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Stream 4 – D4.1.2

***Report on the experimental results from literature of selected chemicals
on the dose-response relationships***

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Executive Summary

This report was written in the context of Task 1.1 of Workpackage 1 of Stream 4, dealing with intercomparison between contaminant thresholds at molecular, individual, population and ecosystem levels. Its main objective is the study of individual responses to chemicals and the establishment of robust dose-response relationships.

The contaminants selected by the Thresholds project were divided in organic: PCBs (polychlorobiphenyls), PBDEs (pentabromodiphenyl ethers), PAHs (polycyclic aromatic hydrocarbons) and metals (cadmium and mercury) (see Milestone 4.2.1). After this selection, it was decided to look for information on their behaviour in the marine environment in order to study ecotoxicity and toxicity data that allow definition of dose-response relationship and derivation of thresholds of no effect.

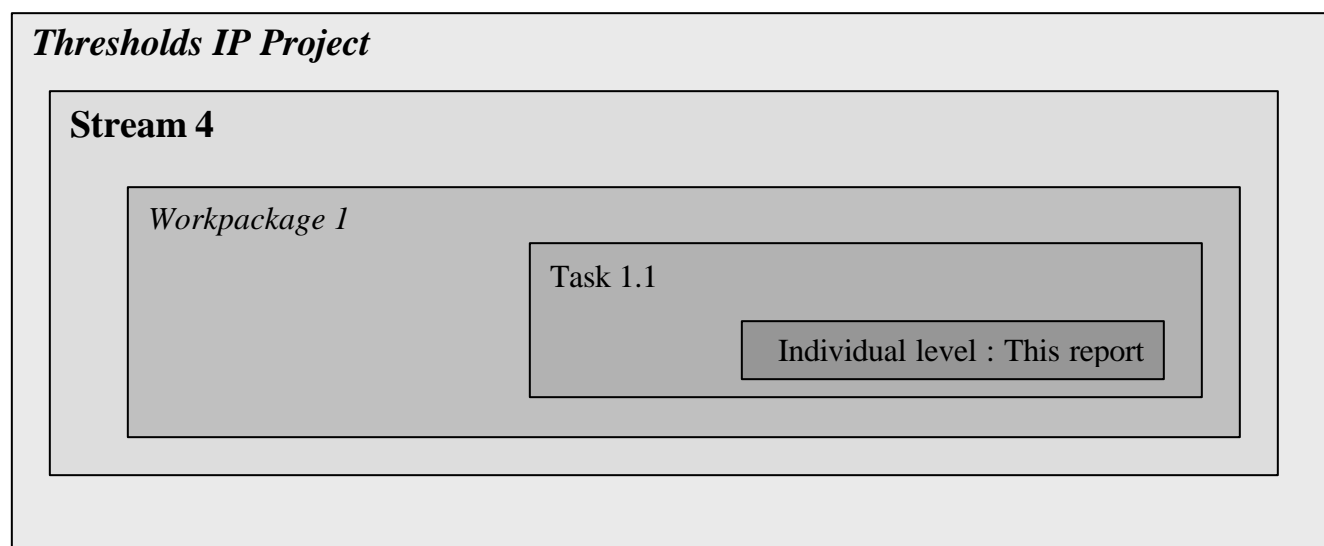
Given the low availability of data it was not possible to define a robust dose-response relationship for none of the substances studied except for cadmium. For the same reason it was not possible to derive thresholds of no effect for most substances. Thresholds could be derived for pelagic organisms for benzo[a]pyrene, benzo[k]fluoranthene, benzo[g,h,i]perylene and cadmium; as well as thresholds of no effect for sediment dwelling organisms for benzo[k]fluoranthene. Pentabromodiphenyl ethers and fluoranthene were the only substances for which thresholds of no effect were derived for the three media: water (pelagic organisms), sediment (benthic organisms) and top predators (secondary poisoning). No thresholds were derived for pyrene, benzo[b]fluoranthene and indeno[1,2,3-cd]pyrene. The most complex substance studied was mercury since it is necessary to consider also secondary poisoning effects and the role of speciation. Given the knowledge on bioaccumulation and toxicity of organic mercury and considering the considerable uncertainties encountered, no reliable overall threshold of no effect of mercury could be derived for the marine environment. It was deemed more appropriate to wait until a decision is taken at the European Commission level in the context of the Water Framework Directive.

1. Introduction

1.1. Context and objectives of the study

This deliverable is included in Stream 4 of the Thresholds Integrated Project, dealing with "*Thresholds and drivers of contaminants*" (Stream leader: JRC), in Workpackage 1 of "*Intercomparison between contaminant thresholds at molecular, individual, population and ecosystem levels*". Objectives of this Workpackage are "*to compare and assess the differences between contaminant thresholds (individual and mixtures) at several levels (molecular, individual, population and ecosystem), to study the effects of the speciation of contaminants and the influence of loading terms (pulse, seasonal, etc.) in their thresholds values*".

