has been shown that the 2-4 ring PAHs with vapour pressure higher than or equal to 10^{-4} Pa are mostly gas phase-related and PAHs of 4 rings or more with vapour pressure below 10^{-4} Pa are particle-associated. In the gas phase PAHs are oxidized by atmospheric hydroxyl (OH) and nitrate radicals and ozone, whereas the particle-associated PAHs are expected to be degraded by direct photolysis and by reaction with ozone (The Netherlands, 2008).

Atmospheric half-lives are given in the Annex XV Transitional Dossier on CTPHT. For the 2-4 ring PAHs (from the 12 indicator PAHs), representative lifetimes with respect to gas-phase reactions range from 2 hours to 2 days for reactions with OH. Few data indicate half-lives from 120 days to 340 days for gas phase nitrate reactions. Under environmental conditions, PAHs of higher molecular mass are almost completely adsorbed onto fine particles. Studies indicate that the degradation rate depends on the particle material, with PAHs being more stable when adsorbed to particles of higher carbon content. Representative lifetimes of the particle-associated PAHs are in the range of 15 minutes to 6-8 days with respect to photolysis (The Netherlands, 2008).

3.2.1.3 Phototransformation in water and soil

PAHs are photo-degraded by two processes, direct photolysis by light with a wavelength < 290 nm and indirect photolysis (photo-oxidation) by at least one oxidizing agent (Volkering and Breure

(2003) cited in The Netherlands, 2008). Singlet oxygen is the main oxidant, but also reactions with nitrite and to a lesser extent with nitrate may take place (Suzuki *et al.*, (1987) cited in The Netherlands, 2008). The degradation rate depends on the content of dissolved oxygen, and may be increased in the presence of humic acid, while it increases exponentially with the temperature (Moore and Ramamoorthy, 1984 cited in The Netherlands, 2008). When PAHs are adsorbed to suspended particles, the accessibility for photochemical reactions will depend on the nature of the particles.

Photodegradation in natural waters takes normally place only in the upper few centimetres of the water-column and is therefore not considered to have significant impact on the overall persistency of PAHs in the aquatic environment. As exposure to light is even more limited in soils, photo-degradation is as well not considered a relevant degradation process in terrestrial environments.

3.2.2 Biodegradation

3.2.2.1 Biodegradation in water

Standard tests for biodegradation in water have demonstrated that PAHs with up to four aromatic rings are biodegradable under aerobic conditions, but that biodegradation rates of PAHs with more aromatic rings are very low (The Netherlands, 2008). In general, the biodegradation rates decrease with increasing number of aromatic rings. This correlation has been attributed to factors like the bacterial uptake rate and the bioavailability. The bacterial uptake rate has been shown to be lower for the higher molecular weight PAHs as compared to the PAHs of lower molecular weight. This may be due to the size of high molecular weight members, which limits their ability to cross cellular membranes. In addition, bioavailability is lower for higher molecular PAHs due to adsorption to organic matter in water and sediment. It has further been shown that half-lives of PAHs in estuarine sediment are proportionally related to the octanol-water partition coefficient (Kow) (Durant *et al*, (1995) cited in The Netherlands, 2008).

3.2.2.2 Biodegradation in sediments

In general, PAHs are considered to be persistent under anaerobic conditions (Neff (1979); Volkering and Breure (2003) cited in The Netherlands, 2008). Aquatic sediments are often anaerobic with the exception of a few millimetre thick surface layer at the sediment-water interface, which may be dominated by aerobic conditions. The degradation of PAHs in aquatic sediments is therefore expected to be very slow.

3.2.2.3 Biodegradation in soil

Biodegradation rates of PAHs in soil depend on several factors related to the soil type, including pH, moisture content, nutrients, oxygen, and the diversity of the soil microbial population. Various species (bacteria, fungi, yeasts and algae) are known to degrade PAHs in soil (The Netherlands, 2008). It has been shown that the number of PAH-degrading microorganisms and the degradation capacity is higher in PAH-contaminated soils than in pristine soils, something explained by the development of an adapted soil microbial community. Several studies have also been demonstrated enhanced PAH-degradation rates when the soil had been enriched with isolated PAH-degrading microorganisms (Davis *et al.* (1993); Grosser *et al.* (1995); Schneider *et al.* (1996) cited in The Netherlands, 2008).

On the basis of a comparison between two studies (Wild *et al.* 1991 and Wild and Jones, 1993) it was illustrated that the half-lives observed under laboratory conditions can be much shorter than those obtained from long-term field studies. This was attributed by the authors to the more optimal conditions (temperature, moisture content, nutrient and oxygen supply) applied in the laboratory tests.

Wild and Jones (1993) and Wild *et al.* (1991) studied the biodegradation of PAHs in soil amended with sewage sludge under laboratory and field conditions, respectively. The half-lives for PAHs determined in the two experiments are presented in Table 3.1. Whereas the half-lives obtained in the laboratory soil microcosms were in the range of days, those representing the field conditions were in the range of years.

Table 3.1: Half-lives for 10 PAHs determined from soil microcosm and long-term field studies

PAH (number of rings)	Half lives obtained from soil microcosms (days) Wild & Jones (1993)	Half lives obtained from long term field experiment (years) Wild *et al* (1991)
Phenanthrene (3)	83-193	5.7
Anthracene (3)	48-120	7.9
Fluoranthene (4)	110-184	7.8
Pyrene (4)	127-320	8.5
Benz(a)anthracene and Chrysene (4)	106-313	8.1
Benzo(b)fluoranthene (5)	113-282	9.0
Benzo(k)fluoranthene (5)	143-359	8.7
Benzo(a)pyrene (5)	120-258	8.2
Benzo(ghi)perylene (6)	365-535	9.1

No experimental data on half-lives for dibenzo(a,h)anthracene (5 rings) and indeno(1,2,3-cd)pyrene (6 rings) were found.

3.2.3 Summary and discussion on degradation

According to Annex XIII of the REACH Regulation, the definitive P criterion is based on half-lives in (fresh, estuarine or marine) water, soils or (fresh, estuarine or marine water) sediments. The degradation kinetics of PAHs in the different environmental compartments are influenced by a number of factors, and to a great extent determined by their very low water solubility and tendency to adsorb to particles and organic matter in the environment. Their low bioavailability (especially of PAHs with more than two aromatic rings) is one of the limiting factors for their biodegradation.

'Aging' is a phenomenon associated with increased residence time of PAHs in soil, which can further decrease the bioavailability of PAHs in the terrestrial environment. Freshly spiked PAHs are more readily desorbed and thus more bioavailable than PAHs that have been in soil or sediment for a longer period of time (The Netherlands, 2008). This means that studies involving artificially added PAHs (e.g. ^{14}C-labelled) often result in biodegradation rates much higher than rates observed for the same substances present in soil as part of a contamination by coal tar.

In the assessment for persistence of the PAHs representing CTPHT, half-lives obtained under realistic conditions, i.e. field conditions, are given priority, as Annex XIII of the REACH Regulation requires the data to be collected under the adequate conditions. The study by Wild *et al.* (1991) reports half-lives in soil for 10 of the 12 PAHs addressed in the present assessment

[anthracene, phenanthrene, fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene and benzo(ghi)perylene] above the P and vP criteria set in the Annex XIII, and it is selected as the key study for the P assessment of CTPHT. Experimental data on half-lives for dibenzo(a,h)anthracene and indeno(1,2,3-cd)pyrene are lacking in this study.

Mackay *et al.* (1992) estimated half-lives in the different environmental compartments based on model calculations and literature search. On the basis of the results of this study, dibenzo(a,h)anthracene and indeno(1,2,3-cd)pyrene are expected to be as well persistent in soil and sediment: the estimated half-lives for the two PAHs were in soil in the range of 420 to 1250 days, and in sediments longer than 1250 days.

3.3 Environmental distribution

3.3.1 Adsorption/desorption

The octanol-water coefficients of the indicator PAH-constituents of CTPHT are shown in Table 3.2. A linear relationship between Kow and the organic carbon-water partitioning coefficient Koc has been demonstrated for PAHs in sediments and soil. The Log Kow values from 4.6 to 6.6 can be translated as a high potential for partitioning to soils and sediments. Partitioning processes like adsorption to airborne particulate matter, as well as accumulation in sludge during wastewater treatment, have been demonstrated especially for high molecular weight PAHs (The Netherlands, 2008).

Table 3.2: Log Kow values of selected PAH-constituents of CTPHT (The Netherlands, 2008)

Substance	Log Kow
Anthracene	4.68
Phenanthrene	4.57
Fluoranthene	5.20
Pyrene	4.98
Benz(a)anthracene	5.91
Chrysene	5.81
Benzo(a)pyrene	6.13
Benzo(b)fluoranthene	6.12
Benzo(k)fluoranthene	6.11
Benzo(ghi)perylene	6.22
Dibenzo(a,h)anthracene	6.50
Indeno(1,2,3-cd)pyrene	6.58

3.3.2 Volatilisation

With their low vapour pressures in the range of 10^{-2}-10^{-10} Pa, the PAHs contained in CTPHT are expected to volatilise very slowly. In the Annex XV Transitional Dossier on CTPHT it is concluded that, under field conditions, volatilisation of PAHs is insignificant (The Netherlands, 2008).

