Annex XV report

PROPOSAL FOR IDENTIFICATION OF A SUBSTANCE OF VERY HIGH CONCERN ON THE BASIS OF THE CRITERIA SET OUT IN REACH ARTICLE 57

Substance Name: Phenanthrene

EC Number: 201-581-5

CAS Number: 85-01-8

Submitted by: FR-MSCA

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CONTENTS

TABLES

FOREWORD

Phenanthrene belongs to the substance group of Polycyclic Aromatic Hydrocarbons (PAHs) of which many are well-known to be hazardous for human health and the environment. Phenanthrene does not possess a harmonised classification according to the CLP Regulation (EC 1272/2008).

Until now, several Annex XV dossiers for the identification of substances of very high concern (SVHC) were explicitly based on the properties of PAHs as constituents of concern in the identified substances, such as Anthracene, Anthracene Oils, Coal Tar Pitch High Temperature (CTPHT), Benzo[a]pyrene, Benz[a]anthracene and Chrysene.

Phenanthrene is constituent, inter alia, in CTPHT. In the Support Document of CTPHT, it has been concluded by the Member State Committee (MSC) that phenanthrene fulfils the vPvB criteria of Annex XIII to the REACH Regulation (ECHA, 2009). However, phenanthrene and further PAHs whose properties have already been agreed on by the MSC in the CTPHT SVHC identification process have not yet been proposed for formal SVHC identification and inclusion in the Candidate List.

Phenanthrene was assessed with respect to vPvB properties based on the MSC Support Document for identification of CTPHT as SVHC (ECHA, 2009). For the purpose of the present SVHC proposal for phenanthrene, a supplementary literature search was made. The search identified only few studies not included in the EU Risk Assessment Report on CTPHT (European Commission, 2008) and the Annex XV Transitional Dossier on CTPHT (The Netherlands, 2008). Thus, the assessment of the vPvB properties in the present dossier and the conclusion that phenanthrene fulfils the criteria in Article 57 (e) was based mainly on the information in the MSC Support Document on CTPHT (ECHA, 2009) and supplemented with information from newer studies that are presented as further evidence as they do not trigger a need to modify the conclusions taken by authorities earlier on.

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- It is proposed to identify the substance as very persistent and very bioaccumulative (vPvB) according to Article 57 (e) of Regulation (EC) No 1907/2006 (REACH).

Summary of how the substance meets the criteria set out in Article 57 of the REACH Regulation

The assessment of the PvB properties in the present dossier and the conclusion that phenanthrene fulfils the criteria in Article 57 (e) were based mainly on the information in the MSC Support Document on CTPHT (ECHA, 2009) and supplemented with information from newer studies. All available information (such as the results of standard tests, modelling and (Q)SAR results) were considered together in a weight-of-evidence approach.

Persistence

The available experimental information show that phenanthrene degrades very slowly in soil with half-life greater than 180 d. The predicted half-lives for soils were between 125 to 420 days. Ultimately, a field study highlighted a half-life of phenanthrene of more than 5.7 years under field conditions.

Thus, the P and the vP criteria of REACH Annex XIII are fulfilled by phenanthrene.

Bioaccumulation

A substance fulfils the B criterion when the bioconcentration factor in aquatic species is greater than 2 000, and the vB criterion when the bioconcentration factor in aquatic species is greater than 5 000. The bioaccumulation of phenanthrene was measured in three studies with fish (BCFs ranging from 2 229 to 6 760 L/kg), two studies with crustacean (BCFs ranging from 5 513 to 28 145 L/kg), two studies with copepod (BCFs ranging from 5 252 to 71 077 L/kg) and one study with an oligochaete species (BCF = 5 222 L/kg). Thus, BCFs greater than 2 000 and 5 000 were obtained.

Thus, the B and the vB criteria of REACH Annex XIII are fulfilled by phenanthrene.

Overall conclusion:

In conclusion, phenanthrene meets the criteria for a vPvB substance according to Article 57 (e) of REACH by comparing all relevant and available information according to the criteria set out in the Annex XIII of REACH in a weight-of-evidence determination.

Registration dossiers submitted for the substance? No

PART I

Justification

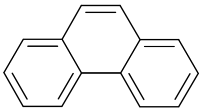
1. Identity of the substance and physical and chemical properties

1.1 Name and other identifiers of the substance

Table 1: Substance identity

EC number:	201-581-5
EC name:	Phenanthrene
CAS number (in the EC inventory):	85-01-8
CAS number: Deleted CAS numbers:	
CAS name:	Phenanthrene
IUPAC name:	Phenanthrene
Index number in Annex VI of the CLP Regulation	No harmonised classification
Molecular formula:	$C_{14}H_{10}$
Molecular weight range:	178.229 g.mol^{-1}
Synonyms:	*o*-diphenyleneethylene, phenanthren, phenanthrin

Structural formula:



1.2 Composition of the substance

Name: Phenanthrene

Description: Phenanthrene belongs to the group of Polycyclic Aromatic Hydrocarbons (PAHs). Phenanthrene is not produced intentionally but does occur as a constituent in UVCB[1] – often together with other PAHs - mainly derived from the coal and petroleum stream. The dossier addresses the substance phenanthrene as a substance itself.

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[1] Substances of Unknown or Variable composition, Complex reaction products or Biological materials

Substance type: mono-constituent

1.3 Physicochemical properties

Table 2: Overview of physicochemical properties

Property	Value [Unit]	Reference/source of information
Physical state at 20°C and 101.3 kPa	solid	INERIS, 2010
Melting/freezing point	100.5 °C	ECHA, 2009
Boiling point	340°C	ECHA, 2009
Vapour pressure	2.6 x 10^{-2} Pa at 25°C	ECHA, 2009
Density	0.980 Kg.L^{-1} at 20°C	ECHA, 2009
Water solubility	0.95 mg.L^{-1} at 24°C	ECHA, 2009
Partition coefficient n-octanol/water (Log value)	4.57 at 25°C	ECHA, 2009
Henry's constant	3.7 Pa m^3/mol at 25 °C	ECHA, 2009

2. Harmonised classification and labelling

No harmonised classification for phenanthrene.

3. Environmental fate properties

3.1 Degradation

The data provided on the degradation of phenanthrene in the Support Document for identification of CTPHT as SVHC (ECHA, 2009) are not assessed or discussed again in this dossier but included in order to have access to the full dataset for assessment (flagged by *italic print*). Additional information is available in the EU risk assessment report on CTPHT (EC, 2008) and the Annex XV Transitional Dossier for CTPHT (The Netherlands, 2008). When more recent data were identified, they have been included in the document and cited accordingly.