Figure 2.2.1-1: Deliverable D4.1.2 in Thresholds Integrated Project



The objective of this report is the "*study of individual responses to chemicals*" that allow the "*establishment of robust dose-response relationships*", including reporting on "*differences between size, sex, and morphometrics*".

1.2. Effective work reported

Chemicals effects assessment comprises two steps of the risk assessment procedure: hazard identification and dose-response assessment. At this last step, the Predicted No Effect Concentration (PNEC) shall be determined. This PNEC is considered as the threshold above which an unacceptable effect is most likely to occur. The methodology to derive PNECs is based on a European consensus described in the Technical Guidance Document (TGD) in support of European regulation on new notified, existing substances and biocidal products (European Commission, 2003).

To derive PNECs, it is very important to evaluate ecotoxicity data with respect to their adequacy and completeness. **Adequacy of a test data** can be defined by the **reliability of data**, covering the inherent quality of a test relating to test methodology and the way that the performance and results of the test are described (according to international and/or European guidelines), and the **relevance of data**, covering the extent to which a test is appropriate for a particular hazard or risk assessment (appropriate endpoints studied under relevant conditions, etc.).

Two methods are available to assess dose-response relationships: a method using **assessment factors** and a method using **statistical extrapolation techniques**. To establish **robust dose-response relationships** and derive a Predicted No Effect Concentration from a statistical extrapolation, the method commonly used is Species Sensitivity Distribution, where a large, reliable and relevant dataset of long-term tests is needed. For most of the substances chosen in Thresholds IP, there is an obvious lack of relevant and reliable ecotoxicity data. Indeed, most of the time there is not enough data in the literature to use statistical extrapolation method, nor to study differences between sex or morphometrics. Therefore, when statistical requirements for the use of statistics were not fulfilled, it is proposed to deliver literature based thresholds which are PNECs derived on the basis of assessment factor method, as described in the TGD (European Commission, 2003).

It has to be kept in mind that those PNECs consist in *thresholds of no effect for the marine organisms*, but in no way of *thresholds of no return*, given that data on reversibility of effects were too sparse to be studied.

2. Methodology

2.1. Data collection

Sources used for the collection of physico-chemical properties, ecotoxicity data and toxicity data are:

- Retrospective literature search using public literature and reviews;
- On-line chemicals databases;
- On-line downloaded reports;
- Handbooks of physico-chemical data and environmental fate;

Substantial parts of datasets for HAPs were based on Marchand and Tissier (2002). Where relevant, it is precised when other specific sources are used.

2.2. Guidance for ecotoxicity and toxicity data selection and validation

All the following recommendations are given so as to define "guidance" for the work but in no way they should be taken as compulsory or necessary for studying dose-response relationships or derivation of ecotoxicity thresholds. In fact, it has to be kept in mind that evaluation of ecotoxicity and toxicity data as well as effects assessment must undergo **expert judgement** and can be judged on a case by case basis. Therefore, many of the following recommendations may not be strictly followed as long as every choice is justified.

2.2.1. *Tools for validation*

Validation step of a study is supported by two main technical tools:

- OECD Guidelines for the Testing of Chemicals (OECD, 1981-2004)
- Part II: Assay methods for the classification, packaging and labelling of dangerous substances in the European Union.

2.2.2. *Data validation*

Guidance followed for this study (and generally recommended)

Given that it was decided to use the methodology recommended in the EC TGD (European Commission, 2003), tests taken into account should be monospecific and lead on one substance but not in mixtures.

Data are pooled all together in a database and roughly sorted out. In this database some of the following information is essential and necessary for validation of the test:

Critical Concentration. This is the concentration that permits the derivation of the PNEC. As far as possible, the chronic value should be a "No Observed Effect Concentration" (NOEC), which is preferable to a "Lowest Observed Effect Concentration" (LOEC), and the acute values should be a "Lethal Concentration" or an "Effect Concentration" for 50% of the population (LC₅₀ or EC₅₀).

Test duration and type of toxicity. Toxicity is said to be "chronic" when exposure duration to the chemical is *ca.* the duration of the life cycle of the species studied or longer. It is "acute" in opposite situations. To derive the PNEC, it is always better when chronic toxicity data come together with acute toxicity data. Indeed, when acute toxicity values are such that they confirm long term toxicity (consistency of dataset) it is often possible to lower the assessment factor for PNEC derivation. For effects and risk assessment purposes, tests on algae are considered chronic as soon as the duration is equal or superior to 72 h. On the other hand, for crustaceans and fish, tests are considered chronic from 21 and 28 days, respectively. There is one exception, the case of the crustacean *Ceriodaphnia dubia* which reproduces quicker than other daphnids and for which exposure is considered chronic as soon as the test lasts 7 days.