3.4 Bioaccumulation

3.4.1 Aquatic bioaccumulation

Bioconcentration in aquatic organisms can be determined at steady state conditions as the concentration in the organism divided by the concentration in the water, or as the ratio between the rates of uptake and depuration at non steady state conditions. The bioconcentration factor (BCF) is linearly correlated with the Kow up to log Kow values in the range of 5 - 6. At higher log Kow values, the BCF tends to stay constant or may even decrease with increasing log Kow (The Netherlands, 2008). This is explained by characteristics like lipid solubility variations, slow desorption, low bioavailability, and reduced membrane passage due to the molecular size, usually associated with molecules having a very high Kow. As for PAHs, this trend has been observed in studies of bioaccumulation potential in fish but not in studies with molluscs or crustaceans.

Potential for biotransformation of substances in exposed species is also an important factor in assessing bioaccumulation. BCF values may be higher in early life stages of an organism than in the adult stage. Whereas fish, and to some extent also molluscs, have the ability to metabolise PAHs, no evidence of metabolism of PAHs has been observed in algae, or oligochaeta.

As part of the Annex XV Transitional Dossier on CTPHT (The Netherlands, 2008), data from studies on bioaccumulation of the 16 representative PAHs were collected. The quality of the studies was evaluated and each study was given a reliability score. Only studies evaluated as reliable and relevant are included for the 12 PAHs addressed in this report (valid without restrictions or valid with restriction; see Tables 3.3 & 3.4).

For each substance, a key study representative for the bioaccumulation potential has been selected. The studies preferred as key studies are equilibrium studies performed with fish and with chemical analysis of the substance in water and in the organism, showing high bioconcentration. However, in addition to data on fish, BCF values for molluscs and crustaceans are considered in the assessment of the bioaccumulation potential of the PAHs as well. In Tables 3.3 and 3.4 the selected key studies are highlighted by bold font of the reference. Justification for choosing the highlighted studies is provided in the notes to the tables.

Bioaccumulation and the role of biotransformation in the bioaccumulation process of PAHs were studied in a static experimental set-up with fathead minnows (*Pimephales promelas*) (De Maagd, 1996). The results indicated that biotransformation did influence the bioaccumulation of benz(a)anthracene, but had no effect on the accumulation of phenanthrene and anthracene. The uptake of fluoranthene, however, could be better modelled if biotransformation was taken into account. The calculated BCF values when biotransformation was inhibited were 6,800 for phenanthrene and anthracene, 3,400 for fluoranthene, and 200 for benz(a)anthracene.

In a second study by De Maagd *et al.* (1998), with fathead minnows, benz(a)anthracene was tested in a flow-through study resulting in BCF values of 262-265.

In another study with fathead minnows (Weinstein and Oris, 1999), juvenile fish (48 hours post-hatching) were exposed in a static system to four concentrations of fluoranthene. The determined BCF value was 9,054 ± 555.

A regular semi-static (renewal) bioaccumulation test was carried out by De Voogt *et al.* (1991). The BCF was determined by dividing the final concentration in fish by the average concentration in

water during the last renewal period. The BCF values determined were 4,550 for anthracene and 11,300 for pyrene.

De Voogt *et al.* (1991) also performed a static experiment. The BCF value determined for anthracene as the concentration in fish divided by the concentration in water at the end of the static experiment was 6000.

Jonsson *et al.* (2004) exposed the fish *Cyprinodon variegatus* for 36d to phenanthrene and pyrene in a continuous flow system with seawater, followed by 8d of depuration. BCFs ranged from 700 to 2,229 for phenanthrene, and from 50 to 145 for pyrene.

Table 3.3: Experimentally obtained BCF values of PAHs in fish or mollusks

Substance	Species	BCF (L/kg)	Val	Test system	Type	Chem. analysis	References
Anthracene	Mollusca						
	U. imbecilis (larv.)	345 (highest 420)	2	R	Equi (parent)		Weinstein & Polk (2001)
	Fish						
	L. macrochirus	900	2	S	k_1/k_2 (total)	^{14}C	Spacie *et al.*, 1983
	P. promelas	6760	2	S	k_1/k_2 (parent)	HPLC	De Maagd *et al.*, 1996
	P. reticulata	4550 (pref)*	2	R	Equi (parent)	HPLC	**De Voogt *et al.*, 1991**
	P. reticulata	6000	2	S	Equi (parent)	HPLC	**De Voogt *et al.*, 1991**
Phenanthrene	Mollusca						
	M. edulis	1240	1	F	k_1/k_2 (parent)	HPLC	McLeese & Burridge, 1987
	M. arenaria	1280	1	F	k_1/k_2 (parent)	HPLC	McLeese & Burridge, 1987
	Fish						
	P. promelas	6760	2	S	k_1/k_2 (parent)	HPLC	**De Maagd *et al.*, 1996**
	C. variegatus	810 (le)	1	CF	k_1/k_2 (parent)	GCMS	Jonsson *et al.*, 2004
	C. variegatus	2229 (he)	1	CF	k_1/k_2 (parent)	GCMS	Jonsson *et al.*, 2004
	C. variegatus	700 (le)	1	CF	Equi (parent)	GCMS	Jonsson *et al.*, 2004
	C. variegates	1623 (he)	1	CF	Equi (parent)	GCMS	Jonsson *et al.*, 2004
Fluoranthene	Mollusca						
	M. edulis	5920	1	F	k_1/k_2 (parent)	HPLC	McLeese & Burridge, 1987
	M. arenaria	4120	1	F	k_1/k_2 (parent)	HPLC	McLeese & Burridge, 1987
	Fish						
	P. promelas	9054	2	S	Equi (parent)	HPLC	**Weinstein & Oris, 1999**
	P. promelas	3388	2	S	k_1/k_2 (parent)	HPLC	De Maagd *et al.*, 1996
Pyrene	Mollusca						
	M. arenaria	6430	1	F	k_1/k_2 (parent)	HPLC	McLeese & Burridge, 1987
	M. edulis	4430	1	F	k_1/k_2 (parent)	HPLC	McLeese & Burridge, 1987
	D. polymorpha	16000 (21h)	2	S	k_1/k_2 (total=parent)	LSC	Bruner *et al.*, 1994
	D. polymorpha	13000 (21l)	2	S	k_1/k_2 (total=parent)	LSC	Bruner *et al.*, 1994
	D. polymorpha	35000 (15)	2	S	k_1/k_2 (total=parent)	LSC	Bruner *et al.*, 1994
	D. polymorpha	43000 (Av1)	2	S	k_1/k_2 (total=parent)	LSC	Gossiaux *et al.*, 1996
	D. polymorpha	37000 (Av2)	2	S	k_1/k_2 (total=parent)	LSC	Gossiaux *et al.*, 1996
	Fish						
	Poecilia reticulata	11300 (pref)	2	R	Equi (parent)	HPLC	**De Voogt *et al.*, 1991**
	Poecilia reticulata	2700*	2	S	Equi (parent)	HPLC	**De Voogt *et al.*, 1991**

Table 3.3: Experimentally obtained BCF values of PAHs in fish or mollusks

Substance	Species	BCF (L/kg)	Val	Test system	Type	Chem. analysis	References
	C. variegatus	145 (le)	1	CF	k_1/k_2 (parent)	GCMS	Jonsson *et al.*, 2004
	C. variegatus	97 (he)	1	CF	k_1/k_2 (parent)	GCMS	Jonsson *et al.*, 2004
	C. variegatus	50 (le)	1	CF	Equi (parent)	GCMS	Jonsson *et al.*, 2004
	C. variegatus	53 (he)	1	CF	Equi (parent)	GCMS	Jonsson *et al.*, 2004
Benz(a)anthracene	Fish						
	P. promelas	200-265	2	S	k_1/k_2 (parent)	HPLC	De Maagd *et al.*, 1996, 1998
Benzo(a)pyrene	Mollusca						
	D. polymorpha	84000 (21h)	2	S	k_1/k_2 (total=parent)	LSC	Bruner *et al.*, 1994
	D. polymorpha	41000 (21l)	2	S	k_1/k_2 (total=parent)	LSC	Bruner *et al.*, 1994
	D. polymorpha	77000 (15)	2	S	k_1/k_2 (total=parent)	LSC	Bruner *et al.*, 1994
	D. polymorpha	133000 (Av3)	2	S	k_1/k_2 (total=parent)	LSC	**Gossiaux *et al.*, 1996**
	D. polymorpha	142000 (Av4)	2	S	k_1/k_2 (total=parent)	LSC	Gossiaux *et al.*, 1996

S. static exposure system; C: Continuous; F, flow-through system; R, static renewal system; k_1/k_2, kinetic: uptake rate/depuration rate. Equi: equilibrium, Val = Validity (1: Reliable without restrictions, 2: Reliable with restrictions, 3: Not reliable, 4: Not assignable); dw = based on dry weights; pref = preferred by the author; lw = based on lipid weights; le: low exposure concentration; he: high exposure concentration; HPLC: High Performance Liquid Chromatography; GCMS: Gas Chromatography Mass Spectrometry; LSC: Liquid Scintillation Counting

21h = 21 mm size class with high lipid content

21l = 21 mm size class with low lipid content

15 = 15 mm size class

Av1 = average BCF obtained from 4 experiments at ambient field temperatures (individual BCFs were 33000, 22000, 77000, and 39000)

Av2 = average BCF obtained from 6 experiments after acclimatisation to lab temperatures (individual BCFs were 32000, 48000, 41,000, 39000, 24000, and 39000)

Av3 = average BCF obtained from 11 experiments at ambient field temperatures (individual BCFs were 77000, 49000, 191000, 167000, 132000, 165000, 150000, 197000, 40000, 24000, and 273000)

Av4 = average BCF obtained from 12 experiments after acclimatisation to lab temperatures (individual BCFs were 190000, 83000, 61000, 197000, 220000, 116000, 40000, 147000, 215000, 270000, 107000, and 62000)

* The BCF value of 4550 is considered the preferable on by de Voogt et al. (1991) as it was determined in a semi-static test by dividing the final concentration in the fish by the average concentration in water during the last renewal period wheras the other BCF (6000) was determined based on a static test (i.e. calculated from the concentration in the fish divided by the concentration in the water at the end of the test).

