5-6 RINGS POLYAROMATIC HYDROCARBONS (PAH)

This EQS dossier was prepared by the Sub-Group on Review of the Priority Substances List (under Working Group E of the Common Implementation Strategy for the Water Framework Directive).The dossier was reviewed by the Scientific Committee on Health and Environmental Risks (SCHER), whose comments did not necessitate any changes

Context

In the EQS fact sheet published in 2005 which addresses 5-6 rings PAHs, 3 EQS values are reported for the following compounds:

- benzo[a]pyrene,
- sum of benzo[b]fluoranthene and benzo[k]fluoranthene,
- sum of benzo[g,h,i]perylene and indeno[1,2,3-cd]pyrene.

Directive 2008/105/EC states that "*for the group of priority substances of polyaromatic hydrocarbons (PAH) (No 28), each individual EQS is applicable, i.e. the EQS for Benzo(a)pyrene, the EQS for the sum of Benzo(b)fluoranthene and Benzo(k)fluoranthene and the EQS for the sum of Benzo(g,h,i)perylene and Indeno(1,2,3-cd)pyrene must be met.*"

These EQS are based on direct toxicity to pelagic organisms only because no data were available for protection of top predators from secondary poisoning or for protection of human health from consumption of fishery products at the time the fact sheet was elaborated (except for benzo[a]pyrene where a $QS_{biota,\ hh}$ is mentioned but not taken into account when deriving the overall QS).

Since this fact sheet was published in 2005, a final draft European Union Risk Assessment Report has become available in the context of assessment of existing chemicals (Regulation 793/93/EEC), addressing Coal Tar Pitch High Temperature (Final EU-RAR CTPHT, E.C., 2008a). By addressing CTPHT, this report provides useful information on the 5 substances addressed in the present fact sheet which are benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[g,h,i]perylene and indeno[1,2,3-cd]pyrene. Moreover, documents relevant to the derivation of an EQS for 5-6 rings PAHs have become available from RIVM (Baars *et al.*, 2001) and EFSA (EFSA, 2008). Finally, an unpublished report from RIVM (Verbruggen, in prep.) was provided by the main author to allow a dataset as complete as possible for the aquatic and benthic effects assessment section.

During the review process of the existing EQS, it was proposed to consider the derivation of a single EQS applying to 5-6 rings Polyaromatic Hydrocarbons, or at least to the four carcinogenic PAHs.

New available data and scientific considerations

Based on the new documents, an attempt was made to review the EQS for the 5 substances.

With regard to aquatic toxicity, enough data are available to derive $MAC\text{-}QS_{water,\ eco}$ as well as $AA\text{-}QS_{water,\ eco}$ values for each compound, except for indeno[1,2,3-cd]pyrene.

For the 4 carcinogenic compounds, the existing reviews, which have focused on carcinogenic properties, did not report any appropriate validated data that could be used to derive QS values for protection of top predators from secondary poisoning.

As regards the protection of human health from consumption of fishery products, it has to be considered that benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene and indeno[1,2,3-cd]pyrene are known to be carcinogenic substances, while no potential for carcinogenicity is demonstrated for benzo[g,h,i]perylene. According to the RIVM report (Baars *et al.*, 2001), benzo[a]pyrene is 10 times more potent for carcinogenic effects than the 3 other compounds.

Regulation 1881/2006/EC sets maximum levels for certain contaminants in foodstuffs and states that "*benzo(a)pyrene, for which maximum levels are listed, is used as a marker for the occurrence and effect of carcinogenic polycyclic aromatic hydrocarbons. These measures therefore provide full harmonisation on polycyclic aromatic hydrocarbons in the listed foods across the Member States*".

In an attempt to build a single EQS for 5-6 rings PAHs, the difference of toxicity (1 non-carcinogenic, 4 carcinogenic, one of those being significantly more toxic) should be taken into account.

As a consequence of these considerations and of the dataset available, different options arose during the review process:

1) Should EQS be derived from a food standard or from TDI values available?
2) Should a Toxic Unit (TU) or Toxic Equivalency Factor (TEF) approach be used for the mixture of 5-6 rings PAHs?
3) Should the EQS be based on a worst case assumption (i.e. on benzo[a]pyrene as representative of all compounds)? Should it include the non-carcinogenic PAH?
4) To which monitored compounds should the EQS (based on benzo[a]pyrene) be compared? Benzo[a]pyrene as a marker? To the sum of the 5-6 rings PAHs? To another set of PAHs?

1) Should EQS be derived from a food standard or from TDI values available?

According to the TGD on EQS derivation "*No internationally recognised approach exists for determining the uptake of contaminants from fishery products by humans (...) Therefore, when legislation* [e.g. Reg. 1881/2006/EC] *has already led to the derivation of standards, the $QS_{biota\ hh}$ should refer to the maximum allowable concentration in $\mu g.kg^{-1}_{wet\ weight}$ in the specific tissue or sampling material.*" (E.C., 2011).
In the case of PAHs, this implies the use of benzo(a)pyrene as a marker for the occurrence and effect of carcinogenic polycyclic aromatic hydrocarbons, with two consequences:

- The standard does not apply to one of the five 5-6 rings PAHs addressed by the WFD (benzo[g,h,i]perylene considered as non carcinogenic) for which an individual standard would have to be derived;
- It has to be assumed that the comparison of monitored concentrations of benzo(a)pyrene alone and an EQS also based on benzo(a)pyrene is sufficient to cover the risk related to the five 5-6 rings PAHs.

Despite the recommendation of the TGD to use the existing food standard (and thus benzo(a)pyrene as a marker for the other PAHs), the following questions were also examined.

2) Should a Toxic Unit (TU) or Toxic Equivalency Factor (TEF) approach be used for the mixture of 5-6 rings PAHs?

In order to address the toxicity of a mixture of compounds from the same family, the application of a Toxic Unit (TU) or Toxic Equivalency Factor (TEF) approach is recommended. Two essential drawbacks were however identified:
In its Scientific Opinion on Polycyclic Aromatic Hydrocarbons in Food (EFSA, 2008), EFSA states that the TEF approach "*is not scientifically valid because of the lack of data from oral carcinogenicity studies on individual PAHs, their different modes of action and the evidence of poor predictivity of the carcinogenic potency of PAH mixtures based on the currently proposed TEF values*".
In addition to the lack of individual toxicity data, it was noted that the occurrence of PAHs in environmental compartments varies too much to define an averaged distribution of individual compounds, which also makes difficult the use of the TEF approach.
Hence, there is up to now no international or European consensus on the use of the TEF approach in the risk characterisation of PAHs mixtures in food.

3) Should the EQS be based on a worst case assumption (i.e. on benzo[a]pyrene as representative of all compounds)? Should it include the non-carcinogenic PAH?

Use of the toxicity value for benzo[a]pyrene for the three other carcinogenic compounds would be consistent with Regulation 1881/2006/EC, which states that "*benzo(a)pyrene, for which maximum levels are listed, is* *used as a marker for* *<u>the occurrence and effect</u>* *of carcinogenic polycyclic aromatic hydrocarbons.*". However, since benzo[a]pyrene is 10 times more potent for carcinogenic effects than the 3 other compounds, the EQS for benzo(a)pyrene would necessarily be over-protective of the **effects** of the other three, assuming that their actual **occurrence** were measured and compared with the EQS. The EQS would on this basis also be too protective of the effects of the non-carcinogenic compound (benzo[g,h,i]perylene), which indeed is not included in Regulation 1881/2006/EC. However, if benzo(a)pyrene were the only measured PAH (i.e. the marker for the occurrence of all) the EQS might not be protective – see question 4.

4) <u>To which monitored compounds should the EQS (based on benzo[a]pyrene) be compared? Benzo[a]pyrene as a marker? To the sum of the 5-6 rings PAHs? To another set of PAHs?</u>

The suitability of using benzo(a)pyrene as a marker for the occurrence of the PAHs has been called into question by the Scientific Opinion of the EFSA Panel on Polycyclic Aromatic Hydrocarbons in Food (EFSA, 2008) which stated that "*benzo[a]pyrene is not a suitable indicator for the occurrence of PAHs in food*" based particularly on a 2007 evaluation where EFSA demonstrated that benzo[a]pyrene could be detected in about 50% of food samples analysed, but in about 30% of all the samples other carcinogenic and genotoxic PAHs were detected despite testing negative for benzo[a]pyrene. In other words, even the EQS for benzo(a)pyrene might not be protective of the less toxic PAHs if it does not always "mark" their presence.

EFSA recommends in its Scientific Opinion of 2008 the possible use of 3 different criteria as indicators of the occurrence of PAHs in food, i.e.:

(i) PAH8: the sum of benzo[a]pyrene, benz[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[ghi]perylene, chrysene, dibenz[a,h]anthracene and indeno[1,2,3-cd]pyrene,
(ii) PAH4: the sum of benzo[a]pyrene, chrysene, benz[a]anthracene and benzo[b]fluoranthene or
(iii) PAH2: the sum of benzo[a]pyrene and chrysene;

also noting "*PAH8 not providing much added value compared to PAH4*".

As summarised in the following table, only PAH8 covers the 5 compounds currently addressed by the WFD:

PolyAromatic Hydrocarbons		PAH8	PAH4	PAH2
WFD 5-6 rings PAHs	**benzo[a]pyrene**	**X**	**X**	**X**
	benzo[b]fluoranthene	**X**	**X**	
	benzo[k]fluoranthene	**X**		
	benzo[ghi]perylene	**X**		
	indeno[1,2,3-cd]pyrene	**X**		
Non WFD PAHs	benz[a]anthracene	X	X	
	chrysene	X	X	X
	dibenz[a,h]anthracene	X		

For none of these groups of indicators does a regulatory maximum level in foodstuffs yet exist. However, the question remains as to whether the EQS for benzo(a)pyrene should be used in conjunction with a the sum of the concentrations of the five PAHs on the Priority Substances list instead of the concentration of benzo(a)pyrene alone, even though this would probably lead to over-protection.

<u>Back calculation from food standard to water:</u>

During discussions of the PS review, it was commented that a default value of 115 g of daily fishery products consumption is overestimated and should be refined for PAHs. However, in order to adapt the default value for an EU EQS, the food basket should in theory be homogeneous over EU MS, which is not the case, *i.e.* mean consumption in the EU is 20 to 30 g of fish per day while the maximum level in Norway is 70 $g.d^{-1}$.

Although it was agreed that the average daily consumption of fishery products is overestimated, no consensus was reached on the refined value to be used.

Also, it was agreed that the standards for PAHs in fish and molluscs should be used to calculate a standard in water on the basis of a standard food basket (*i.e.* contribution of fish versus mussels). The respective BCF/BAF values for fish and molluscs should be used for the conversion. However, in absence of any consensus on a standard food basket for the moment the calculation has used the single BCF values as recommended by the TGD-EQS.

Choices made and conclusions

It is noted that:

- the TGD-EQS recommends[1] the use of maximum levels in foodstuffs, which implies the monitoring of benzo[a]pyrene and its comparison with the EQS based on benzo[a]pyrene toxicity as covering all 5-6 rings PAHs.
- the highest toxicity potential comes from benzo(a)pyrene, but it may not be the best marker of PAHs occurrence and effects,
- if benzo[a]pyrene represents between 10 and 24% of PAH8 in food (EFSA, 2008), the use of benzo[a]pyrene as a marker of exposure and effects of benzo[b]fluoranthene, benzo[k]fluoranthene and indeno[1,2,3-cd]pyrene may be under-protective when dealing with compliance checking of samples which do not contain any benzo(a)pyrene but contain non-negligible concentrations of benzo[b]fluoranthene, benzo[k]fluoranthene and/or indeno[1,2,3-cd]pyrene.
- if the benzo[a]pyrene TL_{hh} were set for the rest of PAHs as if they were equally toxic, although it is known that they are less toxic, then the option of using an EQS based on benzo[a]pyrene to be compared to the sum of 5-6 rings PAHs could be over-protective of the risk to or via the aquatic environment and lead to false-positives.