Tests for which test duration is lower than 24 hours can be considered as acceptable but are not usually used as valid data for PNEC derivation.

Media type. The media in which exposure takes place can be freshwater or saltwater. It is obviously better to have saltwater data to derive PNEC_{marine} but there is a serious lack of data in this domain.

Organisms tested. Obviously, freshwater organisms must be tested in freshwater and marine and estuarine species in salted water. Moreover, some species are recommended by OECD guidelines, like for example freshwater green algae *Selenastrum capricornutum*, *Scenedesmus subspicatus* and *Chlorella vulgaris* for growth inhibition tests, and *Daphnia magna* for bioassays on invertebrates. Concerning marine species, no species are recommended by OECD yet among algae and invertebrates. Among fish, the only marine recommended species is *Cyprinodon variegatus*. On the other hand, freshwater fish species are very numerous (e.g. *Brachydanio rerio*, *Pimephales promelas*, *Oryzias latipes*, *Cyprinus carpio*, *Lepomis macrochirus*, *Oncorhynchus mykiss*, *Poecilia reticulata*). In practice, a considerable amount of other species is reported in literature data.

Endpoint observed and criteria. Given that the main final purpose is the protection of the environment, it is always better to work on sublethal effects than on lethal effects. The effects more frequently observed and taken into account in effects assessment are effects on growth (total body weight, absolute and relative organ weight), reproduction and larval development.

Tests for which endpoints are not likely to cause adverse effects at populational scale (e.g. effects on enzymatic activities, endocrine disrupting effects, histological effects, etc.) can be considered as acceptable but are not usually used as valid data for PNEC derivation.

Controls. Exposing organisms to the media without chemical is one of the *sine qua non* conditions to the validation of the test. Controls are necessary to validate experimental conditions, i.e. to verify that no invisible event (e.g. contamination by another chemical than the one studied, sudden change of temperature, etc.) has occurred during the test being the possible cause for adverse effects or mortality of organisms. Furthermore, observation of controls allows the differentiation of natural mortality from mortality only due to occurrence of the chemical. Finally, in the case of use of another solvent than water it is of prime necessity that controls with solvent are made to deny toxicity of the latter in the conditions of the test. Low mortality of controls (generally $\leq 10\%$) is a prime criterion for validity of tests.

Analysis of chemical. In aquatic media, diverse degradation processes can occur and it is thus important to report actual concentrations to which organisms are exposed so that effect concentration, calculated from concentration-effect curves is not biased. Low variations between measured and nominal concentrations ($\leq 20\%$ variation) is a prime criterion for validity of tests.

Other information. Breeding and culture conditions, conditions of exposure (water temperature, physico-chemical characteristics of water (pH, O₂, salinity, etc.), renewal of exposure media (flow-through, intermittent or static), feeding, etc. are information that can be indicated in the test report. Tests conditions must be as close as possible to living conditions of the organisms in the field (continuous flux of media or static media). Finally, a minimum oxygen concentration in the media of 60% of air saturation is also a prime validity criterion.

Data validation is a complex step of the study that has to be based on expert judgement of all information available in the test report and cited.

Reliability index (Klimisch *et al.*, 1997)

It was decided to use Klimish *et al.* (1997) systematic approach of evaluation of the quality of data in this study. This evaluation is used in hazard and risk assessment and "*intends to harmonize data evaluation processes worldwide*".

The scoring system used to categorize the reliability is as follows:

- **1 = reliable without restrictions:** "*data[...]generated according to generally valid and/or internationally accepted testing guidelines (preferably performed according to GLP) or in which the test parameters documented are based on a specific testing guideline[...]or in which all parameters described are closely related/comparable to a guideline method*";
- **2 = reliable with restrictions:** "*data[...] (mostly not performed according to GLP), in which the test parameters documented do not totally comply with the testing guideline, but are sufficient to accept the data or in which investigations are described which cannot be subsumed under a testing guideline, but which are nevertheless well documented and scientifically acceptable*"
- **3 = not reliable:** "*data[...]in which there were interferences between the measuring system and the test substance or in which organisms/test systems were used which are not relevant in relation to the exposure [...] or which were carried out or generated according to a method which is not acceptable, the documentation of which is not sufficient for assessment and which is not convincing for an expert judgment*"
- **4 = not assignable:** "*data[...]which do not give sufficient experimental details and which are only listed in short abstracts or secondary literature (books, reviews, etc.)*"

2.3. PNEC Derivation according to the TGD methodology (European Commission, 2003)

When validated, data are used for the derivation of the Predicted No Effect Concentration (PNEC). To this aim, critical concentrations (effect and no effect concentrations) have to be observed and interpreted : Is there a sufficient number of data to be used in statistical method of derivation? Are acute and chronic data available for the three main trophic levels (algae, crustaceans, fish)? Are there available data for both freshwater and saltwater species? Are the data consistent between each others? These are some of the main questions that have to be raised when deriving a PNEC.