Marked in bold: Key study. The study by de Voogt *et al*, 1991 was selected as key study for anthracene and pyrene as this was the most reliable one on fish showing BCF > 2000. For phenanthrene the study by de Maagd *et al*, 1996 was the most reliable one with BCF > 2000. The study by Weinstein & Oris, 1999 was chosen as key study as it reports a reliable equilibrium BCF for fluoranthene. For benzo(a)pyrene the study by Gossiaux *et al*, 1996 was chosen among studies on the same organisms and of same validity as key study because it was performed at ambient field temperatures compared to laboratory temperatures.

Table 3.4: Experimentally obtained BCF values of PAHs in Crustaceans						
Substance	**Species**	**BCF (L/kg)**	**Test System**	**Type**	**Chem. analysis**	**References**
Anthracene	*D. magna* *D. pulex* *D. magna*	511 917 970	S S S	k_1/k_2 Equi Equi	^{14}C FS HPLC	McCarthy *et al.*, 1985 Southworth *et al.*, 1978 Newsted & Giesy, 1987
Phenanthrene	*D. pulex* *D. magna*	325 324	S S	Equi Equi	FS HPLC	Southworth *et al.*, 1978 Newsted & Giesy, 1987
Fluoranthene	*D. magna*	1742	S	Equi	HPLC	Newsted & Giesy, 1987
Pyrene	*D. pulex* *D. magna*	2702 2702	S S	Equi Equi	FS HPLC	Southworth *et al.*, 1978 Newsted & Giesy, 1987
Benz(a)-anthracene	*D. magna* *D. pulex* *D. magna*	2920 10109 10226	S S S	k_1/k_2 Equi Equi	^{14}C FS HPLC	McCarthy *et al.*, 1985 Southworth *et al.*, 1978 **Newsted & Giesy, 1987**
Chrysene	*D. magna*	6088	S	Equi	HPLC	**Newsted & Giesy, 1987**
Benzo(a)pyrene	*D. magna*	12761	S	Equi	HPLC	Newsted & Giesy, 1987
Benzo(k)-fluoranthene	*D. magna*	13225	S	Equi	HPLC	**Newsted & Giesy, 1987**
Benzo(ghi)-perylene	*D. magna*	28288	S	Equi	HPLC	**Newsted & Giesy, 1987**
Dibenzo(a,h)-anthracene	*D. magna*	50119	S	Equi	HPLC	**Newsted & Giesy, 1987**

S. static exposure system; k_1/k_2, kinetic: uptake rate/depuration rate. Equi: equilibrium
FS: Fluorescence Spectrophotometry; HPLC: High Performance Liquid Chromatography
Marked in bold: Key study. The study by Newsted & Giesy, 1987 was chosen as the key study for benz(a)anthracene, chrysene, benzo(k)fluoranthene, benzo(ghi)perylene and dibenzo(a,h)anthrancene as the most reliable equilibrium study with BCF >2000.

In a well documented study McLeese and Burridge (1987) determined PAH accumulation in the clam *Mya arenaria* and the mussel *Mytilus edulis* in flow through systems. Concentrations in water and animals were used to calculate k_u and k_e, which were subsequently used to calculate BCFs. The resulting BCFs for phenanthrene were 1,280 and 1,240, for fluoranthene 4,120 and 5,920, and for pyrene 6,430 and 4,430, with the first number representing the value for the mussel and the second for the clam.

Bruner *et al.* (1994) exposed the zebra mussel (*Dreissena polymorpha*) in a static system to ^{3}H–labelled benzo(a)pyrene and pyrene. BCFs were calculated using kinetic rate constants and ranged from 13,000 to 35,000 for pyrene, and 41,000 to 84,000 for benzo(a)pyrene.

Gossiaux *et al.* (1996) exposed the zebra mussel (*Dreissena polymorpha*) in a static system to radio-labelled benzo(a)pyrene in combination with pyrene. In total a number of 23 experiments with benzo(a)pyrene and 10 experiments with pyrene were conducted under either ambient field temperatures or laboratory temperatures. BCFs were calculated using kinetic rate constants and ranged from 37,000 to 43,000 for pyrene, and 133,000 to 142,000 for benzo(a)pyrene.

Experimental BCF values for crustaceans are presented in Table 3.4. Bioaccumulation in *Daphnia magna* has been studied by McCarthy et al (1985) and Newsted & Giesy (1987). In the study by McCarthy the BCF value for benz(a)anthracene was reported as 2,920, determined as the ratio between uptake rate and depuration rate. In the study by Newsted & Giesy (1987) the BCF was determined at steady state in a static system. Bioconcentration was determined for a range of PAHs, with the resulting BCFs being below 2,000 for anthracene, phenanthrene and fluoranthene, and above 2,000 for pyrene, benz(a)anthracene, chrysene, benzo(a)pyrene, benzo(k)fluoranthene, benzo(ghi)perylene, and dibenzo(a,h)anthracene.

In a study by Southworth (1978) the potential for bioaccumulation in *Daphnia pulex* was studied for PAHs in a static system. The bioconcentration factor was determined at steady state conditions and as the ratio between the rates of uptake and elimination at non steady state conditions. The study indicated that the PAH content of Daphnia lipid was in equilibrium with the aqueous PAH concentration. The reported BCF was above 2,000 for pyrene and benz(a)anthracene, and below 2,000 for anthracene and phenanthrene.

3.4.2 Summary and discussion of bioaccumulation

An overview of the BCF values of the selected PAH-constituents of CTPHT determined in the key studies is provided in Table 3.5.

A range of valid experimental fish data were available for phenanthrene, fluoranthene and pyrene, showing BCF values >5,000, and for anthracene above 2,000[5], whereas experimental fish data for benz(a)anthracene and benzo(a)pyrene indicated BCFs below 2,000. Measured BCF values in molluscs were >5,000 for fluoranthene, pyrene and benzo(a)pyrene.

Experimental data from studies on other aquatic organisms, i.e. crustaceans, were considered for the PAHs for which no studies were available with fish or molluscs. For Daphnia experimental data for benz(a)anthracene, chrysene, benzo(a)pyrene, benzo(k)fluoranthene, benzo(ghi)perylene, and dibenzo(a,h)anthracene indicated BCF values > 5,000 and above 2,000 for pyrene. In studies with Daphnia the obtained BCFs for anthracene, phenanthrene and fluoranthene were below 2,000.

[5] The question wether anthracene fulfils both the B and vB criteria or should only be considered as fulfilling the B-criterion was discussed at the Member State Committee meeting in October 2008 in the context of reaching an agreement on the identification of anthracene as a SVHC. Due to uncertainties on the validity of the highest reported BCFvalues (see as well section 3.4.1 of this report) it was concluded to consider anthracene only fulfilling the B-criterion but not the vB-criterion (MSC, 2008).

Table 3.5: Overview of BCF values determined in the key studies		
Substance	**Value**	**Key study endpoint**
Anthracene	4550	Fish: Equi (parent), *P. reticulata*
Phenanthrene	6760	Fish: k_1/k_2 (parent), *P. promelas*
Fluoranthene	9054	Fish: Equi (parent), *P. promelas*
Pyrene	2700-11300	Fish: Equi (parent), *P. reticulata*
Benz(a)anthracene	10226	Crustaceans: Equi, *Daphnia magna*
Chrysene	6088	Crustaceans: Equi, *Daphnia magna*
Benzo(a)pyrene	133000	Mollusca: k_1/k_2 (total=parent), *D. polymorpha*
Benzo(b)fluoranthene	-	*No experimental data available*
Benzo(k)fluoranthene	13225	Crustaceans: Equi, *Daphnia magna*
Benzo(ghi)perylene	28288	Crustaceans: Equi, *Daphnia magna*
Dibenzo(a,h)anthracene	50119	Crustaceans: Equi, *Daphnia magna*
Indeno(1,2,3-cd)pyrene	-	*No experimental data available*

No experimental data on the bioaccumulation potential of benzo(b)fluoranthene and indeno(1,2,3-cd)pyrene were found. On the basis of similarities of their Kow values and molecular sizes with other PAHs for which BCFs above the Annex XIII bioaccumulation criteria have been experimentally confirmed, it is nevertheless anticipated that BCF values for these two substances will be >2000 as well.

4 HUMAN HEALTH HAZARD ASSESSMENT

Information on hazard to human health relevant for the PBT/vPvB assessment of CTPHT and its PAH-constituents is provided in section 2 of this report (classification information).

Supplementary information on the toxicological properties of CTPHT and its PAH-constituents which could be relevant for risk assessment, comparative assessment of alternative substances, or for priority setting in the context of recommending substances for the 'Authorisation List' (Annex XIV of the REACH Regulation) can be found in Annex 1 to this report and the Annex XV Transitional Dossier on CTPHT (The Netherlands, 2008).

5 ENVIRONMENTAL HAZARD ASSESSMENT

As regards environmental toxicity in the context of the PBT assessment in accordance with Annex XIII of the REACH Regulation, the toxicity criterion (T-criterion) refers to effects on aquatic organisms. Therefore, in this section, the toxicity of CTPHT and its PAH-constituents is considered for the aquatic environment only.