Based on the above considerations, and in particular **the recommendation of the TGD-EQS to use existing regulatory values (in this case, Reg 1881/2006/EC)**, **the choice was made to consider the maximum level in foodstuffs for benzo[a]pyrene as the $QS_{biota, hh}$. Therefore, this tentative $QS_{biota, hh}$ value driving the overall QS should be applied as the EQS for compliance with monitored concentrations of benzo[a]pyrene, but covers the risk to or via the aquatic environment for the 3 other carcinogenic PAHs benzo[b]fluoranthene, benzo[k]fluoranthene and indeno[1,2,3-cd]pyrene. This proposed EQS based on the $QS_{biota, hh}$ value for benzo[a]pyrene is recommended for comparison with concentrations in biota.**

During the review process, it was underlined that the current proposal based on the strict application of the TGD-EQS recommendation to use existing standards, might, in some cases, be less conservative than the current approach where the sum of certain PAHs are considered. It is noted that this would be the case in sampling sites where benzo[a]pyrene is not the main (or a) contributor to the PAHs concentration.

A $QS_{biota, hh}$ value is also proposed for the non-carcinogenic benzo[g,h,i]perylene. However, the overall QS for benzo[g,h,i]perylene is not driven by this value but by the AA-$QS_{water, eco}$ value.

It is however noted that the EQS for benzo[a]pyrene would cover the risk for benzo[g,h,i]perylene.

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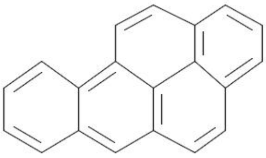
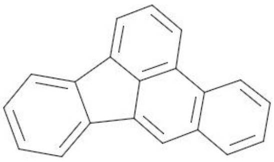
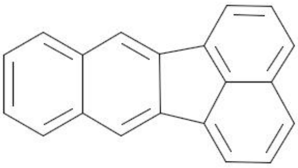
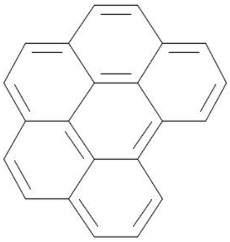
[1] "*No internationally recognised approach exists for determining the uptake of contaminants from fishery products by humans (...) Therefore, when legislation* [e.g. Reg. 1881/2006/EC] *has already led to the derivation of standards, the $QS_{biota\ hh}$ should refer to the maximum allowable concentration in $\mu g.kg^{-1}{}_{wet\ weight}$ in the specific tissue or sampling material.*" (E.C., 2011).

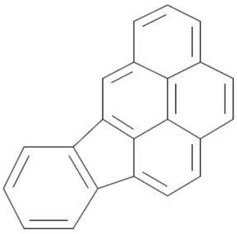
1 CHEMICAL IDENTITY

Common name	Benzo[a]pyrene
Chemical name (IUPAC)	Benzo[def]chrysene
Synonym(s)	B[a]P Benzo[def]chrysene
Chemical class (when available/relevant)	Polyaromatic hydrocarbons (PAH)
CAS number	50-32-8
EC number	200-028-5
Molecular formula	$C_{20}H_{12}$
Molecular structure	
Molecular weight (g.mol^{-1})	252.3

Common name	Benzo[b]fluoranthene
Chemical name (IUPAC)	Benzo[e]acephenanthrylene
Synonym(s)	-
Chemical class (when available/relevant)	Polyaromatic hydrocarbons (PAH)
CAS number	205-99-2
EC number (EINECS)	205-911-9
Molecular formula	$C_{20}H_{12}$
Molecular structure	
Molecular weight (g.mol^{-1})	252.3

Common name	Benzo[k]fluoranthene
Chemical name (IUPAC)	Benzo[k]fluoranthene
Synonym(s)	-
Chemical class (when available/relevant)	Polyaromatic hydrocarbons (PAH)
CAS number	207-08-9
EC number (EINECS)	205-916-6
Molecular formula	$C_{20}H_{12}$
Molecular structure	
Molecular weight (g.mol^{-1})	252.3

Common name	Benzo[g,h,i]perylene
Chemical name (IUPAC)	Benzo[g,h,i]perylene
Synonym(s)	-
Chemical class (when available/relevant)	Polyaromatic hydrocarbons (PAH)
CAS number	191-24-2
EC number (EINECS)	205-883-8
Molecular formula	$C_{22}H_{12}$
Molecular structure	
Molecular weight (g.mol^{-1})	276.3

Common name	Indeno[1,2,3-cd]pyrene
Chemical name (IUPAC)	Indeno[1,2,3-cd]pyrene
Synonym(s)	-
Chemical class (when available/relevant)	Polyaromatic hydrocarbons (PAH)
CAS number	193-39-5
EC number (EINECS)	205-893-2
Molecular formula	$C_{22}H_{12}$
Molecular structure	
Molecular weight (g.mol^{-1})	276.3

2 EXISTING EVALUATIONS AND REGULATORY INFORMATION

Legislation	
Annex III EQS Dir. (2008/105/EC)	No (existing priority substance including in Annex I EQS Dir.)
Existing Substances Reg. (793/93/EC)	CTPHT were investigated, addressing for the purpose of assessment the PAHs studied in the present fact sheet.
Pesticides(91/414/EEC)	No
Biocides (98/8/EC)	None of the 5 substances
PBT substances	None of the 5 substances investigated by EU-PBT Working Group separately. CTPHT were investigated as a whole and it was concluded that CTPHT is considered to be a PBT and a vPvB substance.
Substances of Very High Concern (1907/2006/EC)	CTPHT are included[2] because they are classified “Carc., PBT and vPvB” (articles 57a, 57d and 57e) Date of inclusion: 13.01.2010 Decision number ED/68/2009
POPs (Stockholm convention)	No
Other relevant chemical regulation (veterinary products, medicament, ...)	Regulation 1881/0206/EC

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[2] http://echa.europa.eu/doc/candidate_list/svhc_supdoc_pitch_publication.pdf

Endocrine disrupter (ED)	
E.C., 2004[3]	- Benzo[a]pyrene: Cat. 1 (evidence on ED)
Groshart and Okkerman, 2000	- Investigated, not categorised
Petersen *et al.*, 2007	- Benzo[a]pyrene: * Human health: Cat. 1 (evidence on ED) - * Wildlife: Cat. 2 (potential for ED)

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[3] Commission staff working document on implementation of the Community Strategy for Endocrine Disrupters.

3 PROPOSED QUALITY STANDARDS (QS)

3.1 ENVIRONMENTAL QUALITY STANDARD (EQS)

3.1.1 Benzo[a]pyrene, Benzo[b]fluoranthene, Benzo[k]fluoranthene and Indeno[1,2,3-cd]pyrene

Some MAC values are proposed in the following table, however, due to the high hydrophobicity of 5-6 rings PAHs, acute toxic effects are not expected to occur.

	Value	**Comments**
Benzo[a]pyrene		
Proposed MAC-EQS for [freshwater] [µg.l^{-1}] **Proposed MAC-EQS for [marine water] [µg.l^{-1}]**	**0.27** **0.027**	See section 7.1
Benzo[b]fluoranthene and Benzo[k]fluoranthene		
Proposed MAC-EQS for [freshwater] [µg.l^{-1}] **Proposed MAC-EQS for [marine water] [µg.l^{-1}]**	**0.017** **0.017**	See section 7.1
Indeno[1,2,3-cd]pyrene		
Proposed MAC-EQS for [freshwater] [µg.l^{-1}] **Proposed MAC-EQS for [marine water] [µg.l^{-1}]**	***Insufficient data available***	See section 7.1

As regards chronic effects, QS_{biota_hh} for protection of human health from consumption of fishery products is deemed the “critical QS” for derivation of an Environmental Quality Standard for Benzo[a]pyrene and covering the protection of human health and the environment from long term exposure to the four carcinogenic 5-6 rings PAHs, i.e. benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene and indeno[1,2,3-cd]pyrene). It has to be noticed however that no QS could be derived for the protection of top predators from secondary poisoning and that QS_{biota_hh} is calculated on the basis of maximum levels in foodstuffs (Regulation 1881/2006/EC) (see introductory section and section 7). The proposed value is as follows:

Benzo[a]pyrene	**Value**	**Comments**
Proposed AA-EQS for [biota] [µg.kg$^{-1}_{biota\ ww}$]	**2 for fish** **5 for crustaceans and cephalopods** **10 for molluscs**	Critical QS is $QS_{biota,\ hh}$ See section 7

The proposed values correspond to concentrations in biota and are recommended for comparison with concentrations in fish, crustaceans and cephalopods, or molluscs. Member States may opt to apply EQS for water instead of those recommended above. In this case, they shall convert the values recommended above in biota to their corresponding values in water by dividing them by BCF and BMF values recommended in section 5.3 of the present fact sheet.

Benzo[a]pyrene	**Value**	**Comments**

Corresponding AA-EQS for [freshwater and marine waters] [µg.l^{-1}]	0.015 for fish 4.5 10^{-4} for crustaceans and cephalopods 1.7 10^{-4} for molluscs	Critical QS is $QS_{biota,\ hh}$ See sections 5.3 and 7

3.1.2 Benzo[g,h,i]perylene

As regards chronic effects, AA-$QS_{freshwater\_eco}$ and AA-$QS_{marine\ water\_eco}$ for protection of pelagic organisms are 8.2 10^{-3} and 8.2 10^{-4} $\mu g.l^{-1}$, respectively, and are deemed the "critical QS" for derivation of an Environmental Quality Standard as a first approach. The information available was sufficient to apply assessment factors of 10 and 100 to derive the AA-$QS_{freshwater,\ eco}$ and AA-$QS_{marine\ water,\ eco}$, respectively and these values are deemed reliable.

It has to be noticed however that no QS could be derived for the protection of top predators from secondary poisoning,

As regards acute effects, the information available was sufficient to apply assessment factors of 100 and 1000, but MAC-$QS_{freshwater\_eco}$ and MAC-$QS_{marine\ water\_eco}$ for protection of pelagic organisms resulted in 2 10^{-3} and 2 10^{-4} $\mu g.l^{-1}$, respectively. Therefore, these QS were set equal to AA-$QS_{freshwater,\ eco}$ and AA-$QS_{marine\ water,\ eco}$, respectively.

Benzo[g,h,i]perylene	**Value**	**Comments**
Proposed AA-EQS for [freshwater] [$\mu g.l^{-1}$]	**8.2 10^{-3}**	Critical QS is $QS_{water\ eco}$
Proposed AA-EQS in [marine water] [$\mu g.l^{-1}$]	**8.2 10^{-4}**	See section 7
Proposed MAC-EQS for [freshwater] [$\mu g.l^{-1}$]	**8.2 10^{-3}**	**See section 7.1**
Proposed MAC-EQS for [marine water] [$\mu g.l^{-1}$]	**8.2 10^{-4}**	

3.2 SPECIFIC QUALITY STANDARD (QS)

3.2.1 Benzo[a]pyrene

Protection objective[4]	**Unit**	**Value**	**Comments**
Pelagic community (freshwater) – MAC-QS	[$\mu g.l^{-1}$]	0.27	See section 7.1
Pelagic community (marine water) – MAC-QS	[$\mu g.l^{-1}$]	0.027	
Pelagic community (freshwater) – AA-QS	[$\mu g.l^{-1}$]	0.022	See section 7.1
Pelagic community (marine water) – AA-QS	[$\mu g.l^{-1}$]	0.022	
Benthic community (freshwater)	[$\mu g.kg^{-1}{}_{dw}$]	91.5	See section 7.1
Benthic community (marine)	[$\mu g.kg^{-1}{}_{dw}$]	91.5	
Predators (secondary poisoning)	[$\mu g.kg^{-1}{}_{biota\ ww}$]	*No data available*	See section 7.2
	[$\mu g.l^{-1}$]	*No data available*	
Human health via consumption of fishery products, *valid for the sum of benzo[a]p, benzo[b]f, benzo[k]f and indeno[1,2,3-cd]p (carcinogenic PAHs)*	[$\mu g.kg^{-1}{}_{biota\ ww}$]	- 2 for fish - 5 for crustaceans and cephalopods - 10 for molluscs	See section 7.3
	[$\mu g.l^{-1}$]	1.7 10^{-4} (freshwater and marine water)	

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[4] Please note that as recommended in the Technical Guidance for deriving EQS (E.C., 2011), "EQSs [...] are not reported for 'transitional and marine waters', but either for freshwater or marine waters". If justified by substance properties or data available, QS for the different protection objectives are given independently for transitional waters or coastal and territorial waters.