2.3.1. *PNEC derivation according to the assessment factor method*

Principle

The main principle of PNEC derivation is to divide an effect concentration or a no effect concentration by an assessment factor.

The purpose of the assessment factor is to take into account:

- extrapolation of data :
 - from laboratory studies to the actual environment
 - from acute toxicity to chronic toxicity
 - from freshwater to saltwater (if necessary)
- uncertainty of data :
 - interspecific and intraspecific variations
 - interlaboratories and intralaboratory variations
- low availability of data (if necessary)

PNEC is derived most of the time from the lowest critical concentration reported in the dataset, applying a *minimal* assessment factor of 10 (except case by case), taking into account extrapolation of data from laboratory to the actual environment. Additionally to this minimal assessment factor, other assessment factors are used depending on availability of data (see Table 2.3.1-1, Table 2.3.1-1, Table 2.3.1-3 and Table 2.3.1-4)

It is far better if PNEC for the marine environment are derived from marine and/or relevant estuarine toxicity data. Unfortunately, there is an obvious lack of saltwater ecotoxicity data. Therefore, PNEC for the marine environment are often derived from freshwater data, when there is evidence that no significant difference of sensitivity exists between freshwater and saltwater toxicity data.

Table 2.3.1-1: Assessment factors proposed for deriving $PNEC_{water}$ for saltwater for different data sets (European Commission, 2003)

Data set	Assessment factor
Lowest short-term L(E)C50 from freshwater or saltwater representatives of three taxonomic groups (algae, crustaceans and fish) of three trophic levels	10,000
Lowest short-term L(E)C50 from freshwater or saltwater representatives of three taxonomic groups (algae, crustaceans and fish) of three trophic levels, + two additional marine taxonomic groups (e.g. echinoderms, molluscs)	1000
One long-term NOEC (from freshwater or saltwater crustacean reproduction or fish growth studies)	1000
Two long-term NOECs from freshwater or saltwater species representing two trophic levels (algae and/or crustaceans and/or fish)	500
Lowest long-term NOECs from three freshwater or saltwater species (normally algae and/or crustaceans and/or fish) representing three trophic levels	100
Two long-term NOECs from freshwater or saltwater species representing two trophic levels (algae and/or crustaceans and/or fish) + one long-term NOEC from an additional marine taxonomic group (e.g. echinoderms, molluscs)	50
Lowest long-term NOECs from three freshwater or saltwater species (normally algae and/or crustaceans and/or fish) representing three trophic levels + two long-term NOECs from additional marine taxonomic groups (e.g. echinoderms, molluscs)	10

Table 2.3.1-2 : Assessment factors for derivation of $PNEC_{marine\ sediment}$ from short-term sediment toxicity tests (European Commission, 2003)

Available test results	Assessment factor	$PNEC_{marine\ sediment}$
One acute freshwater or marine test	10,000	Lowest of LC50/10,000 and equilibrium-partitioning method
Two acute tests including a minimum of one marine test with an organism of a sensitive taxa	1000	Lowest of LC50/1000 and equilibrium-partitioning method

Table 2.3.1-3 : Assessment factors for derivation of $PNEC_{marine\ sediment}$ from long-term sediment toxicity tests (European Commission, 2003)

Available test results	Assessment factor
One long-term freshwater sediment test	1000
Two long-term freshwater sediment tests with species representing different living and feeding conditions	500
One long-term freshwater and one saltwater sediment test representing different living and feeding conditions	100
Three long-term sediment tests with species representing different living and feeding conditions	50
Three long-term tests with species representing different living and feeding conditions including a minimum of two tests with marine species	10

Table 2.3.1-4 : Assessment factors for extrapolation of mammalian and bird toxicity data (European Commission, 2003)

TOXoral	Duration of test	AForal
LC50 _{bird}	5 days	3,000
NOEC _{bird}	chronic	30
NOEC _{mammal, food,chr}	28 days	300
	90 days	90
	chronic	30

2.3.2. *PNEC derivation according to the statistical extrapolation method (European Commission, 2003)*

General considerations

If a large dataset from long-term tests for different taxonomic groups is available and therefore the database on Species Sensitivity Distributions (SSDs) is sufficient (OECD, 1992), then statistical extrapolation methods may be used to derive a PNEC.

The main underlying assumptions of the statistical extrapolation methods are that the distribution of species sensitivities follows a theoretical distribution function and that the group of species tested in the laboratory is a random sample of this distribution (OECD, 1992).