5.1 Aquatic compartment (including sediment)

5.1.1 Overview

No adequate information on the environmental hazard of CTPHT is available. Limited data based on the water-accommodated fraction (WAF) approach can be found in the Annex XV Transitional Dossier on CTPHT (chapter B3.2 in Netherlands, 2008). Nevertheless these tests determined acute and not long-term toxicity (as required for comparison with the environmental T-criterion of Annex XIII of the REACH Regulation).

According to the approach followed in the present support document (see section 1.2), the assessment is based on aquatic toxicity data available for the 12 indicator PAHs considered relevant for the PBT assessment of CTPHT.

PAHs can be toxic via different modes of action, such as non-polar narcosis and phototoxicity. Phototoxicity is caused by the ability of PAHs to absorb UVA radiation, UVB radiation, and in some instances, visible light. It may occur as the result of the production of singlet oxygen, which is highly damaging to biological material, or as result of the formation of new, more toxic compounds from the photomodification (usually oxidation) of PAHs (Lampi et al., 2006). Phototoxic effects can be observed after a short period of exposure, which explains why for PAHs like anthracene, fluoranthene and pyrene, where phototoxicity is most evident, the acute toxicity values under simulated solar radiation may be lower than the chronic toxicity values determined under less harsh radiation.

The phototoxicity of PAHs is relevant where the PAHs are exposed to light and UV radiation, and considered to be most important for upper layers of aquatic and terrestrial environments. Although UV penetration depths may vary among PAH-contaminated sites, it is not unlikely that significant portions of the aquatic community may be exposed to UV levels sufficient to induce phototoxicity, as UV levels occurring under normal sun light conditions have been shown to elicit these effects. There is growing evidence which suggests that phototoxic PAHs may be degrading aquatic habitats, particularly those in highly contaminated areas with shallow or clear water. Photo-induced chronic effects have been reported for anthracene at UV intensities occurring at depths of 10-12 m in Lake Michigan (Holst & Giesy, 1989). Phototoxicity of PAHs may also be initiated in aquatic organisms which have accumulated PAHs from the sediment and subsequently are exposed to sun light closer to the surface (The Netherlands, 2008). Phototoxic effects of PAHs are therefore considered relevant in this hazard, respectively T- assessment.

For data on toxicity to aquatic organisms, reference is made to the Annex XV Transitional Dossier on CTPHT (The Netherlands, 2008).

Studies selected as key studies in the Annex XV Transitional Dossier are those providing the lowest reliable value for the most critical effect and endpoint. Therein, due to the high phototoxic potential of some of the PAHs, key studies for derivation of PNEC values have for some of the substances

been short term studies rather than long term studies. Nevertheless, for comparison with the environmental T-criterion of Annex XIII of the REACH Regulation (long-term no effect concentration for marine or freshwater organisms less than 0.01 mg/l), only long term studies have been selected as key studies for PBT assessment. The selected key studies are marked in bold in the Tables 5.1 – 5.11 below.

5.1.2 Toxicity data

5.1.2.1 Anthracene

Anthracene is very phototoxic and acute phototoxic effects are observed after relatively short periods of time (approximately half an hour) upon exposure of test systems to sunlight or artificial light containing UV radiation. Results of studies investigating the aquatic toxicity of anthracene are shown in Table 5.1. The strongest phototoxic effects have been observed in the presence of natural sunlight (The Netherlands, 2008). The results from the acute toxicity studies show a high acute toxicity of anthracene, with EC_{50} values as low as 1 µg/l. Chronic toxicity is comparable with lowest NOECs or EC10s for reproduction of daphnids or growth of the alga *Pseudokirchneriella subcapitata* in the range of 1.4- 2 µg/l. As the EC10s and NOECs for growth of algae have not been obtained in tests of standard duration (72h), the 21 day study with Daphnia magna by Holst & Giesy (1989) is the study providing the lowest reliable long term NOEC and therefore has been chosen as the key study for T-assessment.

Table 5.1: Aquatic Toxicity of Anthracene

Species	Duration	Endpoint	Value	Comment	References
Freshwater organisms, acute					
Daphnia pulex	24.5 h	EC_{50} for immobility	1 µg/l	Dark for 24 h, then exposed to sunlight for 0.5 h	Allred & Giesy, 1985
Freshwater organisms, chronic					
Pimephales promelas	6-w cont. flow	NOEC for hatching	6.7 µg/l	16:8 h light:dark, fluorescent light and UV-A+B radiation	Hall & Oris, 1991
Daphnia magna	21-d static renewal	Lowest NOECs or EC_{10} for reproduction	1.5-1.9 µg/l	16:8 h light:dark and UV-A+B radiation	**Holst & Giesy, 1989** Foran *et al.*, 1991
Pseudokirchneriella subcapitata	34-36 hours static renewal	NOEC or EC_{10} for growth rate orprimary production	1.4-1.5 µg/l	UV-A radiation	Gala & Giesy, 1992
Marine organisms, acute					
Artemia salina	10 hours	EC_{10}	1.7 µg/l	In the dark for 2 h, then exposed to sunlight for 8 h	Peachy & Crosby, 1996

5.1.2.2 Phenanthrene

The lowest chronic toxicity of phenanthrene has been observed by Halling-Sørensen *et al.* (1996) in a growth test with the alga *Pseudokirchneriella subcapitata* (resulting EC_{10} 10 µg/l). However, this test was by far the lowest in a test series in which the authors tested several different experimental set-ups (see Table 5.2) and the result was obtained in a test of only 2-d duration (standard is 72 h). In another recent study the EC_{10} for growth rate of *Pseudokirchneriella subcapitata* was also higher (23 µg/l: Bisson *et al*., 2000). Therefore, the *Ceriodaphnia dubia* study by Bisson *et al*., 2000 is chosen as the key study as it resulted in the lowest reliable long term EC_{10}. The value of this EC_{10} is 13 µg/l and is based on measured concentrations.

Table 5.2: Aquatic Toxicity of Phenanthrene

Species	Duration	Endpoint	Value	Comment	References
Freshwater organisms, chronic					
Pseudokirchneriella subcapitata	2-d	EC_{10} for growth	10 – 720 µg/l	Fluorescent light of 4000 – 8000 lux; to some of the air tight flasks HCO3- was added to control pH	Halling-Sørensen *et al.*, 1996
Pseudokirchneriella subcapitata	72 h	EC_{10} for growth	23 µg/l	Light intensity 6000 – 8000 lux	Bisson *et al.*, 2000
Ceriodaphnia dubia	7-d	EC_{10} for reproduction	13 µg/l	Photoperiod 16:8 h light:dark at less than 500 lux	**Bisson *et al.*, 2000**
Marine organisms, acute					
Neanthes arenaceodentata	96-h	LC_{50}	51 µg/l		Emery & Dillon, 1996
Marine organisms, chronic					
Neanthes arenaceodentata	8 weeks	reproduction	20 µg/l	Some effects, only one sublethal concentration tested – limited validity of test	Emery & Dillon, 1996

5.1.2.3 Fluoranthene

Fluoranthene appears to be extremely phototoxic when organisms are exposed in parallel to ultraviolet radiation, such as in sunlight. The acute $L(E)C_{50}$s of fluoranthene are comparable to the obtained chronic NOEC or $L(E)C_{10}$ values (see Table 5.3).

Numerous long term studies with a range of species representing various taxonomic groups report NOEC or EC_{10} values for fluoranthene below 10 µg/l. Spehar *et al*, 1999 studied both acute and chronic effects of fluoranthene in the presence and absence of UV radiation with different species. The 31d *Mysidopsis bahia* study by Spehar *et al.* (1999) was chosen as key study, as it provided the lowest reliable NOEC (0.6 µg/l).

Table 5.3: Aquatic Toxicity of Fluoranthene					
Species	**Duration**	**Endpoint**	**Value**	**Comment**	**References**
Freshwater organisms, acute					
Utterbackia imbecilis	24-h	LC_{50}	2.45 µg/l	UV-A radiation	Weinstein and Polk, 2001
Lumbriculus variegatus	96-h	LC_{50}	1.2 µg/l	12:12 h light:dark UV-A+B radiation	Spehar *et al.*, 1999
Hydra americana	96-h	LC_{50}	2.2 µg/l	12:12 h light:dark UV-A+B radiation	Spehar *et al.*, 1999
Daphnia magna	48-h	LC_{50}	1.6 µg/l	12:12 h light dark UV-A+B radiation	Spehar *et al.*, 1999
Freshwater organisms, chronic					
Ceriodaphnia dubia	7-d	EC_{10} reproduction	1.2 µg/l	Photoperiod 16:8 h light:dark at less than 500 lux	Bisson *et al.*, 2000
Hyalella azteca	10-d	LC_{10}	1.1 µg/l	16:8 h light:dark UV-A+B radiation	Wilcoxen *et al.*, 2003
Daphnia magna	21-d	NOEC growth	1.4 µg/l	12:12 h light:dark UV-A+B radiation	Spehar *et al.*, 1999
Pimephales promelas	32-d ELS test	NOEC growth	1.4 µg/l	12:12 h light:dark UV-A+B radiation	Spehar *et al.*, 1999
Rana pipiens larvae		NOEC hatching	>25 µg/l	Full sunlight	Hatch & Burton Jr., 1998
Rana pipiens larvae			100 % mortality at 5, 25, and 125 µg/l	Full sunlight	
Marine organisms, acute					
Mulinia lateralis	96-h	LC_{50}	2.8 µg/l	16:8 hours light:dark, laboratory UV A and B light	Spehar *et al.*, 1999
Mysidopsis bahia	96-h	LC_{50}	1.4 µg/l		
Arbacia punctulata	96-h	LC_{50}	3.9 µg/l		
Pleuronectes americanus	96-h	LC_{50}	0.1 µg/l		
Marine organisms, chronic					
Mysidopsis bahia	31-d	NOEC reproduction	11.1 µg/l	16:8 hours light:dark, laboratory fluorescent light	**Spehar *et al.*, 1999**
Mysidopsis bahia	31-d	NOEC reproduction	0.6 µg/l	16:8 hours light:dark, laboratory UV A and B light	

5.1.2.4 Pyrene

With regard to acute effects, the most sensitive freshwater organism appears to be *Daphnia magna*, with EC_{50} values of 1.38 - 20 µg/l (Table 5.4). The lowest acute effect concentrations for embryos/larvae of marine molluscs and neonates/nauplii of crustaceans are reported in the range 0.23-36 µg/l and hence are similar to those observed for fresh water species in the presence of UV-radiation.