3.1.1 Abiotic degradation

3.1.1.1 Hydrolysis

As assessed before in the Support Document for identification of CTPHT as SVHC (ECHA, 2009), phenanthrene does not present functional groups that result in hydrolysis and is therefore expected to be *hydrolytically stable in aquatic systems*. The Support Document furthermore states as a result that *hydrolysis is not expected to contribute to the degradation of PAHs under environmental conditions.*

3.1.1.2 Oxidation

The oxidation of PAHs was assessed in the Annex XV Transitional Dossier for CTPHT (the Netherlands, 2008), and summarised and discussed in the Support Document for identification of CTPHT as SVHC (ECHA, 2009) as follows:

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 oxidised 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). Phenanthrene has 3 aromatic rings and a reported vapour pressure of 2.6 x 10^{-2} Pa at 25°C, which is higher than 10^{-4} Pa. Therefore, it is assumed that phenanthrene is mainly in the gas phase and is degraded mainly by oxidisation and, to a lesser extent, by photolysis. In the gas phase, phenanthrene can undergo oxidation in the presence of OH radicals exhibiting short lifetimes between a few hours to less than two days (ECHA, 2009).

In the atmosphere, phenanthrene can be partitioned in the gas phase and also adsorbed to the particle phase. Among the semi-volatile PAHs, phenanthrene is mainly in the gas phase but a small fraction (up to 12.4%) can be found adsorbed onto particles which reduces the degradation rate due to stabilisation of PAHs (ECHA, 2009). In the atmosphere, phenanthrene reacts with OH radicals and undergoes “alkene-like” reactions with NO_3 or O_3 radicals (Atkinson, 1994). Nevertheless, “alkene-like” reactions are highly variable because NO_3 radical concentrations are very fluctuant due to the fact that their formation requires the presence of both O_3 and NO_2. Furthermore, the NO_3 radical reaction is only a night-time loss process because the NO_3 radical rapidly photolyses. The “alkene-like” reaction that phenanthrene can undergo also contributes to its oxidation in the atmosphere.

3.1.1.3 Phototransformation/photolysis

3.1.1.3.1 Phototransformation in air

Photololysis of PAHs in the atmosphere was already assessed in the EU risk assessment report (2008) and summarised in the Support Document for identification of CTPHT as SVHC (ECHA, 2009) and in the Annex XV Transitional Dossier for CTPHT (The Netherlands, 2008) as follows:

Photolysis in the troposphere results in the formation of reactive hydroxyl (OH) and nitrate (NO_3) *radicals and ozone* (O_3)*, which reacts as oxidizing agent with organic compounds, like PAHs. These radical and ozone reactions comprise mainly degradation of gas-phase PAHs (Calvert et al., 2002). Particle-associated PAHs are expected to degrade in air predominantly via direct photolysis by light with a wavelength < 290 nm (Kamens et al., 1988), although reaction with ozone will also occur (Peters and Seifert, 1980; Grosjean et al., 1983; Pitts et al., 1986; Coutant et al., 1988).*

As stated earlier, phenanthrene in the air is mainly in the gas phase and undergoes oxidisation. The small amount of phenanthrene that is particle-associated undergoes photolysis, with a reaction rate dependent on the type of particle.

3.1.1.3.2 Phototransformation in water

As assessed before in the Support Document for identification of CTPHT as SVHC (ECHA, 2009), *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.* Therefore, aquatic photodegradation is not considered to have a significant impact on the overall persistency of phenanthrene in the environment.

3.1.1.3.3 Phototransformation in soil

As assessed before in the Support Document for identification of CTPHT as SVHC (ECHA, 2009), *as exposure to light is even more limited in soils, photodegradation is as well not considered a relevant degradation process in terrestrial environments.* Thus, photodegradation is not considered a relevant degradation process in soils.

3.1.1.4 Summary on abiotic degradation

It is concluded that in the atmosphere, free PAHs degrade within a range of minutes to days by direct photolysis. The action of an oxidant on phenanthrene is also an important path for its degradation. A very small part of phenanthrene (12.4%) may be particle-associated and when adsorbed onto fine particles, phenanthrene may be more stable in the atmosphere. In water, phenanthrene is not hydrolysed but can be photo-degraded. However, this only appears at the upper few centimetres of a water-column and is therefore not considered having a significant impact on the overall persistence of phenanthrene in the aquatic environment. In soil, exposure to light is even more limited. Thus, photodegradation is not considered as relevant degradation process in water and terrestrial environments. Phenanthrene is hydrolytically stable under environmental conditions.

This conclusion was already drawn in the Support Document for identification of CTPHT as SVHC (ECHA, 2009).

3.1.2 Biodegradation

3.1.2.1 Biodegradation in water and sediments

Regarding the biodegradation in water, as assessed in the Support Document for identification of CTPHT as SVHC (ECHA, 2009):

Experimental information for biodegradation in water has demonstrated that PAH substances with up to four aromatic rings are biodegradable under aerobic conditions, but that biodegradation rates of PAHs with more than four 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). […]

The results from standard tests for biodegradation in water show that PAHs 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 (ECHA, 2009). Regarding biodegradation on sediments, although there is evidence for anaerobic transformation, PAHs are usually considered to be persistent under anaerobic conditions (Neff, 1979; Volkering & Breure, 2003, cited in The Netherlands, 2008), thus a low biodegradation of phenanthrene is expected in sediments.

Although the biodegradation pathway of the different PAHs is very similar, their biodegradation rates differ considerably. In general, the biodegradation rates decreases with increasing number of aromatic rings. Biodegradation rates also are extremely dependent on the (a)biotic 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 PAHs appears to decrease with increase of the residence time of PAHs due to slow sorption onto micropores and organic matter, and polymerisation 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).

As assessed in the Support Document for identification of CTPHT as SVHC (ECHA, 2009) *Mackay et al. (1992) estimated half-lives in the different environmental compartments based on model calculations and literature research. The calculated half-lives of phenanthrene in water and sediments are in the range of 12 to 42 days and longer than 420 to 1250 days respectively*.

In a 28 day ready biodegradability test (MITI I, OECD 301C) using 100 mg/L PAHs and 30 mg/L sludge, phenanthrene did not fulfil the criteria to be considered as readily biodegradable (54% degradation after 4 weeks), similarly to fluorene, carbazole, acenaphthene and dibenzofuran. According to the MITI test, which is suitable for substances with low water solubility, these PAHs are not readily biodegradable (ECHA, 2009).