In general, the method consists in log transforming long-term toxicity data and fitting them according to the distribution function (a prescribed percentile of that distribution is used as criterion).

Guidance

To use statistical extrapolation method, the method commonly used is Species Sensitivity Distribution, where a large, reliable and relevant dataset of long-term tests for different taxonomic groups is needed. The sine qua non conditions are the following:

- Input data : reliable available NOECs from chronic/long-term studies, preferably on full life-cycle or multi-generation studies
- Minimum sample size : at least 10 reliable chronic data (preferably more than 15)
- Taxonomic groups represented: at least 8 taxonomic groups (fish, another vertebrate, crustacean, insect, algae, higher plants, a family in a phylum other than Arthropoda or Chordata, a family in any order of insect or any phylum not already represented).

"Deviations from these recommendations can be made, on a case-by-case basis, through consideration of sensitive endpoints, sensitive species, mode of toxic action and/or knowledge from structure-activity considerations."

Estimation of the PNEC

The PNEC is calculated as: $PNEC = 5\%SSD / AF$

"AF is an appropriate assessment factor between 5 and 1, reflecting the further uncertainties identified. Lowering the AF below 5 on the basis of increased confidence needs to be fully justified. The exact value of the AF must depend on an evaluation of the uncertainties around the derivation of the 5th percentile. As a minimum, the following points have to be considered when determining the size of the assessment factor:

- *the overall quality of the database and the endpoints covered, e.g., if all the data are generated from "true" chronic studies (e.g., covering all sensitive life stages);*
- *the diversity and representativity of the taxonomic groups covered by the database, and the extent to which differences in the life forms, feeding strategies and trophic levels of the organisms are represented;*
- *knowledge on presumed mode of action of the chemical (covering also long-term exposure);*
 - *statistical uncertainties around the 5th percentile estimate, e.g., reflected in the goodness of fit or the size of confidence interval around the 5th percentile, and consideration of different levels of confidence (e.g. by a comparison between the 5% of the SSD (50%) with the 5% of the SSD (95%));*
- *comparisons between field and mesocosm studies, where available, and the 5th percentile and mesocosm/field studies to evaluate the laboratory to field extrapolation."*

Warning

"The approach of statistical extrapolation is still under debate and needs further validation. An advantage of these methods is that they use the whole sensitivity distribution of species in an ecosystem to derive a PNEC instead of taking always the lowest long-term NOEC. However, such methods could also be criticised. Among the most common drawbacks, the reasons put forward are: the lack of transparency by using this method compared to the standard approach, the question of representativity of the selected test species, the comparability of different endpoints, the arbitrary choice of a specific percentile and a statistical confidence level, etc."

3. Selected chemicals

The following chemicals (or families of chemicals) were selected in Stream 4 (see Milestone 4.2.1) :

- Polychlorobiphenyls (PCBs)
- Pentabromodiphenyl Ethers (PBDEs)
- Polycyclic Aromatic Hydrocarbons (PAHs), specifically:
 - Pyrene
 - Fluoranthene
 - Benzo[a]pyrene
 - Benzo[b]fluoranthene
 - Benzo[k]fluoranthene
 - Benzo[g,h,i]perylene
 - Indeno[1,2,3-cd]pyrene
- Cadmium
- Mercury

4. Dose-response relationships and thresholds for chemicals in the marine environment

4.1. General issues

Except where specifically reported:

- all tests were lead with substances pure or almost pure ($\geq 98\%$)
- when several results are given for one reference (several endpoints tested or different values for one endpoint) the worst case has always been taken into account, that is to say the highest toxicity data e.g. the lowest EC or NOEC.

4.2. PolyChloroBiphenyls (PCBs)

4.2.1. *General issues, physico-chemical characteristics and behaviour in the marine environment*

The name PolyChloroBiphenyls (PCBs) denotes a family of organochlorine compounds of high molecular weight, which molecular formula is $C_{12}H_{(10-n)}Cl_n$, n being the number of chlorine atoms which can vary between 1 and 10.

They are manufactured *via* direct chlorination of the biphenyl ring system and this chemical reaction can lead theoretically to the production of 209 discrete congeners (Ballschmiter and Zell, 1980), distinguishable from one to another by the number and the position of chlorine atoms on the molecule.

Ballschmiter and Zell, 1980) introduced the original nomenclature system of PCBs in which congeners are arranged in the ascending numerical order with a number (IUPAC number) based on the number of chlorine atoms and their substitution pattern on the biphenyl ring.