Human health via consumption of water	[µg.l^{-1}]	0.01	

3.2.2 Benzo[b]fluoranthene

Protection objective[4]	**Unit**	**Value**	**Comments**
Pelagic community (freshwater) – MAC-QS	[µg.l^{-1}]	0.017	See section 7.1
Pelagic community (marine water) – MAC-QS	[µg.l^{-1}]	0.017	
Pelagic community (freshwater) – AA-QS	[µg.l^{-1}]	0.017	See section 7.1
Pelagic community (marine water) – AA-QS	[µg.l^{-1}]	0.017	
Benthic community (freshwater)	[µg.kg$^{-1}{}_{\text{dw}}$]	70.7	See section 7.1
Benthic community (marine)	[µg.kg$^{-1}{}_{\text{dw}}$]	70.7	
Predators (secondary poisoning)	[µg.kg$^{-1}{}_{\text{biota ww}}$]	*No data available*	See section 7.2
	[µg.l^{-1}]	*No data available*	
Human health via consumption of fishery products, *valid for the sum of benzo[a]p, benzo[b]f, benzo[k]f and indeno[1,2,3-cd]p (carcinogenic PAHs)*	[µg.kg$^{-1}{}_{\text{biota ww}}$]	- 2 for fish - 5 for crustaceans and cephalopods - 10 for molluscs	See section 7.3
	[µg.l^{-1}]	1.7 10^{-4} (freshwater and marine water)	
Human health via consumption of water, *valid for the sum of benzo[b]f, benzo[k]f, benzo[ghi]p and indeno[1,2,3-cd]p*	[µg.l^{-1}]	0.1	

3.2.3 Benzo[k]fluoranthene

Protection objective[5]	**Unit**	**Value**	**Comments**
Pelagic community (freshwater) – MAC-QS	[µg.l^{-1}]	0.017	See section 7.1
Pelagic community (marine waters) – MAC-QS	[µg.l^{-1}]	0.017	
Pelagic community (freshwater) – AA-QS	[µg.l^{-1}]	0.017	See section 7.1
Pelagic community (marine water) – AA-QS	[µg.l^{-1}]	0.017	
Benthic community (freshwater)	[µg.kg$^{-1}{}_{\text{dw}}$]	67.5	See section 7.1
Benthic community (marine)	[µg.kg$^{-1}{}_{\text{dw}}$]	67.5	
Predators (secondary poisoning)	[µg.kg$^{-1}{}_{\text{biota ww}}$]	*No data available*	See section 7.2
	[µg.l^{-1}]	*No data available*	
Human health via consumption of fishery products, *valid for the sum of benzo[a]p, benzo[b]f, benzo[k]f and indeno[1,2,3-cd]p (carcinogenic PAHs)*	[µg.kg$^{-1}{}_{\text{biota ww}}$]	- 2 for fish - 5 for crustaceans and cephalopods - 10 for molluscs	See section 7.3
	[µg.l^{-1}]	1.7 10^{-4} (freshwater and marine water)	

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[5] Please note that as recommended in the Technical Guidance for deriving EQS (E.C., 2011), "EQSs […] are not reported for 'transitional and marine waters', but either for freshwater or marine waters". If justified by substance properties or data available, QS for the different protection objectives are given independently for transitional waters or coastal and territorial waters.

Human health via consumption of water, *valid for the sum of benzo[b]f, benzo[k]f, benzo[ghi]p and indeno[1,2,3-cd]p*	[µg.l^{-1}]	0.1	

3.2.4 Benzo[g,h,i]perylene

Protection objective[5]	**Unit**	**Value**	**Comments**
Pelagic community (freshwater) – MAC-QS	[µg.l^{-1}]	$8.2\ 10^{-3}$	See section 7.1
Pelagic community (marine water) – MAC-QS	[µg.l^{-1}]	$8.2\ 10^{-4}$	
Pelagic community (freshwater) – AA-QS	[µg.l^{-1}]	$8.2\ 10^{-3}$	See section 7.1
Pelagic community (marine water) – AA-QS	[µg.l^{-1}]	$8.2\ 10^{-4}$	
Benthic community (freshwater)	[µg.kg^{-1} $_{\text{dw}}$]	42	See section 7.1
Benthic community (marine)	[µg.kg^{-1} $_{\text{dw}}$]	4.2	
Predators (secondary poisoning)	[µg.kg^{-1}$_{\text{biota ww}}$]	*No data available*	See section 7.2
	[µg.l^{-1}]	*No data available*	
Human health via consumption of fishery products	[µg.kg^{-1}$_{\text{biota ww}}$]	1 826	See section 7.3
	[µg.l^{-1}]	0.03*	
Human health via consumption of water	[µg.l^{-1}]	0.1	

* Therefore protected by QS$_{\text{biota}}$ of 1.7 10^{-4} µg.l^{-1} for benzo(a)pyrene as a marker for all five PAHs.

3.2.5 Indeno[1,2,3-cd]pyrene

Protection objective[6]	**Unit**	**Value**	**Comments**
Pelagic community (freshwater) – MAC-QS	[µg.l^{-1}]	*No derivation possible*	See section 7.1
Pelagic community (marine water) – MAC-QS	[µg.l^{-1}]		
Pelagic community (freshwater) – AA-QS	[µg.l^{-1}]	*No derivation possible*	See section 7.1
Pelagic community (marine water) – AA-QS	[µg.l^{-1}]		
Benthic community (freshwater)	[µg.kg^{-1} $_{\text{dw}}$]	*No derivation possible*	See section 7.1
Benthic community (marine)	[µg.kg^{-1} $_{\text{dw}}$]		
Predators (secondary poisoning)	[µg.kg^{-1}$_{\text{biota ww}}$]	*No data available*	See section 7.2
	[µg.l^{-1}]	*No data available*	
Human health via consumption of fishery products, *valid for the sum of benzo[a]p, benzo[b]f, benzo[k]f and indeno[1,2,3-cd]p (carcinogenic PAHs)*	[µg.kg^{-1}$_{\text{biota ww}}$]	- 2 for fish - 5 for crustaceans and cephalopods - 10 for molluscs	See section 7.3
	[µg.l^{-1}]	$1.7\ 10^{-4}$ (freshwater and marine water)	
Human health via consumption of water, *valid for the sum of benzo[b]f, benzo[k]f, benzo[ghi]p and indeno[1,2,3-cd]p*	[µg.l^{-1}]	0.1	

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[6] Please note that as recommended in the Technical Guidance for deriving EQS (E.C., 2011), "EQSs [...] are not reported for 'transitional and marine waters', but either for freshwater or marine waters". If justified by substance properties or data available, QS for the different protection objectives are given independently for transitional waters or coastal and territorial waters.

4 MAJOR USES AND ENVIRONMENTAL EMISSIONS

4.1 USES AND QUANTITIES

All data hereunder are extracted from Final CTPHT EU-RAR (E.C., 2008a)

4.1.1 Production

Final CTPHT EU-RAR (E.C., 2008a) states that within the European Union, high temperature coal tar pitch including 5 and 6 rings PAHs is produced "by ten companies at eleven sites in nine countries. The total European Union production capacity in 2004 was 1,127,000 tonnes. The actual production output of coal tar pitch in that year was about 817,800 tonnes. Import from outside the EU was reported to be about 91,600 tonnes per year and export was about 355,600 tonnes per year. The total consumption of coal tar pitch in the EU from these figures is estimated to be about 554,000 tonnes per year."

4.1.2 Uses

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

4.2 ESTIMATED ENVIRONMENTAL EMISSIONS

4.2.1 Sources of PAH emissions (E.C., 2008a)

Industrial sources

"The most important industrial emission sources include coke production, primary aluminium production and creosote and wood preservation. CTPHT is produced at coke plants as such and as a by-product of primary steel production. The main source of PAH emissions in the iron and steel industry is the coke ovens, used to make coke for the steel production. (…) The coke industries improved their PAH emissions markedly by applying modern technology. Nevertheless, old installations still have high PAH emissions, leading to local high ambient air concentrations (E.C., 2001). PAH emissions at steel production using electric arc furnaces originate from the presence of tar in the used refractory material."

"Creosote is a distillation product of coal tar, a by-product of bituminous coal coking. Emissions of PAH take place at all stages of the wood preservation process: impregnation, storage, transport and use. In the creosote and wood preservation industry, wood is mainly impregnated under pressure in vessels, but can also be sprayed or dipped. Since 2003 creosoted wood is only to be used for certain applications by professionals when treated in vacuum/pressure installations. Creosoted wood, which is treated through spraying, brushing or dipping is banned in the European Union. Creosoted wood is completely banned for certain applications like playgrounds, garden and garden furniture according to the EU Directive 2001/90/EC. Consequently wood preservation through spraying and dipping has been phased out in the European Union. Therefore emission from this source is expected to reduce considerably. PAH emissions to air from solvent use, which includes wood impregnation, in the United Kingdom clearly decreased over the period 1990 till 2002 from 104 tonnes to 69 tonnes with no clear decrease in the period 2000 till 2002. From this information it might be concluded that there is not clear direct effect on emissions from PAH resulting from the enforcement of the EU Directive at least in the United Kingdom. Other industrial sources include petrochemical and related industries (refineries), bitumen and asphalt industries (production and use), waste incineration, power plants, rubber tyre production, cement production (combustion of fossil fuels) and motor test rigs."

Domestic sources

"PAH-emissions from domestic sources are predominantly associated with the combustion of solid fuels as wood and coal for heating and cooking purposes. These sources contribute significantly to the total PAH emission. In Europe there is a large geographic variation in these domestic emissions due to climatic differences and to the heating systems in use. In addition to heating purposes, wood, coal or peat are also burned for the decorative effect in open fireplaces."

Mobile sources

"Mobile sources include all modes of transport using a combustion engine. PAH emissions from these sources depend on engine type, fuel type, emission control, outdoor temperature, load of vehicle, age of the car/engine and driving habits. Diesel fuelled vehicles have higher particulate emissions and the emission control equipment is less developed than gasoline vehicles. Therefore, diesel fuelled vehicles are responsible for more PAH emissions on the road. The wear and tear of tyres is also an important source of PAH emissions. Due to the extensive use of catalytic converters and improved diesel quality, the PAH emissions from tyres could even be larger than those from the exhaust of vehicles (Edlund, 2001). Non road transport includes all PAH emissions from combustion engines used by shipping activities, railways and aircrafts."

Agricultural sources

"Agricultural sources involve the burning of organic materials under less optimum combustion activities and therefore produce significant amounts of PAH. These activities include stubble burning, open burning of land for regeneration purposes or the open burning of brushwood, trimmings, straw etc. In some EU countries there are regulations in place regulating these emissions (E.C., 2001)."