In a microcosm study (Bahr et al., 2015), the biodegradation of four PAHs (naphthalene, fluorene, phenanthrene, and acenaphthene added as ^{13}C-labelled substrates) was investigated in groundwater (pH around 7) from an aquifer located at the site of a former gas plant with oxic conditions. ^{13}C-enrichment of the produced CO_2 revealed mineralisation of phenanthrene comprised between 14.2% and 33.1% over a period of 62 days of incubation in the dark at 14°C, in order to approximate field conditions. This study used a BACTRAP® system (composed of activated carbon pellets) that allowed trapping a bacterial community already present in the aquifer by the system for 100 days. In this experiment, the percentage of dissolved oxygen was always recorded to ensure a minimum of 1% content in order to maintain an oxic condition representative of the *in-situ* conditions. The use of an adapted bacterial community may lead to an overestimation of the mineralisation rate in comparison to the situation arising in other aquifer. This study highlighted that phenanthrene degradation was slow in oxic aquifer and possibly persistent. Biodegradation was possible but needed the presence of an adapted bacterial community of sufficient density to achieve mineralisation over a long period of time (100 days of colonisation plus 62 days of exposure to reach 33% of mineralisation).

3.1.2.2 Biodegradation in soil

Biodegradation in soil was assessed in the Support Document for identification of CTPHT as SVHC (ECHA, 2009) as follows:

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 ([...] 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.

Mackay *et al*. (1992) as summarised by The Netherlands (2008) suggested a half-life for phenanthrene in the range of 125 to 420 days in soil. These predictions are in line with half-lives observed under laboratory conditions.

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. They determined a dissipation half-life for phenanthrene of 83 to 193 days in laboratory soil microcosms (three soil types: sandy loams, forest soil, and roadside soil conducted at a range of temperature between 20 and 30°C) and, under field conditions, a half-life of 5.7 years.

Mineralisation of ^{14}C-phenanthrene was investigated with the indigenous microbial communities present in five pristine soils of Livingstone Island, one of the South Shetland Islands separated from the Antarctica Peninsula by the Bransfield Strait. The temperature rarely exceeded 3°C in summer and decreased to -11°C in winter. Mineralisation of ^{14}C-phenanthrene was investigated using respirometric assay at different temperature (4°, 12°, 22°C) and under slurry condition (22°C + Mineral Basal Salt (MBS) medium) in the dark for 35 days. Briefly, 10g of soils were rehydrated to 40-60% water holding capacity and spiked with unlabelled and labelled ^{14}C-phenanthrene. The latter condition (slurry) was not considered due to the adjunction of MBS who improved the bacterial growth, dispersion, accessibility and enhanced phenanthrene bioavailability. The maximum extent of mineralisation of ^{14}C-phenanthrene was 1.14% at 4°C for 35 days, indicating that, in natural temperature conditions of Livingstone Island, phenanthrene mineralisation is extremely slow and may even not occur. At 12°C, maximum mineralisation extent was 35.15 % and 39.09% at 22°C indicating that phenanthrene degradation was limited, which was consistent with the plateau in degradation reached in soil 4 and 5. At 4 and 12 °C, degradation did not start after 35 days of incubation: it was reflected by lag phases (time to reach 5% mineralisation) that were not reached in the 5 soils at 4°C and 3 soils at 12°C and even 2 soils at 22°C. This study supports claims that phenanthrene does not biodegrade in this type of soil and under these conditions (Okere *et al.*, 2012).

In 2017, the same research group evaluated the biodegradation of phenanthrene in the same Antarctic soils over 150 days and at various temperatures. Briefly, 50g of soils were spiked with ^{12}C-phenanthrene and then mixed with 200g of non-spiked soils to avoid adverse effects to bacterial community. Then soils were left incubated in the dark at 4°, 12° and 22°C for 1, 30, 60 and 150 days. These soils were used to determine the catabolic activity of indigenous bacterial community exposed to ^{14}C-phenanthrene using respirometric assay at different temperature (4°, 12°, 22°C) and under slurry condition (22°C + Mineral Basal Salt (MBS) medium). As detailed before, the latter condition was not considered. In the set-up, 10g of soils were rehydrated to 40-60% water holding capacity and spiked with ^{12}C-phenanthrene (>99.6%) and ^{14}C-phenanthrene. The respirometers were stored in the dark, incubated at temperatures set for pre-exposition of the soils for 21 days. The lag phase for bacterial growth (time to reach 5% mineralisation) was never reach for the soils incubated at 4°C, was reach in 4/20 (2 for 60 days of contact and 2 for 150 days of contact) at 12°C and in 6/20 at 22°C (3 for 60 days of contact and 3 for 150 days of contact). At 4°C, the maximum extent of mineralisation of ^{14}C-phenanthrene was 0.46% for 1 day contact soil. At 12°C, the maximum extent of mineralisation of ^{14}C-phenanthrene was 12.21% for 60 day contact soil and was greater than 1% in only 5/20 conditions (2 for 60 days of contact and 3 for 150 days of contact). At 22°C, the maximum extent of mineralisation of ^{14}C-phenanthrene was 24.82% and was greater than 5% in only 6/20 conditions (3 for 60 days of contact and 3 for 150 days of contact). This study highlighted the fact that in soil with poor organic matter content, adsorption of phenanthrene will occur on mineral surfaces, reducing its bioavailability. When increasing temperature and exposure duration, the mineralisation of phenanthrene increases. Nevertheless, in natural conditions that can be found on Livingstone Island, no biodegradation of phenanthrene was observed, indicating that phenanthrene will remain over a long period of time in the environment. Moreover, when the contact time between phenanthrene and soils was increased, the maximum amounts of phenanthrene available for biodegradation was decreased. This was reflected by the plateau of 7% reached at 12°C after 150 days of pre-exposure indicating that soil could accumulate phenanthrene due to ageing (increase in contact time) (Okere *et al.*, 2017).

A microcosm study evaluated a phenanthrene-contaminated Patagonian soil (Pico Truncado, Patagonia, Argentina), maintained under arid conditions and incubated at 20 ± 2°C for 250 days. No biodegradation of phenanthrene measured as primary degradation was observed for 150 days, and this, even with the adjunction of fertilisers at day 86 of treatment, where the microcosms were fertilised with 7.45 g kg^{-1} dry soil of commercial fertiliser Nitrofoska® (BASF, Research Triangle Park, NC), taking the relation C/N/P to 100:5:2. The lack of biodegradation was observed with and without bioaugmentation (adjunction of *Sphingobium sp.* strain 22B, a PAH-degrading strain), indicating that phenanthrene is recalcitrant to biodegradation under arid conditions. After day 150, the water content of soil was increased from 10 % to 15%, drastically increasing the biodegradation of phenanthrene, from no degradation of phenanthrene (day 150) to 98% degradation of the added phenanthrene at the end of the experiment (day 210) (Madueño, Alvarez, and Morelli, 2015).

Furthermore the Support Document for identification of CTPHT as SVHC (ECHA, 2009) discusses "aging" for PAHs as follows:

"'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."