Chronic toxicity data are reported for fresh water species with EC_{10} values of 1.2-2.1 µg/l and for one marine oyster (*Crassostrea*) with a NOEC for shell development of 0.5 µg/l (Lyons *et al.*, 2002). As this latter NOEC value was the lowest one from a reliable study, it was chosen as the key study.

Table 5.4: Aquatic Toxicity of Pyrene

Species	Duration	Endpoint	Value	Comment	References
Freshwater organisms, acute					
Daphnia magna	27 h	EC_{50} immobility	1.38 µg/l	neonates 16:8 hour light:dark for 24 hours UV radiation for 2 hours and 1 h recovery	Wernersson, 2003
Daphnia magna	48 hours	EC_{50} for immobility	2.7 to 20 µg/l	neonates UV-B radiation four times two hours	Nikkilä *et al.*, 1999
Utterbackia imbecilis	24-h	LC_{50}	2.63 µg/l	UV-A radiation	Weinstein & Polk, 2001
Freshwater organisms, chronic					
Pseudokirchneriella subcapitata	72-h	EC_{10} growth	1.2 µg/l	Light intensity 6000 – 8000 lux	Bisson *et al.*, 2000
Ceriodaphnia dubia	7-d	EC_{10} reproduction	2.1 µg/l	Photoperiod 16:8 h light:dark at less than 500 lux	Bisson *et al.*, 2000
Marine organisms, acute					
Artemia salina	3-h	LC_{50}	8 µg/l	2 hours in the dark UV-radiation for one hour	Kagan *et al.*, 1985, 1987
Artemia salina	10-h	LC_{50}	36 µg/l	2 hours in the dark followed by eight hours with UV-radiation	Peachy & Crosby, 1996
Artemia salina	10-h	EC_{50}	3.4 µg/l	2 hours in the dark followed by eight hours with sunlight	Peachy & Crosby, 1996
Mysidopsis bahia	48-h	LC_{50}	0.89 µg/l	16:8 hour light:dark UV-A B radiation	Pelletier *et al.*, 1997
Mulinea lateralis	48-h 96-h	LC_{50}	0.23 µg/l 1.68 µg/l	Embryos/larvae Juveniles 16:8 hour light:dark UV-A B radiation	Pelletier *et al.*, 1997
Marine organisms, chronic					
Crassostrea gigas	48 h	NOEC shell development	0.5 µg/l	Embryos/larvae 12:12 hour light:dark UV-A B radiation	**Lyons *et al.*, 2002**

5.1.2.5 Chrysene

The water solubility of chrysene is about 1.6 µg/l, with a range between 1.0 and 3.3 µg/l (Mackay *et al*., 2000). Around or below this value, no significant effects were observed for any species in a regular toxicity experiment, although chronic toxicity studies were performed with algae, crustaceans (including *Daphnia*) and fish. The only study, that showed a considerable effect of chrysene, was a determination of the median lethal time of neonates of *Daphnia magna* (Newsted & Giesy, 1987). In this experiment, the daphnids were exposed to one concentration of chrysene (measured concentration of 0.7 µg/l). After 24 hours of exposure with a 16:8 h light:dark photoperiod, the animals were exposed to a mix of UV A , UV B and visible light. The median lethal time after UV-radiation started was 24 hours. Thus, after 48 hours, of which the last 24 hours were with UV irradiation, 50% mortality of the daphnids occurred at 0.7 µg/l. This type of study is however not designed to determine dose-response relationships and hence quantitative data on toxicity or toxicity threshold values cannot be derived from the result.

Table 5.5: Aquatic Toxicity of Chrysene

Species	Duration	Endpoint	Value	Comment	References
Freshwater organisms, acute					
Daphnia magna	Until 50 % of the test animals died	LT_{50}	24 h (after commencement of irradiation and exposure to 0.7 µg/l chrysene)	Static renewal test: exposure to 0.7 µg/l chrysene After 16:8 hours light:dark photoperiod irradiation with UV A and B + visible light	**Newsted & Giesy, 1987**

5.1.2.6 Benz(a)anthracene

Data on acute toxicity of benz(a)anthracene are available for algae, crustaceans and amphibians. Effects within the water solubility of the substance have been observed for the crustacean *Daphnia pulex* upon exposure to mixed fluorescent and natural light and for larvae of the amphibian *Pleurodeles waltl* irradiated throughout the experiment with UV-A light (see Table 5.6). The lowest chronic toxicity has been observed for the alga *Pseudokirchneriella subcapitata* with an EC_{10} of 1.2 µg/l for growth inhibition. This study was therefore chosen as key study. For the crustacean *Ceriodaphnia dubia* no effects were observed at the highest test concentration of 8.7 µg/l (Bisson *et al*., 2000). Studies showed that UV irradiation increases the toxicity of benz(a)anthracene (The Netherlands, 2008).

Table 5.6: Aquatic Toxicity of Benz(a)anthracene

Species	Duration	Endpoint	Value	Comment	References
Freshwater organisms, acute					
Daphnia pulex	96 h	EC_{50}	10 µg/l	12:12 h photoperiod to mixed fluorescent and natural light	Trucco *et al*., 1983
Daphnia magna	48 h	EC_{50}	>9.1 µg/l	Dark	Bisson *et al*., 2000

Table 5.6: Aquatic Toxicity of Benz(a)anthracene					
Species	**Duration**	**Endpoint**	**Value**	**Comment**	**References**
Pleurodeles waltl (larvae)	6 d	LC_{50}	at 3.1 µg/l 100% survival; at 6.3 µg/l 100% mortality	Irradiation with UV-A light throughout experiment	Fernandez & L'Haridon, 1992)
Freshwater organisms, chronic					
Pseudokirchneriella subcapitata	72-h	EC_{10} growth	1.2 µg/l	Light intensity 6000 – 8000 lux	**Bisson *et al.*, 2000**

5.1.2.7 Benzo(b)fluoranthene

No effects have been observed at concentrations within the water solubility of benzo(b)fluoranthene, i.e. up to 1.1 - 1.5 µg/l (Mackay et al. 2000 in The Netherlands 2008). An acute study with *Daphnia magna* in the dark showed no effects at the tested concentration of 1.1 µg/l (Bisson *et al.*, 2000). In a 24-h study with the same organism and a photoperiod of 16:8 h light: dark, extended by 2 hours of irradiation with UV light followed by 2 hours of recovery, the EC_{50} for immobilisation was determined as 4.2 µg/l, which is above the water solubility of benzo(b)fluoranthene (Wernersson & Dave, 1997).

5.1.2.8 Benzo(ghi)perylene

Only in a small number of studies effects have been observed at test concentrations within the water solubility limit of benzo(ghi)perylene (Table 5.7). The EC_{50} obtained in the Daphnia test is above the water solubility of 0.14 µg/l. As regards chronic toxicity of benzo(ghi)perylene, no effects were observed in an early life stage study with *Brachydanio rerio* up to concentrations of 0.16 µg/l (Hooftman & Evers-de-Ruiter, 1992). However, effects on the reproduction of the crustacean *Ceriodaphnia dubia* were reported by (Bisson *et al.*, 2000) with a resulting EC_{10} value of 0.082 µg/l. This study was chosen as the key study for T-assessment.

Table 5.7: Aquatic Toxicity of Benzo(ghi)perylene					
Species	**Duration**	**Endpoint**	**Value**	**Comment**	**References**
Freshwater organisms, acute					
Daphnia magna	48 h	EC_{50}	>0.2 µg/l	Dark	Bisson *et al.*, 2000
Pimephales promelas (7-d old larvae)	120 h	LC_{20}	0.15 µg/l	First 24h of exposure to substance without UV radiation in parallel, followed by 96 h exposure with concomittant UV radiation	Oris & Giesy, 1987
Freshwater organisms, chronic					
Ceriodaphnia dubia	7-d	EC_{10} reproduction	0.082 µg/l	Photoperiod 16:8 h light:dark at less than 500 lux	**Bisson *et al.*, 2000**

5.1.2.9 Benzo(k)fluoranthene

In the available studies on acute toxicity to Daphnia magna no effects were observed, which might be attributable to the low water solubility of the substance (The Netherlands 2008).
As regards chronic toxicity, a 7-d reproduction test with *Ceriodaphnia dubia* did not reveal effects either (Bisson *et al.*, 2000) and in a test with the alga *Pseudokirchneriella subcapitata* the EC_{10} for growth was larger than 1 µg/l (Bisson *et al.*, 2000), which is above the water solubility of the substance (about 1 µg/l; Mackay et al. 2000, cited in The Netherlands 2008). However, an early life stage study performed with *Brachydanio rerio* revealed length as the most sensitive endpoint, with an EC_{10} value of 0.17 µg/l (Hooftman & Evers-de Ruiter, 1992; Table 5.8). Due to the good fit of the log-logistic equation, this EC_{10} estimate has a low uncertainty. The study was chosen as the key study for T-assessment.