Selected chemicals

Two criteria have been taken into account for the selection of PCBs congeners to be studied: the hazard or toxicity and the occurrence of monitoring data. Several PCBs congeners are found in the marine environment and the most frequently monitored are the following: 28, 52, 101, 105, 118, 138, 153, 156, 180. As the purpose of this report is the effects of contaminants, it was decided to study only PCB congeners reported as diowin-like compounds i.e. structurally related to polychlorodibenzodioxins (PCDDs) and therefore to possess similar high toxic properties. The mono-*ortho* substituted PCBs 105, 114, 118, 123, 156, 157, 167, 189 as well as a few di-*ortho* substituted PCBs like 170 and 180 are considered “dioxin-like” compounds (Ahlborg *et al.*, 1994). Therefore, crossing the two criteria, PCBs chosen to be studied are the following: pentachlorobiphenyls (PeCB) 105 and 118, hexachlorobiphenyl (HexCB) 156 and heptachlorobiphenyl (HepCB) 180.

PCBs have been widely described in many literature sources, but not always precisely enough so as to get information on specific congeners 105, 118, 156 and 180. Therefore, physico-chemical properties in Table 4.2.1-1 are given for PeCBs, HexCB and HepCB, but for PCBs 105, 118, 156 and 180 specifically only when possible. Moreover, as literature sources are numerous and give slightly different values, it was decided to give ranges with maxima and minima, that is why one source is mainly cited (Mackay *et al.*, 2000) wherein other precise references can be found.

Figure 4.2.1-1 : CAS numbers, structural features and chemical formula of PCBs.

PolyChloroBiphenyls	
$C_{12}H_{(10-n)}Cl_n$	
PCB 105 : CAS n° 32598-40-4 2,3,3',4,4'-Pentachloro-1,1'-biphenyl $C_{12}H_5Cl_5$ (PeCB)	
PCB 118 : CAS n° 31508-00-6 2,3',4,4',5-Pentachloro-1,1'-biphenyl $C_{12}H_5Cl_5$ (PeCB)	
PCB 156 : CAS n° 38380-08-4 2,3,3',4,4',5-Hexachloro-1,1'-biphenyl $C_{12}H_4Cl_6$ (HexCB)	
PCB 180 : CAS n° 35065-29-3 2,2',3,4,4',5,15'-Heptachloro-1,1'-biphenyl $C_{12}H_3Cl_7$ (HepCB)	

Table 4.2.1-1 : Physico-chemical characteristics of PCBs influencing their behaviour in the marine environment.

Properties	Remarks	Molecule	Values	References
Molecular weight ($g \cdot mol^{-1}$)		PeCB HexCB HepCB	326.4 360.9 395.3	-
Water solubility ($\mu g \cdot L^{-1}$)	25°C	PeCB HexCB PCB 180	4 – 72 0.4 – 38 0.31 – 6.56	(Mackay <i>et al.</i> , 2000)
log K_{ow}		PCB 105 PCB 118 HexCB PCB 180	6.53 – 6.93 6.61 – 6.74 6.7 – 7.3 7.14 – 7.36	(Ballschmiter <i>et al.</i> , 2005) (Ballschmiter <i>et al.</i> , 2005) (Mackay <i>et al.</i> , 2000) (Ballschmiter <i>et al.</i> , 2005)
Vapour pressure (mPa)	25°C	PeCB HexCB PCB 180	0.304 – 30 0.2 – 12 0.0858 – 0.506	(Mackay <i>et al.</i> , 2000)
Henry Constant ($Pa \cdot m^3 \cdot mol^{-1}$)		PeCB HexCB PCB 180	12.2 – 151.4 6.7 – 86.0 3.24 – 102	(Mackay <i>et al.</i> , 2000)
log K_{oc} ($L \cdot kg^{-1}$)		PeCB HexCB PCB 180	6.21 4.785 – 6.869 5.5 – 7.3	(Mackay <i>et al.</i> , 2000)

* Based on natural isotopic abundance of carbon, chlorine and hydrogen

PCBs are practically insoluble in water, whereas they dissolve easily in lipids and are readily accumulated in fatty tissues (WHO/EURO, 1987).

Physico-chemical properties of the PCBs are determined by their structural features, that is to say: the number of chlorine atoms and their substitution pattern on the biphenyl ring. The parameters influencing these physico-chemical properties are reported in Table 4.2.1-1. In this table, it is clearly indicated that the higher the chlorination level, the lower the solubility in water, the higher the partition to fatty tissues and the higher the accumulation potential. High chlorinated compounds have also less capacity to evaporate and volatilize.

Therefore, it can be considered that PCBs will not be found in great concentrations in the water column but more likely in sediments and in fatty tissues of aquatic organisms where they highly bioconcentrate.

4.2.2. *Toxicological properties*

Acute toxicity

PCBs often do not appear to be very acutely toxic to aquatic species in static test due to their low solubility in water.