3.1.2.4 Summary and discussion on biodegradation

Regarding water and sediment, Mackay et *al.* (1992) indicated that predicted phenanthrene elimination half-lives ranged between 13 and 42 days and that the substance persisted in sediment with half-lives between 420 to 1250 days. The available ready biodegradability test highlighted that phenanthrene was not ready biodegradable. Nevertheless, considering the chemical structure of phenanthrene that consists of three aromatic rings, standard tests for biodegradation in water demonstrated that phenanthrene biodegradation was possible under aerobic conditions. A microcosm study highlighted that under acidic conditions, at 14°C, mineralisation of phenanthrene could be long, reaching 33% after 62 days and was depending on the presence of an adapted microbial community. Overall, it is concluded that phenanthrene is persistent and very persistent in sediment.

For soil, Mackay et *al.* (1992) indicated that phenanthrene persisted with half-lives between 125 to 420 days. Moreover, laboratory biodegradation studies with soil microcosms showed half-lives ranging between 83 to 193 days (Wild and Jones, 1993). In a microcosm study it was demonstrated that no biodegradation of phenanthrene was observed for 150 days, even with the adjunction of fertilisers and with and without bioaugmentation, indicating that phenanthrene was unlikely to biodegrade under arid conditions (Madueño, Alvarez, and Morelli, 2015). In Antarctic soils, it was demonstrated that no biodegradation occurred at 4°C after 21 or 35 days, respectively. It was demonstrated that increasing temperature enhanced biodegradation but never allowed reaching a sufficient mineralisation level. Moreover, increased contact time (from 1 to 150 days) between soil and phenanthrene decreased its bioavailability by increasing its sequestration into the soils (Okere et al., 2012 and 2017). Finally, biodegradation studies on soil done by Wild *et al.* (1991) demonstrated a phenanthrene half-life of more than 5.7 years under field conditions.

Hence, phenanthrene biodegrades very slowly in soil and field conditions, with different parameters impacting the biodegradation process.

This conclusion was already drawn in the Support Document for identification of CTPHT as SVHC (ECHA, 2009).

3.1.3 Summary and discussion on degradation

In the atmosphere, phenanthrene can be partitioned in the gas phase and, to a fewer extent, also be adsorbed to particulates. Degradation in the gas phase by oxidation in the presence of OH radicals takes place between a few hours to less than two days.

In the water and soil compartments, photolysis is only relevant in the upper few centimeters of the water column and the upper few millimeters of the soil. Thus, photodegradation is not considered as a relevant degradation process in water and terrestrial environments.

In general, PAHs have no functional groups that result in hydrolysis in the water and soil compartments. Therefore, phenanthrene is considered as hydrolytically stable.

Phenanthrene has a low water solubility and shows a high tendency to adsorb to particles and organic matter in the environment due to its Log Kow value of 4.6 (4.57) and Log Koc of 4.36 L/Kg. The resulting low bioavailability is one of the limiting factors of its biodegradation.

The predicted half-lives range between 13 to 42 days for degradation in water and between 420 to 1250 days for sediment. Wild and Jones (1993) reported a dissipation half-life for phenanthrene of 83 to 193 days in a laboratory soil microcosm study. Under field conditions, Wild *et al*. (1991) demonstrated a half-life of more than 5.7 years in soil for phenanthrene.

3.2 Environmental distribution

3.2.1 Adsorption/desorption

In the Support Document for identification of CTPHT as SVHC (ECHA, 2009) the adsorption properties of PAHs are described as follows: "*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)."

Based on the Log K_{ow} of 4.57 for phenanthrene, reported in the Annex XV Transitional Dossier on CTPHT (The Netherlands, 2008), the coefficient of partitioning between organic carbon and water, Log K_{oc}, has been estimated at 4.36 (The Netherlands, 2008) and it is concluded that phenanthrene has a high potential to adsorb to particles in the environment.

3.2.2 Volatilisation

Phenanthrene has a reported vapour pressure of 2.6×10^{-2} Pa at 25°C and a Henry's law constant of 3.7 Pa m^3/mol at 25°C (Mackay et al., 2006, cited by The Netherlands, 2008). Thus, some volatilisation is expected from water or soil surfaces.

3.2.3 Distribution modelling

Mackay Level III fugacity modelling was done using EPI Suite (version 4.11) with default values of environmental emission rates (it is assumed that phenanthrene is released at equal rates to air, water, soil and sediment) (computations done in April 2018). The calculations revealed a distribution of phenanthrene almost exclusively to soil and a small part to sediment and water phases (Table 3).

Table 3: Fugacity Model calculation (EPI Suite, version 4.11) of phenanthrene

Distribution to:	Mass amount (percent)
Air	0.484
Water	9.75
Soil	77.3
Sediment	12.4

3.2.4 Summary and discussion of environmental distribution

Phenanthrene exhibits a high potential to adsorb to organic matter and some volatilisation from soil and water is expected. Furthermore, according to the fugacity model, phenanthrene is expected to be mainly distributed in the soil compartment followed by the sediment and water compartment. The air compartment is not expected to be a relevant route of distribution.

3.3 Bioaccumulation

3.3.1 Bioaccumulation in aquatic organisms (pelagic & sediment organisms)

Experimental studies were available to determine the BCF of phenanthrene in different organisms. They were considered in the Support Document for the identification of CTPHT as SVHC (ECHA, 2009) and reassessed later by the RIVM (Bleeker and Verbruggen, 2009) and completed with a literature search (April 2018). When bioaccumulation data have been reassessed by the RIVM, these are used in preference to the CTPHT data. When more recent supporting data was identified, they were included in the current document and cited accordingly.

BCF values were reported above 2 000 L/kg for sheepshead minnows (*Cyprinodon variegatus* exposed to phenanthrene during 36 days in continuous flow system followed by 8 days of depuration *providing a BCF of* 2 229 L/kg) and fathead minnows (*Pimephales promelas*; BCF_K: 3 611 L/kg). The BCF value obtained with fathead minnows (*Pimephales promelas*; BCF_K: 3 611 L/kg) was reassessed and normalised with a 5% lipid content, providing a BCF value (4 751 L/kg) close to the 5 000 L/kg threshold for vB criteria. For fathead minnows, the study realised by De Maagd and colleagues (De Maagd *et al*., 1996) was used in the European Union Risk Assessment Report on CTPHT (EC, 2008) and provided a BCF value of 6 760 L/kg. However, after reassessing this study, it was concluded that this study cannot any longer be rated as reliability index of 2 but 3 (namely, unreliable) due to uncertainties in the determination method. It was stated by the RIVM that the results from De Maagd (1996) should be considered with care, but are still important as circumstantial evidence in a weight of evidence approach to decide on the bioaccumulation potential of the studies PAHs (Bleeker and Verbruggen, 2009).

Nevertheless, another study is available with phenanthrene providing a final equilibrium BCF value of 5 100 L/kg considered as reliable with restriction (Bleeker and Verbruggen, 2009). In this study, *Fathead minnows* were exposed to a series of PAHs present in lake water, via flow through conditions for 28 days followed by 5 days of depuration (Carlson et al., 1979).