4.2.2 PAH emissions to the different compartments (E.C., 2008a)

Emissions to water

"PAH can be emitted to surface water directly or indirectly via a STP by (industrial) point sources and via atmospheric deposition. Information on PAH emission to surface water for the EU is limited to the EPER database. Based on the emission estimates for 1998 in the Netherlands, road transport is considered to be by far the largest emission source to water, followed by emissions from agriculture and consumers. The emission from industry is relatively small. The European Pollutant Emission Register (EPER, 2004) reports PAH emission of the different point sources for 2001 (see Table below). The largest industrial emission sources to water are the pre-treatment of fibres or textiles, based on the EPER data."

PAH emissions to water in the EU for 2001 (The European Pollutant Emission Register (EPER, 2004)

Source	**Direct (kg)**	**Indirect via STP (kg)**
Industrial processes		
- Iron and steel production	10 271	381
- Petroleum industry	558	151
- Basic organic chemicals	1519	16
- Pharmaceutical products	0	36
- Pre-treatment fibres or textiles	0	12 284
Industrial combustion	1 022	6
- Installations for the production of carbon or graphite	21	0
- Slaughterhouses, plants for the production of milk other animal or vegetable raw materials	267	77
- Industrial plants for pulp from timber or other paper or board production	6	0
Waste disposal	259	80
	6	0
Total	13 923	13 031

5 ENVIRONMENTAL BEHAVIOUR

5.1 ENVIRONMENTAL DISTRIBUTION

Benzo[a]pyrene		**Master reference**
Water solubility (mg.l^{-1})	1.54 10^{-3}	Mackay *et al.*, 1992 *in* E.C., 2008a
Volatilisation	Benzo[a]pyrene is not likely to volatilise from surface water.	
Vapour pressure (Pa)	7.3 10^{-7} at 25°C	Mackay *et al.*, 1992 *in* E.C., 2008a
Henry's Law constant (Pa.m^3.mol^{-1})	0.034 at 20°C	Mackay *et al.*, 1992 *in* E.C., 2008a
Adsorption	**The value of 831 764 is used for derivation of QS**	
Organic carbon – water partition coefficient (K_{OC})	log K_{OC} = 5.92 (*calculated from K_{OW}*) K_{OC} = 831 764	Karickhoff *et al.*, 1979
Sediment – water partition coefficient($K_{sed\text{ -water}}$)	20 795 (*calculated from K_{OC}*)	E.C., 2011
Bioaccumulation	**BCF, BMF_1 and BMF_2 values recommended for back calculation of QS_{biota} values to water reported in the dedicated following section 0.**	
Octanol-water partition coefficient (Log Kow)	6.11 (*estimated*)	Mackay et al., 1992 *in* E.C., 2008a

	6.13 (*experimental*)	US-EPA, 2008

Benzo[b]fluoranthene		**Master reference**
Water solubility (mg.l^{-1})	$1.28\ 10^{-3}$	Mackay *et al.*, 1992 *in* E.C., 2008a
Volatilisation	Benzo[b]fluoranthene is not likely to volatilise from surface water.	
Vapour pressure (Pa)	$3.3\ 10^{-6}$ at 25°C	Mackay *et al.*, 1992 *in* E.C., 2008a
Henry's Law constant (Pa.m^3.mol^{-1})	0.051 at 20°C	Mackay *et al.*, 1992 *in* E.C., 2008a
Adsorption	**The value of 831 764 is used for derivation of QS**	
Organic carbon – water partition coefficient (K_{OC})	log K_{OC} = 5.92 (*calculated from K_{OW}*) K_{OC} = 831 764	Karickhoff *et al.*, 1979
Sediment – water partition coefficient($K_{sed\ -water}$)	20 795 (*calculated from K_{OC}*)	E.C., 2011
Bioaccumulation	**BCF, BMF_1 and BMF_2 values recommended for back calculation of QS_{biota} values to water reported in the dedicated following section 0..**	
Octanol-water partition coefficient (Log Kow)	6.12 (*estimated*)	Mackay *et al.*, 1992 *in* E.C., 2008a
	5.78 (*experimental*)	US-EPA, 2008

Benzo[k]fluoranthene		**Master reference**
Water solubility (mg.l^{-1})	$0.93\ 10^{-3}$	Mackay *et al.*, 1992 *in* E.C., 2008a
Volatilisation	Benzo[k]fluoranthene is not likely to volatilise from surface water.	
Vapour pressure (Pa)	$1.3\ 10^{-7}$ at 25°C	Mackay *et al.*, 1992 *in* E.C., 2008a
Henry's Law constant (Pa.m^3.mol^{-1})	0.043 at 20°C	Mackay *et al.*, 1992 *in* E.C., 2008a
Adsorption	**The value of 794 328 is used for derivation of QS**	
Organic carbon – water partition coefficient (K_{OC})	log K_{OC} = 5.9 (*calculated from K_{OW}*) K_{OC} = 794 328	Karickhoff *et al.*, 1979
Sediment – water partition coefficient($K_{sed\ -water}$)	19 859 (*calculated from K_{OC}*)	E.C., 2011
Bioaccumulation	**BCF, BMF_1 and BMF_2 values recommended for back calculation of QS_{biota} values to water reported in the dedicated following section 0.**	
Octanol-water partition coefficient (Log Kow)	6.11 (*estimated*)	Mackay *et al.*, 1992 *in* E.C., 2008a
	6.11 (*experimental*)	US-EPA, 2008

Benzo[g,h,i]perylene		**Master reference**
Water solubility (mg.l^{-1})	0.14 10^{-3}	Mackay *et al.*, 1992 *in* E.C., 2008a
Volatilisation	Benzo[g,h,i]perylene is not likely to volatilise from surface water.	
Vapour pressure (Pa)	1.4 10^{-8} at 25°C	Mackay *et al.*, 1992 *in* E.C., 2008a
Henry's Law constant (Pa.m^3.mol^{-1})	0.027 at 20°C	Mackay *et al.*, 1992 *in* E.C., 2008a
Adsorption	**The value of 1 023 293 is used for derivation of QS**	
Organic carbon – water partition coefficient (K_{OC})	log K_{OC} = 6.01 (*calculated from K_{OW}*) K_{OC} = 1 023 293	Karickhoff *et al.*, 1979
Sediment – water partition coefficient($K_{sed\ -water}$)	25 583 (*calculated from K_{OC}*)	E.C., 2011
Bioaccumulation	**BCF, BMF_1 and BMF_2 values recommended for back calculation of QS_{biota} values to water reported in the dedicated following section 0.**	
Octanol-water partition coefficient (Log Kow)	6.7 (*estimated*)	Mackay et al., 1992 *in E.C., 2008a*
	6.63 (*experimental*)	US-EPA, 2008

Indeno[1,2,3-cd]pyrene		**Master reference**
Water solubility (mg.l^{-1})	1 10^{-4}	Mackay *et al.*, 1992 *in* E.C., 2008a
Volatilisation	Indeno[1,2,3-cd]pyrene is not likely to volatilise from surface water.	
Vapour pressure (Pa)	1.7 10^{-8} at 25°C	Mackay *et al.*, 1992 *in* E.C., 2008a
Henry's Law constant (Pa.m^3.mol^{-1})	0.046 at 25°C (*estimated*)	Mackay *et al.*, 1992 *in* E.C., 2008a
Adsorption	**The value of** 1 344 229**is used for derivation of QS**	
Organic carbon – water partition coefficient (K_{OC})	log K_{OC} = 6.37 (*calculated from K_{OW}*) K_{OC} = 1 344 229	Karickhoff *et al.*, 1979
Sediment – water partition coefficient($K_{sed\ -water}$)	58 607 (*calculated from K_{OC}*)	E.C., 2011
Bioaccumulation	**BCF, BMF_1 and BMF_2 values recommended for back calculation of QS_{biota} values to water reported in the dedicated following section 0.**	
Octanol-water partition coefficient (Log Kow)	6.7 (*estimated*)	Mackay et al., 1992 *in E.C., 2008a*

5.2 ABIOTIC AND BIOTIC DEGRADATIONS

All information reported hereunder are extracted from Final CTPHT EU-RAR (E.C., 2008a).

Hydrolysis	PAH are chemically stable, with no functional groups that results in hydrolysis. Under environmental conditions, therefore, hydrolysis does not contribute to the degradation of PAH (Howard *et al.*, 1991).
Photolysis	The main abiotic transformation is photochemical decomposition, which in natural water takes place only in the upper few centimetres of the aqueous phase. PAHs are photodegraded by two processes, direct photolysis by light with a wavelength < 290 nm and indirect photolysis by least one oxidizing agent (Volkering and Breure, 2003). Singlet oxygen usually plays the main role in this process and the degradation process is related to the content of oxygen dissolved (Moore and Ranamoorthy, 1984). When PAHs are absorbed on particles, the accessibility for photochemical reactions may change, depending on the nature of the particles. There are great differences in photochemical reactivity between the various PAHs.
Biodegradation	The results from standard test for biodegradation in water show that PAH with up to four aromatic rings are biodegradable under aerobic conditions but that the biodegradation rate of PAH with more aromatic rings is very low (EHC, 1998). Although some evidence for anaerobic transformation of PAHs has been obtained (Coates *et al.*, 1997; Thierrin *et al.*, 1993), PAHs are usually considered to be persistent under anaerobic conditions (Neff, 1979; Volkering and Breure, 2003). Because marine sediments are often anaerobic, degradation of PAHs in this compartment is expected to be very slow.The biochemical pathway for the aerobic biodegradation of PAHs has extensively been investigated. It is understood that the initial step in the aerobic catabolism of a PAH molecule by bacteria occurs via oxidation of the PAH to a dihydrodiol by a multicomponent enzyme system. These dihydroxylated intermediates may then be processed through either an ortho cleavage type of pathway, in which ring fission occurs between the two hydroxylated carbon atoms, or a meta cleavage type of pathway, which involves cleavage of the bond adjacent to the hydroxyl groups, leading to central intermediates such as protocatechates and catechols. These compounds are further converted to tricarboxylic acid cycle intermediates (van der Meer *et al.*, 1992). Although the biodegradation pathway of the different PAHs is very similar their biodegradation rates differ considerably. In general the biodegradation rate decreases with increasing number of aromatic rings. For example, for degradation by bacteria from estuary half lives for B[a]P of more than 1750 days was found (Gerlach, 1981). According to Volkering and Breure (2003), two factors are considered responsible for the difference in degradation rate. First, the bacterial uptake rates of the compounds with higher molecular weight have been shown to be lower than the uptake rates of the low molecular weight PAHs. The second and most important factor is the bioavailability of PAHs, due to sorption on suspended organic matter and sediment. Since the Kow and the Koc are strongly correlated, high molecular weight PAHs will degrade slower than low molecular weight PAHs. This is illustrated by Durant *et al.*, 1995 who found that the half-life of PAHs in estuarine sediment was reversely related to the Kow. Biodegradation rates also are extremely dependent on the (a)biotics conditions both in the lab and in the field. Important influencing factors are (1) the substrate concentration; with low PAH concentrations leading to longer half-lives; (2) temperature, which reversely relates to the half-live and (3) the presence or absence of a lag-phase (De Maagd, 1996). In addition, the desorption rate of PAH appears to decrease with increase of the residence time of PAHs due to slow sorption into micropores and organic matter, and polymerization or covalent binding to the organic fraction. The consequence of this aging process is a decreased biodegradability and a decreased toxicity (Volkering and Breure, 2003).