Table 5.8: Aquatic Toxicity of Benzo(k)fluoranthene

Species	Duration	Endpoint	Value	Comment	References
Freshwater organisms, chronic					
Brachydanio rerio	28 d	LC_{52}	0.58 µg/l	ELS	**Hooftman & Evers-de Ruiter, 1992**
Brachydanio rerio	42 d	LC_{50} EC_{10} weight EC_{10} length	0.65 µg/l 0.31 µg/l 0.17 µg/l	ELS	

5.1.2.10 Benzo(a)pyrene

Table 5.9: Aquatic Toxicity of Benzo(a)pyrene

Species	Duration	Endpoint	Value	Comment	References
Freshwater organisms, acute					
Daphnia magna	27 h	EC_{50}	1.2 µg/l	16:8 hour light:dark followed by 2 hour UV-A B radiation and 1 hour recovery	Wernersson, 2003
Freshwater organisms, chronic					
Pseudokirchneriella subcapitata		EC_{10} growth	0.78 µg/l	Light intensity 6000 – 8000 lux, cool white fluorescent lamps	Bisson *et al.*, 2000
Oncorhynchus mykiss	36 d	NOEC EC_{10} * abnormalities	1.5 µg/l (2.9 µg/l, calculated, above WS)	ELS * determined from presented data with log-logistic dose-response relationship (The Netherlands 2008)	Hannah *et al.*,1982
Ceriodaphnia dubia	7-d	EC_{10} reproduction	0.5 µg/l	Laboratory light Photoperiod 16:8 h light:dark at less than 500 lux	Bisson *et al.*, 2000

Table 5.9: Aquatic Toxicity of Benzo(a)pyrene					
Species	**Duration**	**Endpoint**	**Value**	**Comment**	**References**
Marine organisms, chronic					
Crassostrea gigas	48 h	NOEC shell development EC_{10}	1 µg/l 1.1 µg/l	Embryos 12:12 hour light:dark fluorescent light without UV rad.	Lyons *et al.*, 2002
Crassostrea gigas	48 h	NOEC shell development EC_{10}	0.5 µg/l 0.22 µg/l	Embryos 12:12 hour light:dark UV-A B radiation	**Lyons *et al.*, 2002**

Only acute toxicity studies with exposure to UV-light result in effects at concentrations near the water solubility of 1.2 -1.8 µg/l (Mackay et al. 2000, cited in The Netherlands 2008). Results from studies on the aquatic toxicity of benzo(a)pyrene are shown in Table 5.9. The lowest acute toxicity of benzo(a)pyrene was observed in a test with *Daphnia magna* under exposure to UV radiation.

Chronic toxicity of benzo(a)pyrene was reported for the alga *Pseudokirchneriella subcapitata* with an EC_{10} of 0.78 µg/l, and for reproduction of *Ceriodaphnia dubia* with an EC_{10} of 0.5 µg/l in a 7-d study when exposed to laboratory light without UV (Bisson *et al.*, 2000). In a 28-d early life stage (ELS) study with *Brachydanio rerio* no effects were observed up to the highest test concentration of 4.0 µg/l, which is already above the water solubility of benzo(a)pyrene (Hooftman & Evers-de Ruiter, 1992). In another ELS study with *Oncorhynchus mykiss* a NOEC of 1.5 µg/l was obtained for developmental abnormalities as endpoint (Hannah *et al.*, 1982). Evaluation of the data presented by Hannah *et al.* with a log-logistic relationship resulted in the derivation of an EC_{10} of 2.9 µg/l (The Netherlands 2008), which again is above the water solubility of benzo(a)pyrene.

Furthermore, it has been shown that UV radiation increases the long term toxicity of benzo(a)pyrene. For shell development of *Crassostrea gigas*, when exposed to UV radiation, the calculated EC_{10} was 0.22 µg/l whereas under UV-lacking fluorescent laboratory lighting conditions the resulting EC_{10} was 1.1 µg/l (Lyons *et al.* 2002).

As the study on shell development of the marine mollusc *Crassostrea gigas* resulted in the lowest reliable chronic EC_{10} value (0.22 µg/l) it was chosen as key study for T-assessment.

5.1.2.11 Dibenzo(a.h)anthracene

Results of studies of the aquatic toxicity of dibenzo(a,h)anthracene are provided in Table 5.10. Chronic toxicity studies with fresh water species are available for crustaceans, aquatic plants, and algae. For *Lemna gibba* no effects at concentrations near the water solubility were observed (Huang *et al.*, 1997). No effect was observed at concentrations up to 0.032 µg/l in a 7-d study with *Ceriodaphnia dubia* (Bisson *et al.*, 2000). The 72-h EC_{10} for the growth rate of *Pseudokirchneriella subcapitata* was 0.14 µg/l (Bisson *et al.*, 2000). In both the test with *C. dubia* and *P. subcapitata* concentrations were measured. As the study with *Pseudokirchneriella subcapitata* resulted in the lowest reliable chronic EC_{10} value it was chosen as the key study.

Table 5.10: Aquatic Toxicity of Dibenzo(a,h)anthracene					
Species	**Duration**	**Endpoint**	**Value**	**Comment**	**References**

Table 5.10: Aquatic Toxicity of Dibenzo(a,h)anthracene					
Species	**Duration**	**Endpoint**	**Value**	**Comment**	**References**
Freshwater organisms, acute					
Daphnia magna	27 h	EC_{50}	1.8 µg/l	16:8 hour light:dark followed by 2 hour UV-A B radiation and 1 hour recovery	Wernersson, 2003
Daphnia magna	28 h	EC_{50}	4.6 µg/l	16:8 hour light:dark followed by 2 hour UV-A B radiation and 2 hour recovery	Wernersson & Dave, 1997
Freshwater organisms, chronic					
Pseudokirchneriella subcapitata	72 h	EC_{10} growth	0.14 µg/l	Light intensity 6000 – 8000 lux	**Bisson *et al.*, 2000**

5.1.2.12 Indeno(1,2,3-cd)pyrene

Table 5.11: Aquatic Toxicity of Indeno(1,2,3-cd)pyrene					
Species	**Duration**	**Endpoint**	**Value**	**Comment**	**References**
Freshwater organisms, chronic					
Pseudokirchneriella subcapitata	72 h	EC_{10} growth	1.5 µg/l	Light intensity 6000-8000 lux	**Bisson *et al.*, 2000**
Ceriodaphnia dubia	7-d	EC_{10} reproduction	0.27 µg/l	Photoperiod 16:8 h light:dark at less than 500 lux	

For indeno(1,2,3-cd)pyrene, a chronic EC_{10} value of 1.5 µg/l is reported for growth of the algae *Pseudokirchneriella subcapitata* in a study of 72h duration. The 7-d EC_{10} for reproduction of the crustacean *Ceriodaphnia dubia* was 0.27 µg/l (Bisson *et al.*, 2000; see Table 5.11). In both studies concentrations were measured. The study with the lowest EC_{10}, i.e. reproduction of *Ceriodaphnia dubia*, was chosen as key study for T-assessment.

5.1.3 Summary and discussion on aquatic toxicity

An overview on the aquatic toxicity obtained in the key studies selected for the PAH-constituents of CTPHT is provided in Table 5.12.

Table 5.12: Aquatic toxicity of the PAH-constituents of CTPHT observed in the selected key studies

Substance	Value	Key study endpoint
Anthracene	1.5 µg/l	EC_{10} reproduction, *Daphnia magna,* 21-d
Phenanthrene[6]	13 µg/l	EC_{10} reproduction, *Ceriodaphnia dubia,* 7-d
Fluoranthene	0.6 µg/l	NOEC reproduction, *Mysidopsis bahia,* 31-d
Pyrene	0.5 µg/l	NOEC shell development, *Crassostrea gigas larvae,* 48-h ELS
Benz(a)anthracene	1.2 µg/l	EC_{10} growth, *Pseudokirchneriella subcapitata,* 72-h
Chrysene[7]	-	No significant effects up to the water solubility of the substance detected in any regular toxicity test. Only study in which considerable effects were detected was a median lethal time (LT_{50}) study with Daphnia magna
Benzo(a)pyrene	0.22 µg/l	EC_{10} shell development, *Crassostrea gigas larvae,* 48-h ELS
Benzo(b)fluoranthene	-	*No toxicity has been observed up to the water solubility limit of the substance*
Benzo(k)fluoranthene	0.17 µg/l	EC_{10} growth (length), *Brachydanio rerio,* 42-d
Benzo(ghi)perylene	0.082 µg/l	EC_{10} reproduction, *Ceriodaphnia dubia,* 7-d
Dibenzo(a,h)anthracene	0.14 µg/l	EC_{10} growth, *Pseudokirchneriella subcapitata,* 72-h
Indeno(1,2,3-cd)pyrene	0.27 µg/l	EC_{10} reproduction, *Ceriodaphnia dubia,* 7-d

The experimental data indicate a high chronic and acute toxicity of the PAH consitituents of CTPHT for aquatic organisms. NOEC/EC_{10} values <10 µg/l have been observed for the following PAHs: anthracene, fluoranthene, pyrene, benz(a)anthracene, benzo(a)pyrene, benzo(k)fluoranthene, benzo(ghi)perylene, dibenzo(a,h)anthracene, and indeno(1,2,3-cd)pyrene. For phenanthrene, the EC_{10} value of the selected key study with *Ceriodaphnia dubia* is > 10 µg/l, but for the algae *Pseudokirchnerella subcapitata* a two days growth inhibition study (i.e. exposure time shorter than required according to the guideline) showed EC_{10} values down to 10 µg/l.