In molluscs phenanthrene accumulates, but BCF levels remain below 2 000 L/kg (maximum: 1 280 L/kg). In crustaceans, two studies provided very high BCF values. Landrum *et al*., 2003, conducted a static renewal experiment of toxicity and bioaccumulation with the amphipod *Diporeia spp.* exposed to a range of concentrations of ^{14}C PAHs (from 57.1 to 637.8 µg/L of phenanthrene) for 28 days. The authors determined BCF values for phenanthrene by kinetic approach ranging from 5 513 to 11 440 L/kg (8 889 L/kg) for the tested concentrations. The second one was determined in flow-through systems by the kinetic method with the amphipod *Pontoporeia hoyi* exposed to selected ^{14}C radiolabelled PAHs during 6 hours followed by 14 days of depuration phase. This study provided a BCF value of 28 145 L/kg. The two studies were considered as reliable with restriction and reliable without restriction respectively.

In oligochaete *Stylodrilus heringianus*, a flow-through experiment using the kinetic method rated as reliable with restriction provided a BCF value of 5 222 L/kg (Frank *et al*., 1986, as cited in Bleeker and Verbruggen, 2009).

Regarding *copepods*, a laboratory experiment in *Calanus finmarchicus* conducted a BCF determination in a 192 h semi-static daily renewal exposure with ^{14}C-labeled phenanthrene followed by a 96 h depuration time. Phenanthrene accumulated rapidly, reaching steady state within 96 h and providing, at the end of depuration step, a lipid normalised BCF (with the kinetic method) of 5 252 L/kg (Jensen *et al*., 2012). In a more recent study, BCF determination with the kinetic methodology on arctic copepod species *Calanus hyperboreus* for 4 days of uptake and 3 days depuration provided BCF values ranging from 40 330 to 71 077 L/kg depending on the copepod developmental stage. (Agersted *et al*., 2018).

For insects (*Hexagenia limbata*), BCFs clearly depend on lipid content of the organism, and may reach values as high as 5 697 L/kg.

3.3.2 Bioaccumulation in terrestrial organisms (soil dwelling organisms, vertebrates)

The European Union Risk Assessment Report on CTPHT (EC, 2008) estimated BCF values on earthworm for several PAHs according to the equilibrium portioning approach (EP). For phenanthrene, it was estimated a BCF earthworm of 450 L/kg. This value represents a reasonable worst case (EC, 2008).

3.3.3 Field data

Trophic magnification studies are available for phenanthrene. In the study of Wan *et al*., 2007, not mentioned in the CTPHT Support Document, PAHs concentrations in phytoplankton/seston, zooplankton, invertebrates, fish and one seabird species collected from Bohai Bay on the north of China were analysed. The trophic magnification factor (TMF) calculated for phenanthrene was 0.43. Another study of Nfon *et al*., 2008, calculated a TMF of 0.82 (0.73–0.92) for phenanthrene, referring to a study conducted in a benthic and pelagic food chain from the Baltic Sea. The species of the food chain analysed included pelagic species of phytoplankton, zooplankton and several benthic species. A study investigated the bioaccumulation and biomagnification of PAHs by analyzing 11 finfish species and the blue crab, *Callinectes sapidus*, collected from the fresh-brackish portion of the Passaic River. For phenanthrene, a TMF of 0.34 was calculated (Khairy, Weinstein, and R. Lohmann *et al*., 2014).

The study conducted by Wang (Wang *et al*., 2012) reported estimated TMF values for several PAHs, based on the analysis of several fish species with different feeding behaviours (herbivorous, omnivorous and carnivorus) collected on Taihu Lake in China. A TMF of 1.27 was calculated for phenanthrene, suggesting biomagnification of the chemical through the food chain.

It is mentioned in the chapter R.11 of the ECHA guidance on PBT or vPvB that the results from field studies should be considered as part of the overall evaluation of the bioaccumulation properties of a substance. However, currently there is no consensus about standard methodologies and guidelines for the interpretation of such results, generating uncertainties for the interpretation of those results. In particular, temporal and spatial variability or the inclusion/exclusion of a few or even a single species could affect the outcome of the TMFs. Thus, the data treatment could have a deep impact on the TMF values that were calculated. Ultimately, chapter R.11 of the ECHA guidance on PBT or vPvB indicates that the absence of a biomagnification potential cannot be used on its own to conclude that the B or vB criteria are not fulfilled.

3.3.4 Summary and discussion of bioaccumulation

The bioaccumulation potential of phenanthrene differs between the organisms due to their capacity to metabolise (biotransform) PAHs. It is likely that phenanthrene is transformed in fish using enzymes belonging to the Cytochrome P450 enzymes (Cyt P450) and other mechanisms, resulting in low BCF values. However, invertebrate species may have a lower metabolic capacity than fish species, e.g. as is the case for polycyclic aromatic hydrocarbons (Bleeker and Verbruggen, 2009). Bioaccumulation in these invertebrates may therefore be higher than in fish under the same exposure conditions and this situation should be considered in a Weight-of-Evidence approach.

The bioaccumulation of phenanthrene was measured in fish (BCFs of 2 229 to 6 760 L/kg), crustacean (BCFs of 5 513 to 28145 L/kg), copepod (BCFs of 5 252 to 71 077 L/kg) and oligochaete (BCF of 5 222 L/kg). Thus, the BCFs values were higher than 2000 and 5000.

4. Human health hazard assessment

Not relevant for the identification of the substance as SVHC in accordance with Article 57 point (e) of REACH.

5. Environmental hazard assessment

Not relevant for the identification of the substance as SVHC in accordance with Article 57 point (e) of REACH. Information related to the T criterion of Article 57 (d) of REACH is presented in Annex I as additional information.

6. Conclusions on the SVHC Properties

6.1 CMR assessment

This section is not relevant for the identification of the substance phenanthrene as SVHC in accordance with Article 57 (e).

6.2 PBT and vPvB assessment

6.2.1 Assessment of PBT/vPvB properties

An assessment of the vPvB properties of phenanthrene has already been carried out by the MSC in the context of the identification of CTPHT as SVHC, as documented in the MSC Support Document for identification of CTPHT as SVHC (ECHA, 2009). Additional information was assessed earlier in the EU Risk Assessment Report on CTPHT (European Commission, 2008) and the Annex XV Transitional Dossier on CTPHT (NL, 2008). Moreover, a recent literature search (performed up to April 2018) did not highlight any such new data which would provide contradicting evidence. Both the assessment reports and the more recent literature search support the conclusions on the vPvB properties of phenanthrene, as already drawn in the MSC Support Document on CTPHT.

6.2.1.1 Persistence

Phenanthrene has low water solubility and shows a high tendency to adsorb to particles and organic matter in the environment. The resulting low bioavailability is one of the limiting factors of its biodegradation.