5.3 BIOACCUMULATION AND BIOMAGNIFICATION POTENTIAL

		Master reference
Bioaccumulation	**The BCF values of 57 981 (molluscs), 11 138 (crustaceans and cephalopods) and 135 (fish) for benzo[a]pyrene are used for derivation of $QS_{biota\ sec.\ pois.}$ for all 5-6 rings PAHs and $BMF_1 = BMF_2 = 1$ given the absence of biomagnification (Bleeker, 2009; E.C., 2011).**	
BCF	Values per taxa based on data reported in the BCF dedicated table below for benzo[a]pyrene: - BCF plants = 910 (one value) - BCF annelids = 7 317 (one value) - BCF molluscs = 57 981 (geo. mean) - BCF crustaceans = 11 138 (geo. mean) - BCF insects = 1 080 (geo. mean) - BCF fish = 135 (geo. mean) Moreover, these data demonstrate an absence of biomagnification given that higher trophic levels (fish) present lower BCF values than lower trophic levels such as molluscs or crustaceans. Therefore, trophic dilution seems more likely than biomagnification and BMF values should be set to 1 by default. Values reported for crustaceans for Benzo[k]fluoranthene and Benzo[g,h,i]perylene are of the same order of magnitude compared to Benzo[a]pyrene. The RIVM report considers that trophic dilution is relevant for these PAHs (Bleeker, 2009).	Bleeker, 2009
BSAF anguilla	Sum of 5 rings PAH (including Benzo[b]fluoranthene and Benzo[k]fluoranthene: 0.003 – 0.06 Sum of 6 rings PAH (including Benzo[g,h,i]perylene and Indeno[1,2,3-cd]pyrene: 0.02 – 0.2	van der Oost *et al.*, 1994 *in* E.C., 2008a

Table summarising BCF values for PAH 5-6 rings in several aquatic species (Bleeker, 2009)

Taxa	Species	Test	Chem.	BCF ($l.kg^{-1}$)	Type (c)	Reliability	Reference
Benzo[a]pyrene							
Pisces	*Lepomis macrochirus*	FT	^{14}C	367 – 608[1]	Kin.	2	Jimenez *et al.*, 1987
		FT	^{14}C	30	Kin.	2	McCarthy and Jimenez, 1985
Mollusca	*Dreissena polymorpha*	S	^{3}H	41 000 – 84 000[2]	Kin.	2	Bruner *et al.*, 1994
		S	^{3}H	24 000 – 273 000[3]	Kin.	2	Gossiaux *et al.*, 1996
	Perna viridis	SR	GC	8 500[4]	Equi.	2	Richardson *et al.*, 2005
Crustacea	*Daphnia magna*	SR	HPLC	12 761	Equi.	2	Newsted and Giesy, 1987
		S	^{14}C	2 837	Equi.	2	Leversee *et al.*, 1981
	Eurytemora affinis		GCMS	1 750[5]	Equi.	2	Cailleaud *et al.*, 2009
	Mysis relicta	FT	^{3}H	8 496	Kin.	2	Evans and Landrum, 1989
	Pontoporeia hoyi	FT	^{14}C	73 000	Kin.	1	Landrum, 1988
			^{3}H	48 582	Kin.	2	Evans and Landrum, 1989
Insecta	*Chironomus riparius* (4th instar larvae)	S	^{14}C	650	Equi.	2	Leversee *et al.*, 1982
		S	^{14}C	166	Equi.	2	Leversee *et al.*, 1981
	Hexagenia limbata	FT	^{3}H	2 725 – 11 167[8]	Kin.	2	Landrum and Poore, 1988
Oligochaeta	*Stylodrilus heringianus*	FT	^{3}H	7 317	Kin.	2	Frank *et al.*, 1986
Magnoliophyta	*Lemna gibba*	S	^{14}C	7 – 910[6]	Kin.	2	Duxbury *et al.*, 1997
Benzo[k]fluoranthene							
Crustacea	*Daphnia magna*	SR	HPLC	13 225	Equi.	2	Newsted and Giesy, 1987
Benzo[g,h,i]perylene							
Crustacea	*Daphnia magna*	SR	HPLC	28 288	Equi.	2	Newsted and Giesy, 1987

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[1] BCFs were determined at different feeding regimes, i.e. fed both during uptake and depuration, not fed during uptake but fed during depuration.
[2] BCFs were determined with tested animals that differ in lipid content.
[3] BCFs were determined at different exposure temperatures.
[4] In this study BCF values are based on lipid weight, values given in this table are normalized to 5% lipid content.
[5] BCFs are based on dry weight.
[6] Values represent (a range of) BCF values from (a range of) different exposure concentrations.

a) FT: flow-through system; S: static; SR: static renewal. b) ^{14}C: radioactive carbon in the parent compound; GC: Gas chromatography; GCMS: Gas chromatography with mass spectrometry; Flu.Spec.: fluorescence spectrometry; 3H: radioactive hydrogen in the parent compound; HPLC: high pressure liquid chromatography. c) Kin.: Kinetic BCF, i.e. $k1/k2$; Equi.: BCF at (assumed) equilibrium, i.e. Corganism/Cwater. d) Reliability; 1: valid without restrictions; 2: valid with restrictions.

6 AQUATIC ENVIRONMENTAL CONCENTRATIONS

6.1 ESTIMATED CONCENTRATIONS

As sufficient monitoring data are available no separate calculation of the regional PECs had been performed. Therefore, only C_{local} values are presenting hereunder.

6.1.1 Benzo[a]pyrene

Compartment		**Predicted environmental concentration (PEC)**	**Master reference**
Freshwater (μg.l^{-1})	$C_{\text{local – production}}$	1.7 10^{-8} – 7.6 10^{-3}	E.C., 2008a
	$C_{\text{local – primary Al production}}$	4.6 10^{-4} – 0.46	
Marine waters (μg.l^{-1})	$C_{\text{local – production}}$	6 10^{-6}	E.C., 2008a
	$C_{\text{local – ferro-alloy producing ind.}}$	0.001	
	$C_{\text{local – primary Al production}}$	5.9 10^{-4} – 0.36	
Freshwater sediment (μg.kg^{-1} dw)	$C_{\text{local – production}}$	1.5 10^{-3} – 736	E.C., 2008a
	$C_{\text{local – primary Al production}}$	39 – 38 000	
Marine sediment (μg.kg^{-1} dw)	$C_{\text{local – production}}$	0.27	E.C., 2008a
	$C_{\text{local – ferro-alloy producing ind.}}$	79.7	
	$C_{\text{local – primary Al production}}$	0.012 – 30 000	
Biota (freshwater)		No data available	
Biota (marine)		No data available	
Biota (marine predators)		No data available	

6.1.2 Benzo[b]fluoranthene

Compartment		**Predicted environmental concentration (PEC)**	**Master reference**
Freshwater (μg.l^{-1})	$C_{\text{local – production}}$	1.8 10^{-8} – 1.2 10^{-2}	E.C., 2008a
	$C_{\text{local – primary Al production}}$	9.8 10^{-4} – 0.98	
Marine waters (μg.l^{-1})	$C_{\text{local – production}}$	3 10^{-6}	E.C., 2008a
	$C_{\text{local – ferro-alloy producing ind.}}$	1.9 10^{-3}	
	$C_{\text{local – primary Al production}}$	2.5 10^{-4} – 0.79	
Freshwater sediment (μg.kg^{-1} dw)	$C_{\text{local – production}}$	1.5 10^{-3} – 1 104	E.C., 2008a
	$C_{\text{local – primary Al production}}$	80 – 79 000	
Marine sediment (μg.kg^{-1} dw)	$C_{\text{local – production}}$	0.23	E.C., 2008a
	$C_{\text{local – ferro-alloy producing ind.}}$	153.5	
	$C_{\text{local – primary Al production}}$	0.012 – 64 000	
Biota (freshwater)		No data available	
Biota (marine)		No data available	
Biota (marine predators)		No data available	

6.1.3 Benzo[k]fluoranthene

Compartment		**Predicted environmental concentration (PEC)**	**Master reference**
Freshwater (µg.l^{-1})	$C_{\text{local – production}}$	$1.8\ 10^{-8}$ – $3.8\ 10^{-3}$	E.C., 2008a
Marine waters (µg.l^{-1})	$C_{\text{local – production}}$	$3\ 10^{-6}$	E.C., 2008a
Freshwater sediment (µg.kg^{-1} dw)	$C_{\text{local – production}}$	$1.5\ 10^{-3}$ – 345	E.C., 2008a
Marine sediment (µg.kg^{-1} dw)	$C_{\text{local – production}}$	0.23	E.C., 2008a
Biota (freshwater)		No data available	
Biota (marine)		No data available	
Biota (marine predators)		No data available	

6.1.4 Benzo[g,h,i]perylene

Compartment		**Predicted environmental concentration (PEC)**	**Master reference**
Freshwater (µg.l^{-1})	$C_{\text{local – production}}$	$1.5\ 10^{-8}$ – $4.2\ 10^{-3}$	E.C., 2008a
	$C_{\text{local – primary Al production}}$	$1.6\ 10^{-4}$ – 0.12	
Marine waters (µg.l^{-1})	$C_{\text{local – production}}$	$2\ 10^{-6}$	E.C., 2008a
	$C_{\text{local – ferro-alloy producing ind.}}$	$4\ 10^{-4}$	
	$C_{\text{local – primary Al production}}$	$1.2\ 10^{-4}$ – 0.12	
Freshwater sediment (µg.kg^{-1} dw)	$C_{\text{local – production}}$	$1.6\ 10^{-3}$ – 506	E.C., 2008a
	$C_{\text{local – primary Al production}}$	13 – 12 000	
Marine sediment (µg.kg^{-1} dw)	$C_{\text{local – production}}$	0.30	E.C., 2008a
	$C_{\text{local – ferro-alloy producing ind.}}$	42	
	$C_{\text{local – primary Al production}}$	0.32 – 12 000	
Biota (freshwater)		No data available	
Biota (marine)		No data available	
Biota (marine predators)		No data available	

6.1.5 Indeno[1,2,3]pyrene

Compartment		**Predicted environmental concentration (PEC)**	**Master reference**
Freshwater (µg.l^{-1})	$C_{\text{local – production}}$	$8\ 10^{-9}$ – $2.6\ 10^{-3}$	E.C., 2008a
	$C_{\text{local – primary Al production}}$	$9.2\ 10^{-4}$ – 0.91	
Marine waters (µg.l^{-1})	$C_{\text{local – production}}$	$1\ 10^{-6}$	E.C., 2008a
	$C_{\text{local – ferro-alloy producing ind.}}$	$2\ 10^{-4}$	
	$C_{\text{local – primary Al production}}$	$2.3\ 10^{-6}$ – 0.071	
Freshwater sediment (µg.kg^{-1} dw)	$C_{\text{local – production}}$	$2\ 10^{-3}$ – 690	E.C., 2008a
	$C_{\text{local – primary Al production}}$	21 – 21 000	
Marine sediment (µg.kg^{-1} dw)	$C_{\text{local – production}}$	0.37	E.C., 2008a
	$C_{\text{local – ferro-alloy producing ind.}}$	53.6	
	$C_{\text{local – primary Al production}}$	0.55 – 17 000	
Biota (freshwater)		No data available	
Biota (marine)		No data available	
Biota (marine predators)		No data available	

6.2 MEASURED CONCENTRATIONS

6.2.1 Benzo[a]pyrene

Compartment		**Measured environmental concentration (MEC)**	**Master reference**
Freshwater (µg.l^{-1})		PEC 1: 0.035 PEC 2: 0.025	James *et al.*, 2009$^{(1)}$
Marine waters (coastal and/or transitional) (µg.l^{-1})		No data available	
WWTP effluent (µg.l^{-1})		No data available	
Sediment(µg.kg^{-1} dw)	Sed < 2 mm	PEC 1: 300 PEC 2: 217	James *et al.*, 2009$^{(1)}$
	Sed 20 µm	PEC 1: 1 119 PEC 2: 1 103	
	Sed 63µm	PEC 1: 24 PEC 2: 22	
Biota(µg.kg^{-1} ww)	Invertebrates	PEC 1: 6 PEC 2: 4	James *et al.*, 2009$^{(1)}$
	Fish	PEC 1: 0.014 PEC 2: 0.014	
	Marine predators	No data available	