No toxicity to aquatic organisms has been observed within the water solubility limit of benzo(b)fluoranthene. The same is the case for chrysene, with the exception that in one study aimed at determining the mean lethal time (LT_{50}) of Daphnia magna upon exposure to 0.7 µg/l chrysene considerable toxic effects have been observed. This type of study is however not designed to determine dose-response relationships and hence quantitative data on toxicity like EC_{10} or EC_{50} values or toxicity threshold values like long-term no effect levels cannot be derived from the results. Therefore, the result of this study is not a suitable basis for comparison with the T-criteria of Annex XIII of the REACH Regulation.

6 The lowest chronic values reported are EC_{10} for *Pseudokirchneriella subcapitata* of 10 µg/l (Halling-Sørensen *et al.*, 1996)

7 No results from toxicity studies available that could be used for comparison with the T-criteria of REACH Annex XIII.

6 PBT AND VPVB ASSESSMENT

6.1 PBT / vPvB assessment

6.1.1 Assessment of PBT/vPvB properties – comparison with the criteria of Annex XIII

No information on persistence, potential for bioaccumulation and aquatic toxicity was found for CTPHT itself. Therefore, the PBT assessment for CTPHT focuses on the assessment of its PAH-constituents present in concentrations ≥ 0.1% (see Section 1.2).

6.1.1.1 Persistence

Half-lives in soil for the following 10 PAH-constituents of CTPHT have been reported to be in the range of 5.7 to 9.1 years under field conditions:

Anthracene	Chrysene
Phenanthrene	Benzo(a)pyrene
Fluoranthene	Benzo(b)fluoranthene
Pyrene	Benzo(k)fluoranthene
Benz(a)anthracene	Benzo(ghi)perylene

As these half-lives observed in soil exceed the P- and vP-criteria (half lives of 120, respectively 180 days in soil), it is concluded that the vP criterion is fulfilled by all 10 above listed PAH substances.

No experimental data on persistence were found for dibenzo(a,h)anthracene and indeno(1,2,3-cd)pyrene. A final conclusion on the P- or vP-properties of these substances can therefore not be drawn. Estimated half-lives > 400 days in soil for dibenzo(a,h)anthracene and indeno(1,2,3-cd)pyrene (Mackay *et al.*, 1992) indicate however that the two PAHs are presumably persistent in sediments and soils as well.

6.1.1.2 Bioaccumulation

Experimentally obtained BCF values above 5,000 are reported for the following 9 PAH-constituents of CTPHT:

Matrix: **fish**

Fluoranthene	Pyrene
Phenanthrene	

Matrix: **molluscs:**

Fluoranthene	Benzo(a)pyrene
Pyrene	

Matrix: **crustaceans:**

Benz(a)anthracene	Benzo(k)fluoranthene
Chrysene	Benzo(ghi)perylene
Benzo(a)pyrene	Dibenzo(a,h)anthracene

As the BCF values of the above PAH substances exceed the B- and vB criteria (measured BCF values in aquatic species > 2000, respectively > 5000), it is concluded that the vB-criterion is fulfilled by all 9 substances.

Furthermore, experimentally obtained BCF value above 2000 have been reported for anthracene and it has already been agreed by the Member State Committee (MSC, 2008) that anthracene fulfils the PBT-criteria and, hence, the B-criterion.

No experimental data on the bioaccumulation potential of benzo(b)fluoranthene and indeno(1,2,3-cd)pyrene were found. A final conclusion on the B- or vB-properties of these substances can therefore not be drawn. However, on the basis of similarities of their Kow values and molecular sizes with other PAHs for which BCFs above the Annex XIII bioaccumulation criteria have been experimentally confirmed, it is anticipated that these two substances will at least fulfill the B-criterion (i.e. BCF >2000) as well.

6.1.1.3 Toxicity

Experimental data of aquatic species referring to chronic toxicity endpoints (NOEC/EC_{10}) < 0.01 mg/l) are available for 9 of the PAH-constituents of CTPHT, namely:

Anthracene	Benzo(a)pyrene
Fluoranthene	Benzo(k)fluoranthene
Pyrene	Benzo(ghi)perylene
Benz(a)anthracene	Dibenzo(a,h)anthracene
	Indeno(1,2,3-cd)pyrene

For phenanthrene the reported values for chronic toxicity are > 10 µg/l. For benzo(b)fluoranthene no toxicity was observed within the limits of its water solubility. The same applies for chrysene with the exemption of one study, which however is not suitable to determine a (no)effect level (see sections 5.1.2.5 and 5.1.3).

Some of the PAH-constituents of CTPHT are classified as a carcinogen, mutagen or as toxic to reproduction in Annex VI of Regulation (EC) No 1272/2008.

Table 6.1: Classification of PAH-constituents of CTPHT as Carcinogen, Mutagen or as Toxic to Reproduction

Substance	**Carcinogen** ***(Category 2, Respectively 1B)***	**Mutagen** ***(Category 2, Respectively 1B)***	**Toxic To Reproduction** ***(Category 2, Respectively 1B)***
Benz(a)anthracene	X		
Chrysene	X	X	
Benzo(a)pyrene	X	X	X
Benzo(b)fluoranthene	X		
Benzo(k)fluoranthene	X		
Dibenzo(a,h)anthracene	X		

Based on the available experimental aquatic toxicity data and the data on classification, it is concluded that 11 of the 12 indicator PAH-constituents relevant for the assessment of CTPHT

(apart phenanthrene) fulfil the T-criteria of Annex XIII of the REACH Regulation [long term NOEC for aquatic organisms < 0.01 mg/l or substance classified as carcinogenic (cat. 1 or 2), mutagenic (cat. 1 or 2) or toxic to reproduction (cat. 1, 2 or 3) or there is evidence of chronic toxicity as identified by the classifications T, R48 or Xn, R48 according to Directive 67/548/EEC[8]].

6.1.2 Summary and overall conclusions on the PBT, vPvB or equivalent level of concern properties

An overview on the conclusions drawn on persistence, potential for bioaccumulation and toxicity to human health and the environment based on comparison of the data presented for the 12 indicator PAH-constituents of CTPHT with the PBT/vPvB criteria of Annex XIII of the REACH Regulation is provided in Table 6.2.

Table 6.2: Overview on Conclusions on Fulfilment of the (v)P-, (v)B- or T-criteria for the 12 Indicator PAH-constituents of CTPHT

Substance	Persistence	Bioaccu-mulation	Toxicity Human health	Toxicity Aquatic Environment	Conclusion
Anthracene	vP	B	-	T	PBT
Phenanthrene	vP	vB	-	-	vPvB
Fluoranthene	vP	vB	-	T	PBT/vPvB
Pyrene	vP	vB	-	T	PBT/vPvB
Benz(a)anthracene	vP	vB	T	T	PBT/vPvB
Chrysene	vP	vB	T	-	PBT/vPvB
Benzo(a)pyrene	vP	vB	T	T	PBT/vPvB
Benzo(b)fluoranthene	vP	No experimental data	T	- (No signs of toxicity up to limit of water solubility)	-
Benzo(k)fluoranthene	vP	vB	T	T	PBT/vPvB
Benzo(ghi)perylene	vP	vB	-	T	PBT/vPvB
Dibenzo(a,h)anthracene	No experimental data	vB	T	T	-
Indeno(1,2,3-cd)pyrene	No experimental data	No experimental data	-	T	-

Based on the data available, it is concluded that 7 of the 12 PAH-constituents present in CTPHT in concentrations equal to or above 0.1% are to be considered as both vPvB and PBT substances. These are: fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(a)pyrene, benzo(k)fluoranthene and benzo(ghi)perylene.

[8] In the CLP Regulation (1272/2008), classifications [T, R48] and [Xn, 48] have been replaced by [STOT RE 1, H372] and [STOT RE 2, H373] ([Hazard Class, Hazard statement]) respectively. No one of the PAHs addressed in this PBT assessment is classified as such.

STOT RE 1,2: Specific target organ toxicity – repeated exposure; H372: Causes damage to organs through prolonged or repeated exposure; H373: May cause damage to organs through prolonged or repeated exposure.

Phenanthrene fulfils the vPvB criteria, but not the PBT criteria. Anthracene fulfils the PBT criteria, but not the vPvB criteria.

For benzo(b)fluoranthene, dibenzo(a,h)anthracene, and indeno(1,2,3-cd)pyrene no definitive conclusion on their PBT/vPvB properties is possible, due to lack of data relevant for P/vP and/or B/vB assessment in accordance with Annex XIII of the REACH Regulation.

For coal tar pitch, high temperature, the above conclusion on the vPvB and PBT properties of its PAH-constituents has the consequence that the substance needs to be considered as a substance with both vPvB and PBT properties. It is concluded that CTPHT is a substance containing at least 5 to 10 % of PAH-constituents with both vPvB and PBT properties.

This assessment relies only on the indicator PAH-constituents of CTPHT. It should however be considered that residual constituents of CTPHT may have similar structure with the indicator PAHs selected and, therefore, fractions of these residual constituents may have PBT and / or vPvB properties as well.

REFERENCES

Allred PM, Giesy JP (1985): Solar radiation-induced toxicity of anthracene to *Daphnia pulex*. Environ Toxicol Chem 4: 219-226.