Regarding water and sediment, Mackay et *al.* (1992) indicated that predicted phenanthrene elimination half-lives range between 13 and 42 days and it persists in sediment with half-lives comprised between 420 to 1250 days. The ready biodegradability test available highlighted that phenanthrene is not readily biodegraded. Nevertheless, considering the chemical structure of phenanthrene that consists of three aromatic rings, standard tests for biodegradation in water demonstrated that phenanthrene biodegradation is possible under aerobic conditions. A microcosm study highlighted that under oxic condition, at 14°C, mineralisation of phenanthrene can be long, reaching 33% after 62 days and depending on the presence of an adapted microbial community. Overall, it is concluded that phenanthrene is persistent and very persistent in sediment.

For soil, Mackay et *al.* (1992) indicated that phenanthrene persists with half-lives comprised between 125 to 420 days. Moreover, biodegradation studies in laboratory soil microcosms showed half-lives ranging between 83 to 193 days (Wild and Jones, 1993). In a microcosm study it was demonstrated that no biodegradation of phenanthrene was observed for 150 days even with the adjunction of fertilisers and with and without bioaugmentation, indicating that phenanthrene did not biodegrade under arid conditions (Madueño, Alvarez, and Morelli, 2015). In Antarctic soils, it was demonstrated that no biodegradation occur at 4°C after neither 21 nor 35 days. It was demonstrated that increasing temperature enhanced biodegradation but never allowing reaching sufficient mineralisation. Moreover, increasing contact time (from 1 to 150 days) between soil and phenanthrene decreased its bioavailability by increasing its sequestration into the soils (Okere *et al*., 2012 and 2017). Finally, biodegradation studies on soil carried out by Wild *et al.* (1991) demonstrated a half-life of phenanthrene of more than 5.7 years under field conditions. Overall, it is concluded that phenanthrene is persistent and very persistent in soils.

Therefore it is concluded that phenanthrene fulfils the P and vP criteria for soil according to REACH Annex XIII. This conclusion was already drawn by the MSC in the context of the identification of CTPHT as SVHC (ECHA, 2009). New data retrieved in the literature search done in April 2018 did not challenge the previous conclusion.

6.2.1.2 Bioaccumulation

Experimentally obtained BCF values > 2 000 and 5 000 are reported with phenanthrene in fish (2 229 to 6 760 L/kg), crustacean (5 513 to 28 145 L/kg), copepod (5 252 to 71 077 L/kg) and oligochaete (5 222 L/kg). In accordance to REACH Annex XIII, phenanthrene fulfils the B and vB criteria. This conclusion was already drawn by the MSC in the context of the identification of CTPHT as SVHC (ECHA, 2009). New data retrieved in the literature search done in April 2018 have been included in the current report and did not challenge the previous conclusion.

6.2.2 Summary and overall conclusions on the PBT and vPvB properties

The assessment of the PvB properties in the present dossier and the conclusion that phenanthrene fulfils the criteria in Article 57 (e) were based mainly on the information in the MSC Support Document on CTPHT (ECHA, 2009) and supplemented with information from newer studies. All available information (such as the results of standard tests, modelling and (Q)SAR results) were considered together in a weight-of-evidence approach.

Persistence

The available experimental information shows that phenanthrene degrades very slowly in soil with half-life greater than 180 d. The predicted half-lives for soils were between 125 to 420 days. Ultimately, a field study highlighted a half-life of phenanthrene of more than 5.7 years under field conditions.

Thus, the P and the vP criteria of REACH Annex XIII are fulfilled by phenanthrene.

Bioaccumulation

A substance fulfils the B criterion when the bioconcentration factor in aquatic species is greater than 2 000, and the vB criterion when the bioconcentration factor in aquatic species is greater than 5 000. The bioaccumulation of phenanthrene was measured in three studies with fish (BCFs ranging from 2 229 to 6 760 L/kg), two studies with crustacean (BCFs ranging from 5 513 to 28 145 L/kg), two studies with copepod (BCFs ranging from 5 252 to 71 077 L/kg) and one study with an oligochaete species (BCF = 5 222 L/kg). Thus, BCFs greater than 2 000 and 5 000 were obtained.

Thus, the B and the vB criteria of REACH Annex XIII are fulfilled by phenanthrene.

Overall conclusion:
In conclusion, phenanthrene meets the criteria for a vPvB substance according to Article 57 (e) of REACH by comparing all relevant and available information according to the criteria set out in the Annex XIII of REACH in a weight-of-evidence determination.

6.3 Assessment under Article 57(f)

This section is not relevant for the identification of the substance phenanthrene as SVHC in accordance with Article 57 (e) of REACH.

Part II

7. Registration and C&L notification status

7.1 Registration status

Phenanthrene is not produced intentionally and is not registered under REACH.

7.2 CLP notification status

Table 4: CLP notifications

	CLP Notifications[2]
Number of aggregated notifications	13
Total number of notifiers	439

8. Total tonnage of the substance

Phenanthrene is not produced intentionally and is not registered under REACH. In general, PAHs occur as constituents in substances from the coal and petroleum stream. Such substances are mostly well-defined Multi-Constituent Substances (MCSs) or Substances of Unknown or Variable composition, Complex reaction products or Biological materials (UVCB substances).

9. Information on uses of the substance

There are numerous UVCB petroleum and coal stream substances that contain PAHs in variable concentrations, including phenanthrene. Among these PAH-containing petroleum substances, some have wide dispersive uses. Among the reported uses are: Uses in Coatings and paints, uses in road and construction application, in binders or release agents, uses in lubricants, in cleaning agents (BAUA, 2017). Those uses can lead to significant environmental releases.

Information on tonnage per identified use for the substance is limited. The use pattern of “Pitch, coal tar, high-temp” (CAS: 65996-93-2) was analysed and discussed in detail in the Risk Assessment Report of CTHPH (EC, 2008). It is reported that CTPHT is mainly used as a binding agent for anodes and electrodes. Taking the use as binding agent for refractory materials into account, these applications covered 94 % of the sales in the EU in 2003.

10. Information on structure of the supply chain

The structure of the supply chain and downstream users is complex. The primary producers of UVCBs containing phenanthrene are organised in industry consortia like

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[2] C&L Inventory database, https://echa.europa.eu/fr/information-on-chemicals/cl-inventory-database/-/discli/details/109754 (accessed 11 July 2018). The following hazard classes are listed in the different notifications: Skin irritation, Eye irritation, Respiratory irritation, Acute toxicity, Carcinogenicity, Aquatic Acute toxicity, Aquatic Chronic toxicity.

CONCAWE[3], Cefic[4], LOA[5] and others. According to information from an industry sector organisation the knowledge of uses decreases with the increase in the level of downstream uses.