(1) data originating from EU monitoring data collection

6.2.2 Benzo[b]fluoranthene

Compartment		**Measured environmental concentration (MEC)**	**Master reference**
Freshwater (µg.l^{-1})		PEC 1: 0.036 PEC 2: 0.05	James *et al.*, 2009$^{(1)}$
Marine waters (coastal and/or transitional) (µg.l^{-1})		No data available	
WWTP effluent (µg.l^{-1})		No data available	
Sediment(µg.kg^{-1} dw)	Sed < 2 mm	PEC 1: 422 PEC 2: 310	James *et al.*, 2009$^{(1)}$
	Sed 20 µm	PEC 1: 1 428 PEC 2: 1 238	
	Sed 63µm	PEC 1: 54 PEC 2: 47	

Biota($\mu g.kg^{-1}$ ww)	Invertebrates	PEC 1: 23 PEC 2: 11	James *et al.*, 2009$^{(1)}$
	Fish	No data available	
	Marine predators	No data available	

$^{(1)}$ *data originating from EU monitoring data collection*

6.2.3 Benzo[k]fluoranthene

Compartment		**Measured environmental concentration (MEC)**	**Master reference**
Freshwater (μg.l^{-1})		PEC 1: 0.03 PEC 2: 0.025	James *et al.*, 2009$^{(1)}$
Marine waters (coastal and/or transitional) (μg.l^{-1})		No data available	
WWTP effluent (μg.l^{-1})		No data available	
Sediment(μg.kg^{-1} dw)	Sed < 2 mm	PEC 1: 219 PEC 2: 135	James *et al.*, 2009$^{(1)}$
	Sed 20 μm	PEC 1: 589 PEC 2: 586	
	Sed 63μm	PEC 1: 23 PEC 2: 19	
Biota(μg.kg^{-1} ww)	Invertebrates	PEC 1: 15 PEC 2: 13	James *et al.*, 2009$^{(1)}$
	Fish	No data available	
	Marine predators	No data available	

$^{(1)}$ *data originating from EU monitoring data collection*

6.2.4 Benzo[g,h,i]perylene

Compartment		**Measured environmental concentration (MEC)**	**Master reference**
Freshwater (μg.l^{-1})		PEC 1: 0.031 PEC 2: 0.05	James *et al.*, 2009$^{(1)}$
Marine waters (coastal and/or transitional) (μg.l^{-1})		No data available	
WWTP effluent (μg.l^{-1})		No data available	
Sediment(μg.kg^{-1} dw)	Sed < 2 mm	PEC 1: 249 PEC 2: 180	James *et al.*, 2009$^{(1)}$
	Sed 20 μm	PEC 1: 753 PEC 2: 715	
	Sed 63μm	PEC 1: 20 PEC 2: 19	
Biota(μg.kg^{-1} ww)	Invertebrates	PEC 1: 8 PEC 2: 7	James *et al.*, 2009$^{(1)}$
	Fish	No data available	
	Marine predators	No data available	

$^{(1)}$ *data originating from EU monitoring data collection*

6.2.5 Indeno[1,2,3-cd]pyrene

Compartment		**Measured environmental concentration (MEC)**	**Master reference**
Freshwater (µg.l^{-1})		PEC 1: 2.6 PEC 2: 0.025	James *et al.*, 2009(1)
Marine waters (coastal and/or transitional) (µg.l^{-1})		No data available	
WWTP effluent (µg.l^{-1})		No data available	
Sediment(µg.kg^{-1} dw)	Sed < 2 mm	PEC 1: 218 PEC 2: 171	James *et al.*, 2009(1)
	Sed 20 µm	PEC 1: 740 PEC 2: 735	
	Sed 63µm	PEC 1: 32 PEC 2: 34	
Biota(µg.kg^{-1} ww)	Invertebrates	PEC 1: 8 PEC 2: 7	James *et al.*, 2009(1)
	Fish	No data available	
	Marine predators	No data available	

(1) *data originating from EU monitoring data collection*

7 EFFECTS AND QUALITY STANDARDS

Final CTPHT EU-RAR (E.C., 2008a) states that “PAHs can be toxic via different mode of actions, such as non-polar narcosis and phototoxicity. The last is caused by the ability of PAHs to absorb ultraviolet A (UVA) radiation (320–400 nm), ultraviolet B (UVB) radiation (290–320 nm), and in some instances, visible light (400–700 nm). This toxicity may occur through two mechanisms: photosensitization, and photomodification. Photosensitization generally leads to the production of singlet oxygen, a reactive oxygen species that is highly damaging to biological material. Photomodification of PAHs, usually via oxidation, results in the formation of new compounds and can occur under environmentally relevant levels of actinic radiation (Lampi et al., 2005). The phototoxic effects can be observed after a short period of exposure, which explains why for PAHs like anthracene, fluoranthene and pyrene, where photoxicity is most evident, the acute toxicity values are even lower than the chronic toxicity values. According to Weinstein and Oris (1999) there is a growing body of evidence which suggests that phototoxic PAHs may be degrading aquatic habitats, particularly those in highly contaminated areas with shallow or clear water. For example, the photoinduced chronic effects of anthracene have been reported at those UV intensities occurring at depths of 10 to 12 m in Lake Michigan (Holst & Giesy, 1989). In addition to direct uptake of PAHs from the water column, another potential route of exposure for aquatic organisms is their accumulation from sediments (see e.g. Clemens et al., 1994; Kukkonen & Landrum, 1994), followed by subsequent solar ultraviolet radiation exposures closer to the surface. Ankley et al. (2004) also concluded in their peer review that PAHs are present at concentrations in aquatic systems such that animals can achieve tissue concentrations sufficient to cause photoactivated toxicity. Although UV penetration can vary dramatically among PAH-contaminated sites, in their view it is likely that at least some portion of the aquatic community will be exposed to UV radiation at levels sufficient to initiate photoactivated toxicity. They do recognize that at present time, the ability to conduct PAH photoactivated risk assessment of acceptable uncertainty is limited by comprehensive information on species exposure to PAH and UV radiation during all life stages. PAH exposure and uptake, as well as UV exposure, are likely to vary considerably among species and life stages as they migrate into and out of contaminated locations and areas of high and low UV penetration. For all but sessile species, these patterns of movements are the greatest determinant of the risk for photoactivated toxicity. Despite these uncertainties, it is thought that the phototoxic effects cannot be ignored in the present risk assessment. Therefore these effects are also considered in deriving the PNECs for aquatic species. It should be noted that the UV exposure levels of the selected studies did not exceed the UV levels under natural sun light conditions.

7.1 ACUTE AND CHRONIC AQUATIC ECOTOXICITY

Ecotoxicity data reported in the tables hereunder were extracted exclusively from the finalised version of CTPHT EU-RAR (E.C., 2008a) and an RIVM report in preparation (Verbruggen, in prep.).

In the table below, all data reported were considered valid for effects assessment purpose, i.e. could be given a reliability index (Klimisch code) of 1 or 2, or were considered useful as supporting information for effects assessment purpose, i.e. could be given a reliability index (Klimisch code) of 2/3. Information on reliability were retrieved from finalised version of CTPHT EU-RAR (E.C., 2008a) and an RIVM report in preparation (Verbruggen, in prep.).

Averaged measured concentrations are tagged as (mm).

7.1.1 Benzo[a]pyrene

ACUTE EFFECTS – Benzo[a]pyrene			**Klimisch code**	**Master reference**
Bacteria **(mg.l^{-1})**	**Freshwater**	*Vibrio fischeri* / 30mn $EC_{10 – bioluminescence}$ > water solubility	2 acc^{ing} to RIVM	Loibner *et al.*, 2004
	Marine			
Algae & aquatic plants **(mg.l^{-1})**	**Freshwater**	No information available		
	Marine	No information available		
Invertebrates **(mg.l^{-1})**	**Freshwater**	*Daphnia magna* (<24h) / 48h / (1) EC_{50} >2.7 10^{-3} No effects observed	2 acc^{ing} to RIVM	Bisson *et al.*, 2000b
		Daphnia pulex **(1.9-2.1mm) / 96h / (2)** **LC_{50} = 5 10^{-3}**	2/3 acc^{ing} to RIVM	Trucco *et al.*, 1983
	Marine	No information available		
	Sediment	No information available		
Fish **(mg.l^{-1})**	**Freshwater**	*Pimephales promelas* (larvae) / 120h / (3) LC_{50} < 5.6 10^{-3}	2/3 acc^{ing} to RIVM	Oris and Giesy, 1987
	Marine	No information available		
	Sediment	No information available		

(1) exposure in the dark

(2) 12:12 h photoperiod, with mixed fluorescent and natural light.

(3) LT50 study, at the end of the 96-h test period no mortality effect was found for phenanthrene and dibenzo[a,h]anthracene and less than 20% for benzo[ghi]perylene; simulated UV-A at 95 µW/m2 and UV-B at 20 µW/m2; 24 h preincubation with toxicant without light; only 1 concentration tested

CHRONIC EFFECTS – Benzo[a]pyrene			**Valid according to**	**Master reference**
Algae & aquatic plants **(mg.l^{-1})**	**Freshwater**	*Pseudokirchneriella subcapitata* / 72h (1) $EC_{10-\text{growth}} = 7.8\ 10^{-4}$	2 acc^{ing} to RIVM and EU-RAR	Bisson *et al.*, 2000a
	Marine	No information available		
Invertebrates **(mg.l^{-1})**	**Freshwater**	*Ceriodaphnia dubia* / 7d / (2) $EC_{10-\text{reproduction}} = 5\ 10^{-4}$	2 acc^{ing} to RIVM and EU-RAR	Bisson *et al.*, 2000a
	Marine	*Crassostrea gigas* / 48h / (1) $NOEC_{\text{abnormal shells}} = 1\ 10^{-3}$	2/3 acc^{ing} to RIVM and EU-RAR	Lyons *et al.*, 2002 *in* E.C., 2008a
		***Crassostrea gigas* / 48h / (2)** $\mathbf{NOEC_{\text{abnormal shells}} = 5\ 10^{-4}}$ $\mathbf{EC_{10-\text{abnormal shells}} = 2.2\ 10^{-4}}$	2/3 acc^{ing} to RIVM and EU-RAR	
		Crassostrea gigas / 48h / (2) $EC_{10-\text{larval development}} \geq 1.6\ 10^{-3}$ (mm)	2 acc^{ing} to RIVM	AquaSense, 2004
		Strongylocentrus purpuratus (eggs and sperm) / 48h $NOEC_{\text{gastrula deformities}} = 5\ 10^{-4}$	2 acc^{ing} to RIVM	Hose *et al.*, 1983
		Psammechinus miliaris / 48h / (2) $EC_{10-\text{larval development}} \geq 1.6\ 10^{-3}$ (mm)	2 acc^{ing} to RIVM	AquaSense, 2005
	Sediment	No information available		
Fish **(mg.l^{-1})**	**Freshwater**	*Brachydanio rerio* / 42d / (3) $NOEC_{ELS} \geq 4\ 10^{-3}$ (one conc. tested) No effects observed	2 acc^{ing} to RIVM	Hooftman and Evers-de Ruiter, 1992
		Brachydanio rerio (larvae) / 168d / (3) $NOEC_{\text{malformation}} \geq 4.4\ 10^{-4}$ (one conc. tested) No effects observed	2 acc^{ing} to RIVM	Petersen and Kristensen, 1998
		Oncorhynchus mykiss / 36d $EC_{10-ELS-\text{abnormalities}} \geq 2.9\ 10^{-3}$	2 acc^{ing} to RIVM	Hannah *et al.*, 1982
	Marine	*Psettichtys melanostichus* / 6d $NOEC_{\text{hatchability}} < 1\ 10^{-4}$ (one conc. tested)	2/3 acc^{ing} to RIVM	Hose *et al.*, 1982
	Sediment	No information available		

(1) 6000-8000 lux on the level of the solutions

(2) 16:8 h photoperiod.