Sea urchin embryos exposed 72h to PCBs showed irregular mass of lysed or undifferentiated cells (posthatch malformation) and other type of abnormalities e.g. prehatch malformations, skeletal abnormalities, gut abnormalities and development retardation (Schweitzer *et al.*, 1997). The effects of an exposure of developing tadpoles to acute and high concentrations of Aroclor 1254 (containing ca. 14% of PCB 118 and 7% of PCB 105) have also been reported to cause significant reductions in survival and body size, histological abnormalities, including aberrant tail tip, myotomal, and melanocyte morphologies (Fisher *et al.*, 2003).

Chronic toxicity

- Mechanism of toxicity mediated by the Ah-receptor (AhR)

Dioxin-like PCBs (coplanar) are reported to work in a similar manner as dioxins, that is to say to bind to AhR, leading *via* the ADN traduction process to the production of anormal proteins which can induce pathologies, development disorders, etc.

- Reproductive toxicity and immunotoxicity

It is well-known that PCBs and their metabolites have potentialities to alter the reproductive processes by interfering with endocrine function in human (Kester *et al.*, 2000; Portigal *et al.*, 2002), and in fish (Fossi *et al.*, 2004; Örn *et al.*, 1998; Thomas, 1988; Thomas, 1989; Vaccaro *et al.*, 2005), e.g. by feminisation of fish (US-EPA, 1997) of altering sex ratio (Matta *et al.*, 1998). It has also been demonstrated that PCBs may impair lipid metabolism and reproductive success in oysters (Chu *et al.*, 2003).

Some PCBs are reported to strongly bind to Ah-Receptor (AhR) and have anti-estrogenic effects in fish (Vaccaro *et al.*, 2005) whereas others do not bind to AhR and have strong estrogenic effects (Vega-Lopez *et al.*, 2006). PCBs are also likely to affect hormone metabolism by interfering with CYP1A1 (Yeung *et al.*, 2003).

In mammals, numerous studies have been undertaken to demonstrate that PCBs can alter hormonally mediated effects on reproduction and developments. In particular, many studies have been carried out to show that PCBs may be cofactor of immunotoxic effects to marine mammals such as seals (Barron *et al.*, 2003; Brouwer *et al.*, 1989; Reijnders, 1986), but the establishment of a credible dose-effect relationship in mammalian population had not been reported until recently. In fact, a study lead by Levin *et al.* has demonstrated for the first time causal relationship between exposure to non-coplanar PCBs and impaired immune function in dolphins and belugas (Levin *et al.*, 2004).

Carcinogenicity and mutagenicity

PCB are classified in Group 2A by IARC, as ‘*probably carcinogenic to humans*’ (IARC, 1987). In fact, IARC reports that there is “*limited evidence of carcinogenicity*” in humans and “*sufficient evidence of carcinogenicity*” in experimental animals.

Carcinogenic effects are observed at the individual levels but there occurrence and possible consequences on populations are not well known for the moment. This is the reason why such effects are not taken into account in data set and derivation of thresholds for the marine environment.

4.2.3. *Effects on organisms*

Many reports have linked endocrine effects with environmental and experimental exposures to PCBs mixtures, but few have examined congener-specific effects, and while data on bioaccumulation of PCBs in aquatic organisms are fairly numerous, occurrence of congener-specific effects data issued from valid bioassays is very low.

Moreover, data on ecotoxicity of PCBs are often reported from studies that have not been realised according to International or European guidelines and which therefore do not fit for risk assessment purposes and use in determination of reliable thresholds.

Therefore, data reported thereafter do not represent an exhaustive list of ecotoxicity data for PCBs but the data which could be considered as relevant for risk assessment purposes for the marine environment.

Effects on pelagic organisms

Few valid ecotoxicity data of PCBs to pelagic organisms are reported. Actually, only one of the tests reported in Table 4.2.3-1 has been validated according to OECD Guidelines for PCB 105 (Mayer *et al.*, 1998). Other data, reliable with restriction, are nevertheless reported in this table. All values reported in Table 4.2.3-1 have been considered as valid in the RIVM report on Maximum Permissible Concentrations for PCBs (RIVM, 1999).

Effects on benthic organisms

There is no data available in the literature issued from valid water-sediment toxicity tests, reporting toxicity of sediment spiked with PCBs to benthic organisms.