11. Additional information

11.1 Substances with similar hazard and use profiles on the Candidate List

Phenanthrene is not produced intentionally but occurs together with other PAHs as constituent of coal and petroleum stream UVCB substances. Among the PAHs benzo[a]pyrene (B[a]P, EC number: 200-028-5), chrysene (EC number 205-923-4), benz[a]anthracene (B[a]A, EC number 200-280-6) and anthracene (EC number: 204-371-1) are included in the Candidate List due to PBT and vPvB properties already.

Further UVCBs like CTPHT (EC number: 266-028-2) and five anthracene oil-derivatives (EC numbers: 292-604-8, 295-278-5, 295-275-9, 292-603-2, and 292-602-7) are listed in the Candidate List due to assessment of the intrinsic properties of its PAH constituents. Phenanthrene was one of its constituents which lead the inclusion of CTPH into the Candidate List based on its vPvB properties.

11.2 Alternatives

It is possible to considerably decrease the PAH content of UVCB substances derived from coal or mineral oil (see for example use of low aromatic oils in tires, KEMI, 2003). Furthermore, there seems to be no unique, essential technical function of PAHs in PAH-containing UVCB substances in most cases. Currently, in most of the cases, alternatives to PAH-containing substances seem to be available, e.g. for binding material used in certain electrodes in the aluminium production.

It is important to stress that the complete picture of uses of phenanthrene-containing UVCB
substances remains unclear as it is not possible to identify all of these substances themselves. Further regulatory actions on these substances might be warranted in the future.

11.3 Existing EU legislation

Phenanthrene has no harmonised classification and is not subject to specific regulatory measures.

11.4 Previous assessments by other authorities

Phenanthrene belongs to the substance group of PAHs of which many are well-known to be hazardous for human health and the environment. Several PAHs: (Benz(a)pyrene (50-32-8, Benzo(e)pyrene (192-97-2), Benzo(a)anthracene (56-55-3), Chrysene (218-01-9), Benzo(b)fluoranthene (205-99-2), Benzo(j)fluoranthene (205-82-3), Benz(k)fluoranthene (207-08-9) and Dibenzo(a,h)anthracene (53-70-3)), but not phenanthrene, are already classified as CMR substances. Until now, several Annex XV dossiers for the identification of PAHs as substances of very high concern were explicitly based on their intrinsic

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[3] Concawe is a division of the European Petroleum Refiners Association and supports members in implementation of the REACH regulation

[4] European Chemical Industry Council

[5] Lower Olefins and Aromatics Reach Consortium

properties (anthracene, B[a]P, B[a]A, chrysene) or on their PAH constituents (Anthracene Oils, CTPHT).

In the Support Document of Pitch, coal tar, high temp. (CTPHT) it has been concluded by the Member State Committee (MSC) that phenanthrene fulfils the vPvB criteria of Annex XIII to the REACH Regulation (ECHA, 2009). However, phenanthrene and further PAHs whose properties have already been agreed on by the MSC in the CTPHT SVHC identification process have not been proposed (before the submission of the current Annex XV report) so far for formal SVHC identification and inclusion in the Candidate List.

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Annex I – Environmental Hazard Assessment

In the current Annex XV report, Phenanthrene is assessed with respect to its vPvB properties based on the MSC Support Document for identification of CTPHT as a SVHC according to the criteria set out in the Annex XIII (ECHA, 2009). As this dossier only focuses on the identification of phenanthrene as a SVHC substance according to article 57 (e), the toxicity data presented here are only informative.

Thus, several environmental toxicity studies have been assessed in the Annex XV Transitional Dossier for CTPHT (The Netherlands, 2008) and summarised in the Support Document for identification of CTPHT as SVHC (ECHA, 2009). As the data presented in the following sections is based on these documents, they will not be assessed and discussed again within this dossier. Additional relevant studies were retrieved in a bibliographic search in April 2018 and have been included in the analysis hereafter.

1.1 Aquatic compartment (including sediment)

The Support Document for the identification of CTPHT as SVHC summarises the following on environmental hazard assessment for the aquatic compartment. *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 phenanthrene acute as well as chronic toxicity data are available for fresh water algae, crustaceans including daphnids, fish, and insects. In addition, chronic toxicity data are also available for protozoans, cyanobacteria, aquatic plants, and insects.

1.1.1 Fish

1.1.1.1 Short-term toxicity to fish

A test performed with *Danio rerio* according to the OECD 236 FET test, provided an 96h-LC_{50} of 11 µg/L (Alves *et al*., 2017). The 96h UV-enhanced LC_{50} for zebrafish (*Danio rerio*) for phenanthrene was 271 µg/L (Willis and Oris 2014). The available data in the literature provides values ranging from up to 10 µg/L to phenanthrene solubility value and even higher (Black *et al*., 1983; Seiler *et al*., 2014; Turcotte *et al*., 2010; Hodson, 2017;

Verbruggen and van Herwijnen, 2011).

For marine water, data were available with red sea bream (*Pagrosomus major*) providing values of toxicity ranging from 0.15 mg/L for larvae NOEC to 48h-LC_{50} of 1.97 mg/L for embryos (Zhao *et al*., 2017). In turbot embryos (*Psetta maxima*), tested according to the early life stage OECD guideline, the values for hatching success 48h-EC_{10} were of 102.5 and 42.9 µg/L under light and black condition respectively. The embryos survival 96h-EC_{10} values were 4.5 and 6.66 µg/L under light and black condition respectively (Mhadhbi, Boumaiza and Beiras, 2010). Moreover, the FET with *Danio rerio* provides an effluent soluble fraction of 96h-LC_{50} of 11 µg/L and a 96h-LC_{50} of 4.9 µg/L for 50 % frequency of fish without an inflated swim bladder (Alves et al., 2017).

1.1.1.2 Long-term toxicity to fish

Regarding long-term toxicity, data for fishes were assessed by Verbruggen and van Herwijnen in 2011 for the RIVM (Verbruggen and van Herwijnen, 2011). In their report, they provide a NOEC or EC_{10} value ranging from 11 µg/L and 93 µg/L for mortality in an ELS test with the largemouth bass *Micropterus salmoides* and *Oryzias latipes* (based on the most sensitive parameters, malformations) in freshwater. The chronic toxicity data assessed by the RIVM for fish ranged from 11 µg/L to up to 560 µg/L. An assay with the zebrafish embryos larval survival assay provides a 30d-LC_{10} value of 44 µg/L (Butler *et al*., 2013) and was highlighted to be above 756 µg/L in 25d-LC_{50} medaka embryos assay (Mu *et al*., 2014). In marine water, NOEC and EC10 values ranged from 68 to 168 µg/L (Verbruggen and van Herwijnen, 2011).