(3) 16:8 h photoperiod, yellow light

Acute studies for freshwater species are available for crustaceans and fish. Chronic studies for fresh water species are available for algae, crustaceans, and fish. In addition, chronic studies for marine species are available for molluscs, echinoderms, and fish.

The acute test led by Bisson et al. (2000) on *Daphnia magna* did not result in any toxic effects. The 48h-EC_{50} of 2.7 µg.l^{-1} for crustacean *Daphnia magna* can however be used as endpoint for MAC-$QS_{\text{water, eco}}$ derivation. Assessment factors of 10 and 100 can reasonably be applied on this data to derive $MAC_{\text{freshwater, eco}}$ and $MAC_{\text{marine water, eco}}$, respectively.

Many data are available that correspond to studies where no effects were observed. The EC$_{10}$ of 0.22 µg.l^{-1} for shell development of the marine mollusc *Crassostrea gigas* is used as the most critical endpoint to use for AA-QS$_{water,\ eco}$ derivation. Because additional chronic toxicity data are available for two groups of typical marine species, the assessment factor deemed necessary for both freshwater and marine water is 10.

Tentative QS$_{water}$ Assessment factor method	**Relevant study for derivation of QS**	**AF**	**Tentative QS**
MAC$_{freshwater,\ eco}$	*Daphnia magna* / 24h EC$_{50}$ > 2.7 10^{-3} mg.l^{-1}	10	0.27 µg.l^{-1}
MAC$_{marine\ water,\ eco}$		100	0.027 µg.l^{-1}
AA-QS$_{freshwater,\ eco}$	*Crassostrea gigas* / 48h EC$_{10\ –\ abnormal\ shells}$ = 2.2 10^{-4} mg.l^{-1}	10	0.022 µg.l^{-1}
AA-QS$_{marine\ water,\ eco}$		10	0.022 µg.l^{-1}
AA-QS$_{freshwater,\ sed.}$	No data available for sediment-dwelling organisms. Therefore, EqP method was applied to derive the AA-QS	EqP	35.2 µg.kg$^{-1}_{ww}$ 91.5 µg.kg$^{-1}_{dw}$
AA-QS$_{marine\ water,\ sed.}$			

7.1.2 Benzo[b]fluoranthene and Benzo[k]fluoranthene

Data usable to derive the QS for benzo[b]fluoranthene are scarce. Because the two substances are mostly reported together and have structural similarities, it is proposed to combine benzo[b]fluoranthene and benzo[k]fluoranthene ecotoxicological data to derive a common QS$_{water,\ eco}$.

ACUTE EFFECTS – Benzo[b]f. and Benzo[k]f.			**Klimisch code**	**Master reference**
Bacteria (mg.l^{-1})	**Freshwater**	No information available		
	Marine	*Vibrio fischeri* / 30mn EC$_{10\ –\ bioluminescence}$ > water solubility	2 acc^{ing} to RIVM	Loibner *et al.*, 2004
Algae & aquatic plants (mg.l^{-1})	**Freshwater**	No acute data are available but that “chronic data for *Pseudokirchneriella subcapitata* indicate an EC$_{10\ –\ growth\ –\ 72h}$ > 1 10^{-3} and acute data is expected to be higher”.		
	Marine	No information available		
Invertebrates (mg.l^{-1})	**Freshwater**	Data are available for [b] and [k] isomer for *Daphnia magna* only but that no effects were observed (>1.1 10^{-3} mg.l^{-1}) in the two available studies (Bisson *et al.*, 2000a; Verrhiest *et al.*, 2001) and that “due to the low solubility of benzo(k)fluoranthene of about 1 µg.l^{-1} (Mackay and al., 2000), acute effects are not anticipated”.		
	Marine	No information available		
	Sediment	No toxicity was observed up to highest concentrations tested on *Rhepoxynius abronius* (test with benzo[b]fluoranthene), nor on *Hyalella azteca* and *Chironomus riparius* (test with benzo[k]fluoranthene)	2 acc^{ing} to RIVM	Boese *et al.*, 1998; Verrhiest *et al.*, 2001
Fish (mg.l^{-1})	**Freshwater**			
	Marine	No information available		
	Sediment	No information available		

CHRONIC EFFECTS – Benzo[b]f. and Benzo[k]f.			**Valid according to**	**Master reference**
Algae & aquatic plants **(mg.l^{-1})**	**Freshwater**	*Pseudokirchneriella subcapitata* / 72h / [b] and [k] $EC_{10 – growth} > 1\ 10^{-3}$	2 acc^{ing} to RIVM and EU-RAR	Bisson *et al.*, 2000a
	Marine	No information available		
Invertebrates **(mg.l^{-1})**	**Freshwater**	*Ceriodaphnia dubia* (<24h) / 7d / [b] and [k] $EC_{10 – reproduction} > 1.08\ 10^{-3}$	2 acc^{ing} to RIVM and EU-RAR	Bisson *et al.*, 2000a
		Daphnia magna (<24h) / 21d / [k] $EC_{10 – mortality, offspring intrinsic growth rate} > 2.2\ 10^{-3}$ (mm)	2 acc^{ing} to RIVM	AquaSense, 2004
	Marine	*Crassostrea gigas* / 48h / [k] $EC_{10 – larval development} > 2.6$ (mm)	2 acc^{ing} to RIVM	AquaSense, 2004
		Psammechinus miliaris / 48h / [k] $EC_{10 – larval development} > 2.6$ (mm)	2 acc^{ing} to RIVM	AquaSense, 2004
	Sediment	No information available		
Fish **(mg.l^{-1})**	**Freshwater**	*Brachydanio rerio* / 42d / [k] $EC_{10 – length} = 1.7\ 10^{-4}$ $EC_{10 – weight} = 3.1\ 10^{-4}$	2 acc^{ing} to RIVM and EU-RAR	Hooftman and Evers-de Ruiter, 1992
	Marine	No information available		
	Sediment	No information available		

No acute data is available for fish for benzo[b]fluoranthene and benzo[k]fluoranthène while fish is shown to be the most sensitive taxa in the chronic dataset. Therefore, it is decided to set the MAC-QS$_{water, eco}$ at the level of the AA-QS$_{water, eco}$.

As regards chronic toxicity, data are available for algae, crustaceans and fish. In addition, additional marine data are available for molluscs and specific marine taxa echinoderm. The lowest EC$_{10}$ value is found for *Brachydanio rerio* at 0.17 µg.l^{-1}. Because additional chronic toxicity data are available for two groups of marine species, the assessment factor deemed necessary for both freshwater and marine water is 10.

Tentative QS$_{water}$ **Assessment factor method**	**Relevant study for derivation of QS**	**AF**	**Tentative QS**	
MAC$_{freshwater, eco}$	*Insufficient data available*	-	MAC-QS is set equal to AA-QS: 0.017 µg.l^{-1}	
MAC$_{marine water, eco}$		-	MAC-QS is set equal to AA-QS: 0.017 µg.l^{-1}	
AA-QS$_{freshwater, eco}$	*Brachydanio rerio* / 42d $EC_{10 – length} = 1.7\ 10^{-4}$ mg.l^{-1}	10	0.017 µg.l^{-1}	
AA-QS$_{marine water, eco}$		10	0.017 µg.l^{-1}	
			B[b]fluo.	B[k]fluo.
AA-QS$_{freshwater, sed.}$	No toxicity was observed up to highest concentrations tested. Therefore, EqP method was applied to derive the AA-QS	EqP	27.2 µg.kg$^{-1}_{ww}$ 70.7 µg.kg$^{-1}_{dw}$	26.0 µg.kg$^{-1}_{ww}$ 67.5 µg.kg$^{-1}_{dw}$
AA-QS$_{marine water, sed.}$			27.2 µg.kg$^{-1}_{ww}$ 70.7 µg.kg$^{-1}_{dw}$	26 µg.kg$^{-1}_{ww}$ 67.5 µg.kg$^{-1}_{dw}$

7.1.3 Benzo[g,h,i]perylene

ACUTE EFFECTS – Benzo[g,h,i]p.			**Klimisch code**	**Master reference**
Bacteria **(mg.l^{-1})**	**Freshwater**	No information available		
	Marine	*Vibrio fischeri* / 30mn EC$_{10 – \text{bioluminescence}}$ > water solubility	2 acc$^{\text{ing}}$ to RIVM	Loibner *et al.*, 2004
Algae & aquatic plants **(mg.l^{-1})**	**Freshwater**	No acute data are available but chronic data for *Pseudokirchneriella subcapitata* indicate an EC$_{10\text{–growth–72h}}$ > 1.6 10^{-4} mg.l^{-1} and acute data is expected to be higher.		
	Marine	No information available		
Invertebrates **(mg.l^{-1})**	**Freshwater**	*Daphnia magna* / 48h EC$_{50 – \text{immobility}}$ > 2 10^{-4} No effects observed	2 acc$^{\text{ing}}$ to RIVM and EU-RAR	Bisson *et al.*, 2000a
	Marine	No information available		
	Sediment	No information available		
Fish **(mg.l^{-1})**	**Freshwater**	*Pimephales promelas* (larvae) / 120h / (1) <20% mortality at 1.5 10^{-4}	2 acc$^{\text{ing}}$ to RIVM and EU-RAR	Oris and Giesy, 1987
	Marine	No information available		
	Sediment	No information available		

(1) absence of UV-radiation and thereafter exposed to UV-light with an intensity of 20 µW/cm^2 UV-B (290-336 nm), 95 µW/cm^2 UV-A (336-400 nm). After the incubation time of 24 hours, the medium was renewed every 12 hours and exposure in combination with UVradiation lasted for 96 hours.

CHRONIC EFFECTS – Benzo[g,h,i]p.			**Valid according to**	**Master reference**
Algae & aquatic plants **(mg.l^{-1})**	**Freshwater**	*Pseudokirchneriella subcapitata* / 72h EC$_{10 – \text{growth}}$ > 1.6 10^{-3} No effects observed	2 acc$^{\text{ing}}$ to RIVM	Bisson *et al.*, 2000a
	Marine	No information available		
Invertebrates **(mg.l^{-1})**	**Freshwater**	*Ceriodaphnia dubia* (<24h) / 7d EC$_{10 – \text{reproduction}}$ = 8.2 10^{-5}	2 acc$^{\text{ing}}$ to RIVM and EU-RAR	Bisson *et al.*, 2000a
	Marine	No information available		
	Sediment	No information available		
Fish **(mg.l^{-1})**	**Freshwater**	*Brachydanio rerio* / 42d NOEC$_{\text{ELS}}$ ≥ 1.6 10^{-4}	2 acc$^{\text{ing}}$ to RIVM and EU-RAR	Hooftman and Evers-de Ruiter, 1992
	Marine	No information available		
	Sediment	No information available		

Beside the toxicity on marine bacterium *Vibrio fisheri*, no additional data on marine species are available.

Acute and chronic toxicity data are available for crustaceans and fish. Algae are not represented in the acute dataset but the chronic data show that crustaceans represent the most sensitive taxa so the dataset is considered complete.

The acute test led by Bisson et al. (2000) on *Daphnia magna* did not result in any toxic effects. The higher than 48h-EC$_{50}$ of 0.2 µg.l^{-1} for crustacean *Daphnia magna* can however be used as endpoint for MAC-QS$_{\text{water, eco}}$ derivation. Assessment factors of 10 and 100 can reasonably be applied on this data to derive MAC$_{\text{freshwater, eco}}$ and MAC$_{\text{marine water, eco}}$, respectively.

The lowest EC_{10} of 0.082 µg.l^{-1} is found for reproduction of *Ceriodaphnia dubia*. Assessment factors of 10 and 100 can be applied to this data to derive the $AA\text{-}QS_{\text{freshwater, eco}}$ and $AA\text{-}QS_{\text{marine water, eco}}$, respectively.