Bisson M, Dujardin R, Flammarion P, Garric J, Babut M, Lamy M-H, Porcher J-M, Thybaud É, Vindimian É (2000): Complément au SEQ-Eau: méthode de détermination des seuils de qualité pour les substances génotoxiques. Verneuil-en-Halatte, France: Institut National de l'Environnement Industriel et des Risques (INERIS), Agence de l'eau Rhin-Meuse.

Bruner KA, Fisher SW, Landrum PF (1994): The role of the Zebra Mussel, *Dreissena polymorpha*, in contaminant cycling: I. The effect of body size and lipid content on the bioconcentration of PCBs and PAHs. J. Great Lakes Res. 10(4): 725-734.

De Maagd PGJ (1996): Polycyclic aromatic hydrocarbons: fate and effects in the aquatic environment. Academic Thesis, Rijksuniversiteit Utrecht, The Netherlands

De Maagd PGJ, Sinnige TL, Schrap SM, Opperhuizen A, Sijm DTHM (1998): Sorption coefficient of polycyclic aromatic hydrocarbons for two lake sediments: influence of the bacteriocide sodium zide. Environ. Toxicol., Chem 17, 1899-1907,

De Voogt P, Van Hattum B, Leonards P, Klamer JC, Govers, H (1991): Bioconcentration of polycyclic heteroaromatic hydrocarbons in the guppy (*Poecilia reticulatea*). Aquat. Toxicol., 20, 169-194

Emery Jr. VL, Dillon TM (1996): Chronic toxicity of phenanthrene to the marine polychaete worm, *Nereis (Neanthes) arenaceodentata*. Bull Environ Contam Toxicol 56: 265-270.

Foran JA, Holst LL, Giesy JP (1991): Effects of photoenhanced toxicity of anthracene on ecological and genetic fitness of *Daphnia magna*: A reappraisal. Environ Toxicol Chem 10: 425-427.

Gala WR, Giesy JP (1992): Photo-induced toxicity of anthracene to the green alga, Selenastrum capricornutum. Arch Environ Contam Toxicol 23: 316-323.

Gossiaux DC, Landrum PF, Fisher SW (1996): Effect of temperature on the accumulation kinetics of PAHs and PCBs in the Zebra Mussel, *Dreissena polymorpha.* J. Great Lakes Res. 22 (2): 379-388

Hall AT, Oris JT (1991): Anthracene reduces reproductive potential and is maternally transferred during long-term exposure in fathead minnows. Aquat Toxicol 19: 249-264.

Halling-Sørensen B, Nyholm N, Baun A (1996): Algal toxicity test with volatile and hazardous compounds in air-tight test flasks with CO2 enriched headspace. Chemosphere 32: 1513-1526

Hannah JB, Hose JE, Landolt ML, Miller BS, Felton SP, Iwaoka WT (1982): Benzo(a)pyrene-induced morphologic and developmental abnormalities in rainbow trout. Arch Environ Contam Toxicol 11: 727-734.

Hatch AC, Burton Jr. GA (1998): Effects of photoinduced toxicity of fluoranthene on amphibian embryos and larvae. Environ Toxicol Chem 17: 1777-1785

Holst LL, Giesy JP (1989): Chronic effects of the photoenhanced toxicity of anthracene on *Daphnia magna* reproduction. Environ Toxicol Chem 8: 933-942.

Hooftman RN, Evers-de Ruiter A (1992): Early life stage tests with Brachydanio rerio and several polycyclic aromatic hydrocarbons using an intermittent flow-through system (draft OECD guideline). Delft, the Netherlands: TNO Environmental and Energy Research, TNO Institute of Environmental Sciences. TNO-report IMW-R 92/210.

Jonsson G, Bechmann RK, Bamber SD, Baussant T (2004): Bioconcentration, biotransformation, and elimination of polycyclic aromatic hydrocarbons in sheepshead minnows (*Cyprinodon variegatus*) exposed to contaminated seawater. Environ Toxicol Chem 23: 1538-1548

Kagan J, Kagan ED, Kagan IA, Kagan PA (1987): Do polycyclic aromatic hydrocarbons, acting as photosensitizers, participate in the toxic effects of acid rain? In: Zika RG, Cooper WJ, eds. Photochemistry of environmental aquatic systems. ACS Symposium Series 327. Washington, DC: American Chemical Society. pp (191-204.

Kagan J, Kagan ED, Kagan IA, Kagan PA, Quigley S (1985): The phototoxicity of non-carcinogenic polycyclic aromatic hydrocarbons in aquatic organisms. Chemosphere 14: 1829-1834

Lyons BP, Pascoe CK, McFadzen IRB (2002): Phototoxicity of pyrene and benzo(a)pyrene to embryo-larval stages of the pacific oyster *Crassostrea gigas*. Mar Environ Res 54: 627-631.

Mackay, D, Shiu, WY, and Ma, KC (1992): Illustrated Handbook of Physical–Chemical Properties and Environmental Fate of Organic Chemicals. Lewis Publishers, Boca Raton, FL.

McCarthy JF, Jimenez BD, and Barbee T (1985): Effect of dissolved humic material on accumulation of polycyclic aromatic hydrocarbons: Structure-activity relationships. Aquat Toxicol, 7, 15-24.

McLeese DW and Burridge LE (1987): Comparative accumulation of PAHs in four marine invertebrates. In: Capuzzo IM & Kester DR ed. Oceanic processes in marine pollution. Malabar, Florida, Kirger RE, 109-118.

MSC (2008). Member State Committee Support Document for Identification of Anthracene as a Substance of Very High Concern. Adopted on 8 October 2008. http://echa.europa.eu/doc/candidate_list/svhc_supdoc_anthracene_publication.pd

The Netherlands (2008): Annex XV Transitional Dossier. Coal Tar Pitch High Temperature (November 2008). Rapporteur: The Netherlands. Documentation of the work done under the Existing Substance Regulation (EEC) No 793/93 and submitted to the European Chemicals Agency according to Article 136(3) of Regulation (EC) No 1907/2006. Published by the European Chemicals Agency at: http://echa.europa.eu/doc/trd_substances/pitch_coal_tar_high_temp/ann_xv_trd/trd_netherlands_pitch.pdf

The Netherlands (2008b): European Union Risk Assessment Report (RAR), Coal-Tar Pitch, High Temperature (CAS No: 65996-93-2, EINECS No: 266-028-2), Risk Assessment – Human Health, April 2008.

Newsted JL, Giesy JP (1987): Predictive models for photoinduced acute toxicity of polycyclic aromatic hydrocarbons to *Daphnia magna*, Strauss (*Cladocera, crustacea*). Environ Toxicol Chem 6: 445-461.

Nikkilä A, Penttinen S, Kukkonen JVK (1999): UV-B induced acute toxicity of pyrene to the waterflea *Daphnia magna* in natural freshwaters. Ecotoxicol Environ Saf 44: 271-279.

Peachey RL, Crosby DG (1996): Phototoxicity in tropical reef animals. Mar Environ Res 42: 359-362

Pelletier MC, Burgess RM, Ho KT, Kuhn A, McKinney RA , Ryba SA (1997): Phototoxicity of individual polycyclic aromatic hydrocarbons and petroleum to marine invertebrate larvae and juveniles. Environ Toxicol Chem 16: 2190-2199

Southworth GR, Beauchamp JJ, & Schmieder PK (1978): Bioaccumulation potential of polycyclic aromatic hydrocarbons in *Daphnia pulex*. Water Res, 12: 973-977.

Spacie A, Landrum PF, & Leversee GJ (1983): Uptake, depuration, and biotransformation of anthracene and benzo(a)pyrene in bluegill sunfish. Ecotoxicol Environ Saf, 7: 330-341.

Spehar RL, Poucher S, Brooke LT, Hansen DJ, Champlin D, Cox DA (1999): Comparative toxicity of fluoranthene to freshwater and saltwater species under fluorescent light. Arch Environ Contam Toxicol 37: 496-502.

Trucco RG, Engelhardt FR, & Stacey B (1983): Toxicity accumulation and clearance of aromatic hydrocarbons in *Daphnia pulex***.** Environ Pollut, A31: 191-202

Weinstein JE, Oris JT (1999): Humic acids reduce the bioaccumulation and photoinduced toxicity of fluoranthene to fish. Environ. Toxicol. Chem., 18, 2087-2094.

Weinstein JE, Polk KD (2001): Phototoxicity of anthracene and pyrene to glochidia of the freshwater mussel *Utterbackia imbecilis*. Environ Toxicol Chem 20: 2021-2028.

Wernersson A-S (2003): Predicting petroleum phototoxicity. Ecotoxicol Environ Saf 54: 355-365.

Wernersson A-S, Dave G (1997): Phototoxicity identification by solid phase extraction and photoinduced toxicity to *Daphnia magna*. Arch Environ Contam Toxicol 32: 268-273

Wilcoxen SE, Meier PG, Landrum PF (2003): The toxicity of fluoranthene to *Hyalella azteca* in sediment and water-only exposures under varying light spectra. Ecotoxicol Environ Saf 54: 105-117.

Wild SR, Berrow ML, Jones, KC (1991): The persistence of polynuclear aromatic hydrocarbons (PAHs) in sewage sludge amended agricultural soils. Environ. Pollut., 72, 141-157.

Wild SR, Jones, KC (1993): Biological and abiotic losses of polynuclear aromatic hydrocarbons (PAHs) from soils feshly amended with sewage sludge. Environ Toxicol Chem 12: 5-12.