1.1.2 Aquatic invertebrates

Toxicity data of phenanthrene on aquatic invertebrates provides quite similar values when tested with daphnia (*Daphnia magna*). The available data, when performing acute tests, provide values ranging from 48h-EC_{50} of 0.34 mg/L (OECD 202, Zindler *et al*., 2016), 48h-EC_{50} of 0.48 mg/L (Smith *et al*., 2010), 48h-EC_{50} of 0.55 mg/L (Zhang *et al*., 2014) to 48h-EC_{50} of 0.59 mg/L (Ma *et al*., 2016). Verbruggen and van Herwijnen in 2011 report values ranging from 140 µg/L to more than 1200 µg/L in daphnia magna 48h-LC_{50}.

In marine environment, the model marine zooplankton *Artemia salina* provide a 48h-LC_{50} of 0.49 mg/L (Lu *et al*., 2018). A study with the mollusc *Mytilus galloprovincialis*, performed in the dark, gives a NOEC/EC_{10} value of 29 µg/L and the crustacean *Acartia tonsa* a value of phenanthrene toxicity of 69 µg/L (Verbruggen and van Herwijnen, 2011). An acute 24h-EC_{50} embryo-larval development assessment of phenanthrene on the pacific oyster *Crassostrea gigas* provide a value of 1.91µg/L and was performed according to the standard procedure AFNOR XP T90-382 (Afnor, 2009). Photo-enhanced toxicity of phenanthrene was assessed by exposing 3-days-old mysid shrimp (*Americamysis bahia*) under artificial ultraviolet light or in the dark during a 48-h acute toxicity test. The 96h-LC_{50} was 22.8 µg/L and expressed no phototoxicity (Finch *et al*., 2017).

Despite the recent literature search (April 2018), no new long term data were highlighted to be used to provide a more restrictive classification regarding the toxicity of phenanthrene. The data already assessed and described in the CTPHT and in the report of the RIVM are the most sensitive for phenanthrene on aquatic invertebrates. These reports provide the lowest EC_{10} value for reproduction of *Ceriodaphnia dubia* in a 7d toxicity test. The value of this EC_{10} is 13 µg/L and is based on measured concentrations.

1.1.3 Algae and aquatic plants

A 48h-EC_{50} assay performed with *Pseudokirchneriella subcapitata* provides a toxicity value of 438.3µg/L. An OECD 201 algae assay performed with *T. chuii* at 20°c and 25°C provide value of 96h-IC_{50} of 1.316 and 0.262 mg/L, respectively (Vieira and Guilhermino 2012).

For the marine microalgae *Phaeodactylum tricornutum,* the effect of phenanthrene was determined at 22 ± 2 °C and result in a 96 h IC_{50} of 0.347 mg L^{-1} (Okay and Karacik, 2007). For chronic toxicity data, the lowest 48h-EC_{10} value available in the literature is 10 µg/L and was obtained for growth rate of the algae *P. subcapitata* (Halling-Sørensen *et al*., 1996). The values of chronic toxicity to algae and macrophytes were ranging from EC_{10} of 10 to 4910 µg/L (Verbruggen and van Herwijnen, 2011).

1.1.4 Sediment organisms

Phenanthrene toxicity to sediment was evidenced with different species (Evans and Nipper, 2007, Verbruggen and van Herwijnen 2011, ECHA, 2009). It is stated in CTPHT that “For sediment data are available for both fresh water sediment and marine sediment. The data for fresh water sediment include chronic tests with annelids, crustaceans and insects. The lowest NOEC is 50 mg/kg dw, recalculated to sediment with 10% organic carbon, for mortality and growth of both *Hyalella azteca* exposed for 14 days and *Chironomus riparius*, exposed for 10 days (Verrhiest *et al.*, 2001). Effect concentrations are based on measured concentrations. In another 28-d study with *Chironomus riparius*, emergence appeared to be somewhat less sensitive (Bleeker *et al*, 2003).

For marine sediment toxicity data are available for two species of crustaceans. Effect concentrations for the Amphipod *Rhepoxynius abronius* (Swartz *et al*., 1997; Boese *et al*., 1998) appeared to be all above 200 mg/kg dw, recalculated to sediment with 10% organic carbon.” The most sensitive assay was performed with *Schizopera knabeni* and provides a NOEC/EC_{10} value of 7.8 mg/kg dw based on the most sensitive parameter, the reproduction (Verbruggen and van Herwijnen, 2011).

1.2 Terrestrial compartment

The environmental hazard assessment for phenanthrene was previously done for the identification
of CTPHT as SVHC (ECHA, 2009). It was reported that “chronic toxicity data for phenanthrene in soil are available for annelids, collembola, plants, crustaceans, and microbial processes. Again for phenanthrene, the EC_{10} for reproduction of *Folsomia fimetaria* was the lowest EC_{10} or NOEC (Sverdrup *et al*., 2001, 2002, 2002c). Four EC_{10} for Folsomia in sandy loam soil were available. The difference between the four values was the ageing of phenanthrene in the soil. Soils were spiked and toxicity testing started after 0, 10, 40, or 120 days after spiking. The EC_{10s} for these cases were 29, 18, 18, and 12 mg/kg dw, recalculated to a soil with 2% organic carbon. The EC_{10s} were based on measured concentrations. The geometric mean of these EC_{10s} is 18 mg/kg dw. This value was based on measured concentrations”.

This data is the lowest available for phenanthrene toxicity on soil organisms. Indeed, recent literature search (done in April 2018) highlight other phenanthrene toxicity data. Nevertheless, those data, described later, provide higher effect concentrations on different organisms. In a study with the predatory mite *Hypoaspis aculeifer*, performed according to the OECD guideline 226, the 14d-LC_{50} was 684 mg/kg. When focusing on the reproduction, the 14d-EC_{50} was 49 mg/kg and the avoidance 48h-EC_{50} was 26 mg/kg (Owojori, Waszak, and Roembke, 2014). In an OECD 220 assay, the 21d-EC_{10} was 37 mg/kg for *Enchytraeus crypticus* (Roelofs *et al*., 2016). For *E. albidus*, the 3w-LC_{50} was 135 mg/kg dry soil (Amorin *et al*., 2011). According to an experiment realised in microcosm according to the ISO 11268 with *Eisenia fetida*, the 4w-EC_{50} was 40.67 mg/kg (Wu *et al*., 2012). One other study with *E. fetida* gives a NOEC/EC_{10} value of 36 mg/kg (Verbruggen and van Herwijnen, 2011). A study with *Folsomia candida*, performed according to the ISO 11267, gives an EC_{10} value of 24.95 mg/kg (Droge *et al*., 2006).

1.3 Summary and discussion of the environmental hazard assessment

In the Support Document for identification of CTPHT as SVHC (ECHA, 2009), the issue has already been summarised and discussed as follows:

The experimental data indicate a high chronic and acute toxicity of the PAH constituents of CTPHT for aquatic organisms.

The reassessment of toxicity data by the RIVM (Verbruggen and van Herwijnen, 2011) and the recent literature search performed in April 2018 and included in the current report did not challenge this conclusion for phenanthrene.