Tentative QS$_{\text{water}}$ **Assessment factor method**	**Relevant study for derivation of QS**	**AF**	**Tentative QS**
MAC$_{\text{freshwater, eco}}$	*Daphnia magna* / 48h EC$_{50\text{ – immobility}}$ > 2 10^{-4} mg.l^{-1}	100	MAC-QS = 0.002 µg.l^{-1} but can not be lower than AA-QS. Therefore MAC-QS is set equal to AA-QS = 8.2 10^{-3} µg.l^{-1}
MAC$_{\text{marine water, eco}}$		1000	MAC-QS = 2 10^{-4} µg.l^{-1} but can not be lower than AA-QS. Therefore MAC-QS is set equal to AA-QS = 8.2 10^{-4} µg.l^{-1}
AA-QS$_{\text{freshwater, eco}}$	*Ceriodaphnia dubia* / 7d EC$_{10\text{ – reproduction}}$ = 8.2 10^{-5}	10	8.2 10^{-3} µg.l^{-1}
AA-QS$_{\text{marine water, eco}}$		100	8.2 10^{-4} µg.l^{-1}
AA-QS$_{\text{freshwater, sed.}}$	No data available for sediment-dwelling organisms. Therefore, EqP method was applied to derive the AA-QS	EqP	16.1 µg.kg$^{-1}_{\text{ww}}$ 42 µg.kg$^{-1}_{\text{dw}}$
AA-QS$_{\text{marine water, sed.}}$			1.6 µg.kg$^{-1}_{\text{ww}}$ 4.2 µg.kg$^{-1}_{\text{dw}}$

7.1.4 Indeno[1,2,3-cd]pyrene

ACUTE EFFECTS –Indeno[1,2,3-cd]p.			**Klimisch code**	**Master reference**
Bacteria **(mg.l^{-1})**	**Freshwater**	No information available		
	Marine	*Vibrio fischeri* / 30mn EC$_{10\text{ – bioluminescence}}$ > water solubility	2 acc$^{\text{ing}}$ to RIVM	Loibner *et al.*, 2004
Algae & aquatic plants **(mg.l^{-1})**	**Freshwater**	No information available		
	Marine	No information available		
Invertebrates **(mg.l^{-1})**	**Freshwater**	No information available		
	Marine	No information available		
	Sediment	No information available		
Fish **(mg.l^{-1})**	**Freshwater**	No information available		
	Marine			
	Sediment			

CHRONIC EFFECTS –Indeno[1,2,3-cd]p.			**Valid according to**	**Master reference**
Algae & aquatic plants **(mg.l^{-1})**	**Freshwater**	*Pseudokirchneriella subcapitata* / 72h $EC_{10 \text{ – growth}}$ = 1.5 10^{-3}	2 acc^{ing} to RIVM and EU-RAR	Bisson *et al.*, 2000a
	Marine	No information available		
Invertebrates **(mg.l^{-1})**	**Freshwater**	*Ceriodaphnia dubia* / 7d $EC_{10 \text{ – reproduction}}$ = 2.7 10^{-4}	2 acc^{ing} to RIVM and EU-RAR	Bisson *et al.*, 2000a
	Marine	No information available		
	Sediment	No information available		
Fish **(mg.l^{-1})**	**Freshwater**	No information available		
	Marine			
	Sediment			

Acute data set for indeno[1,2,3-cd]pyrene is not sufficient to derive MAC-QS values. The chronic base-set is as well not complete for indeno[1,2,3-cd]pyrene, with missing information on chronic toxicity to fish. Therefore, no quality standard can be derived.

Tentative QS_{water} **Assessment factor method**	**Relevant study for derivation of QS**	**AF**	**Tentative QS**
$MAC_{freshwater, eco}$	*Insufficient data available*	-	*No sufficient data available*
$MAC_{marine water, eco}$		-	
$AA\text{-}QS_{freshwater, eco}$	*Insufficient data available*	-	*Insufficient data available*
$AA\text{-}QS_{marine water, eco}$		-	
$AA\text{-}QS_{freshwater, sed.}$	No data available for sediment-dwelling organisms.		-
$AA\text{-}QS_{marine water, sed.}$			-

7.2 SECONDARY POISONING

Data on the PAH toxicity to birds are scarce (Albers and Laoughlin, 2003; Patton and Dieter, 1980) and Final CTPHT EU-RAR (E.C., 2008a) states that "from these data it is not possible to derive a NOAEL for birds for either of the PAHs". "Also relevant toxicity data to mammals is limited. Almost all of the long term studies reported were designed to assess carcinogenic potency of PAH and are not considered appropriate for secondary poisoning assessment.

Only for B[a]pyrene reprotoxicity data are available. Most severe effect were observed after administration of 10 mg.kg^{-1} to CD-1 mice by gavage during gestation which produced decreased gonadal weights and reduced fertility and reproductive capacity in the offspring. Higher doses (40 mg.kg^{-1}) caused almost complete sterility in both sexes of offspring (Mackenzie and Angevine, 1981b). As no concentrations are tested a NOAEL can not be determined and consequently no QS can be derived.

Other mammalian toxicity data for Benzo[a]pyrene from 90 days studies with mice resulted in higher NOAELs (Mackenzie and Angevine, 1981a). Whilst QS could be derived from these data in the usual way, the reprotoxicity data for Benzo[a]pyrene suggest that such a value might not be adequately protective and the ecological relevance of the adverse effect on which some of the NOAELs are based, might also be questionable.

Based on the available information $QS_{biota,\ sec.\ pois.}$ values for the individual PAHs can not be derived.

Secondary poisoning of top predators		**Master reference**
Mammalian oral toxicity	Mice / gavage during gestation LOEC = 10 mg.kg$^{-1}{}_{food}$	Mackenzie and Angevine, 1981b

Avian oral toxicity	No available information

Tentative $QS_{biota\ secpois}$	**Relevant study for derivation of QS**	**AF**	**Tentative QS**
Biota	No available information		

7.3 HUMAN HEALTH

Human health via consumption of fishery products				Master reference
Mammalian oral toxicity	Benzo[a]pyrene, Benzo[b]fluoranthene, Benzo[k]fluoranthene and Indeno[1,2,3-cd]pyrene are carcinogenic (cf. below). No test results usable as such are available for assessment purpose of possible effects to human *via* the consumption of fishery products for these carcinogenic substances. Benzo[g,h,i]perylene is a non carcinogenic substances (cf. below). Therefore, it is deemed acceptable to use a TDI. A RIVM report (Baars *et al.*, 2001) has used the TPHCWG method (TPHCWG, 1997) (1) to calculate a TPH fraction specific RfD for non carcinogenic PAHs, which is deemed applicable to benzo[g,h,i]perylene. The TL_{hh} proposed by RIVM is 0.03 $mg.kg^{-1}_{bw}.d^{-1}$			
CMR[13]	Carc.	Muta.	Repr.	
Benzo[a]pyrene	1B	1B	1B	E.C., 2008b
	1	-	-	IARC, 2009
	B2	-	-	EPA, 1986[14]
Benzo[b]fluoranthene	1B	nc	nc	E.C., 2008b
	2B	-	-	IARC, 2009
	B2	-	-	EPA, 1986[14]
Benzo[k]fluoranthene	1B	nc	nc	E.C., 2008b
	2B	-	-	IARC, 2009
	B2	-	-	EPA, 1986[14]
Benzo[g,h,i]perylene	nc	nc	nc	E.C., 2008b
	3	-	-	IARC, 2009
	nc	-	-	EPA, 1986[14]
Indeno[1,2,3-cd]pyrene	nc	nc	nc	E.C., 2008b
	2B	-	-	IARC, 2009
	B2	-	-	EPA, 1986[14]

For the four carcinogenic substances (Benzo[a]pyrene, Benzo[b]fluoranthene, Benzo[k]fluoranthene and Indeno[1,2,3-cd]pyrene), there are no test results available which are usable as such for assessment purpose of possible effects to human *via* the consumption of fishery products. However, Regulation 1881/2006/EC sets maximum levels for certain contaminants in foodstuffs. In Section 6 of its Annex, Polycyclic Aromatic Hydrocarbons are addressed and maximum levels are given for foodstuffs content of benzo[a]pyrene.

Maximum levels given for “fresh” (other than smoked) aquatic resources are the following:

- Fish: 2 $µg.kg^{-1}_{ww}$

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[13] nc: not classified; According to E.C., 2008b – Carc./Muta/Repr. 1B: presumed to have carcinogenic/mutagenic/reprotoxic effects; According to EPA, 1986 – Carc. B2: probable carcinogen; According to IARC, 2009 – 1: Carcinogenic to humans; 2B: Possibly carcinogenic to humans; 3: Not classifiable as to its carcinogenicity to humans.

[14] U.S. EPA. 1986. Guidelines for Carcinogen Risk Assessment. 51 FR 33992-34003

- Crustaceans and cephalopods: 5 $\mu g.kg^{-1}_{ww}$
- Bivalve molluscs: 10 $\mu g.kg^{-1}_{ww}$

As not other data are available up to date to assess protection of human health from consumption of fishery products containing 5-6 rings carcinogenic PAHs, it seems relevant to make use of these maximum levels to estimate a possible $QS_{biota, hh}$.

Footnote of the Regulation 1881/2006/EC Annex indicates that "Benzo(a)pyrene, for which maximum levels are listed, is used as a marker for the occurrence and effect of carcinogenic polycyclic aromatic hydrocarbons. These measures therefore provide full harmonisation on polycyclic aromatic hydrocarbons in the listed foods across the Member States."

Given that information, and the considerations raised in the introductory section of the present fact sheet, it is deemed relevant to use these maximum level in foodstuffs value for derivation of a $QS_{biota, hh}$ value for Benzo[a]pyrene.

For the back calculation of $QS_{biota, hh}$ into water, the BCF values of 57 981, 11 138 and 135 are used for mollusc, crustaceans and fish, respectively. BMF_1 and BMF_2 values are equal to 1 (cf. section 5.3).

Tentative $QS_{biota\ hh}$	**Relevant data for derivation of QS**	**AF**	**Threshold Level** (mg.kg$^{-1}_{ww}$)	**Tentative $QS_{biota, hh}$**
Human health	Maximum levels given for foodstuffs content of benzo[a]pyrene: - 0.002 mg.kg$^{-1}_{ww}$ for fish - 0.005 mg.kg$^{-1}_{ww}$ for crustaceans and cephalopods - 0.01 mg.kg$^{-1}_{ww}$ for molluscs			- fish: 2 $\mu g.kg^{-1}_{ww}$ corresponding to 0.015 $\mu g.l^{-1}$ - molluscs: 10 $\mu g.kg^{-1}_{ww}$ corresponding to 1.7 10^{-4} $\mu g.l^{-1}$ - crustaceans and cephalopods: 5 $\mu g.kg^{-1}_{ww}$ corresponding to 4.5 10^{-4} $\mu g.l^{-1}$
	-	-	B[g,h,i]perylene: TL_{hh} proposed by RIVM = 0.03 mg.kg$^{-1}_{ww}$	1 826 $\mu g.kg^{-1}_{ww}$ corresponding to 0.03 $\mu g.l^{-1}$ (using molluscs BCF) 13.5 $\mu g.l^{-1}$ (using fish BCF)

For corresponding values in water, the worst case values of 1.7 10^{-4} and 0.03 $\mu g.l^{-1}$ are retained for the carcinogenic substances and benzo[g,h,i]perylene, respectively. With benzo(a)pyrene as a marker for the 5 PAHs, the value of 1.7 10^{-4} $\mu g.l^{-1}$ should therefore be protective for all.

Human health via consumption of drinking water		**Master reference**
Existing drinking water standard(s)	0.1 $\mu g.l^{-1}$ for the sum of concentrations of: - benzo[b]fluoranthene, - benzo[k]fluoranthene, - benzo[ghi]perylene, - indeno[1,2,3-cd]pyrene.	Directive 98/83/EC
	0.01 $\mu g.l^{-1}$ for benzo[a]pyrene	

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