Table 4.2.3-1 : Acute and chronic toxicity of PCB to pelagic organisms

Chemicals	Taxa	Species ^a	EC type ^b	EC/NOEC value (µg.L ⁻¹)	Expo. Conc. ^c (µg.L ⁻¹)	Expo. Type ^d	RI ^e	References
PCB 105	Algae	<i>Selenastrum capricornutum</i> (FW)	EC ₅₀ (48h) GRO _b	4.6	nr	S/M	1	(Mayer <i>et al.</i> , 1998)
PCB 105	Fish	<i>Brachydanio rerio</i> (FW)	EC ₅₀ (7d) nr	1.3	nr	nr	4 ^f	(Petersen <i>et al.</i> , subm.)
PCB 118	Invertebrates Crustaceans	<i>Daphnia magna</i> (FW)	NOEC (21d) nr	>1 ^g	-	nr	3 ^f	(Dillon <i>et al.</i> , 1990)
PCB 156	-	-	-	-	-	-	-	-
PCB 180	Fish	<i>Pimephales promelas</i> (FW)	NOEC (13wk) MOR, GRO, REP	< 2.5 ^h	2.5, 25	C/N/O	3 ^f	(Suedel <i>et al.</i> , 1997)

^a FW : fresh water organisms; SW : marine and estuarine organisms.

^b EC : Effect Concentration; EC₅₀ : EC for 50% of the population; NOEC : No Observed Effect Concentration; GRO : growth; GRO_b : growth for which endpoint criterion is biomass; MOR : mortality; REP : reproduction.

^c Expo. Conc. : Concentration of the substance to which organisms were exposed during the test.

^d S : static exposition; C : continuous/flow-through exposition; N : EC/NOEC value based on nominal concentrations; M : EC/NOEC value based on measured concentrations; O : open vessel.

^e RI : Reliability Index (Klimish *et al.*, 1997); 1 : Valid without restriction; 2 : Valid with restriction; 3 : Not reliable; 4 : Not assignable.

^f Information on methodology was not available (RI=4) or could not be validated according to OECD guidelines (RI=3) but test was considered as « acceptable » given that it is used in RIVM report (RIVM, 1999).

^g No effects were observed, even at the highest concentration tested.

^h Effects were observed at lowest concentration tested.

Effects on top predators : secondary poisoning

Many ecotoxicity data of PCBs to avian and mammalian species indicated in the RIVM report on Maximum Permissible Concentrations for PCB (RIVM, 1999) have been considered as reliable enough to be used to derive MPCs. According to the TGD (European Commission, 2003), only toxicity studies reporting on dietary and oral exposure are relevant as the pathway for secondary poisoning is referring exclusively to the uptake through the food chain. Therefore, in this report, it was chosen not to report all of the data indicated in RIVM report, because it is not considered reliable to take into account data exported from tests where animals have been exposed via intraperitoneal injections. In fact, this kind of exposure is not representative of what happens in the actual environment. For avian species, absolutely no ecotoxicity data could be validated for PCB 105, 118, 156 and 180 according to OECD Guidelines 205 (OECD, 1984a) and 206 (OECD, 1984b). For mammals, it was decided to report as “acceptable” the 7 ecotoxicity data that are indicated in Table 4.2.3-2, of which 1 is related to effects of PCB 105, 4 to effects of PCB 118 and 2 to effects of PCB 156. Within the 4 data for PCB 118, one of them could be validated according to OECD guidelines (OECD, 1981-2004), however with some restrictions. No validated or “acceptable” ecotoxicity data could be reported for PCB 180.

Table 4.2.3-2 : Toxicity of PCB to mammalian species

Chemicals	Species	EC type ^a	EC/NOEC value ^b (mg.kg ⁻¹ food, ww.)	Expo. Conc. ^c (mg.kg ⁻¹ food, ww.)	Expo. Type ^d	RI ^e	References
PCB 105	Rat	ED ₅₀ (nr) <i>HRM</i>	0.5	0.4, 1, 2.5	O-nr/nr	4 ^f	(Moore <i>et al.</i> , 1996)
PCB 118	Rat	NOEC (90d) <i>BCM_{1-VITA}</i>	≥2 ^g	0.002, 0.02, 0.2, 2	O-D/nr	4 ^f	(Håkanson <i>et al.</i> , 1994)
PCB 118	Rat	LOEC (90d) <i>HST_{1-cell.abn.}</i>	0.002	0.002, 0.02, 0.2, 2	O-D/nr	4 ^f	(MacLellan <i>et al.</i> , 1994)
PCB 118	Rat	NOEC (90d) <i>GRO_{bw}* , GRO_{ow}, ENZ, HRM</i>	0.2 (f) 0.1 (m)	0.002, 0.02, 0.2, 2 (f) 0.001, 0.01, 0.1, 1 (m)	O-D/M	2	(Chu <i>et al.</i> , 1995)
PCB 118	Rat	NOEC (10-16 d) <i>GRO_{bw}* , GRO_{ow}, HRM</i>	4	4, 16	O-G/na	3 ^f	(Ness <i>et al.</i> , 1993)
PCB 118	Rat	NOEC (90d) <i>BCM_{1-prot}</i>	3	3, 7.5, 15, 30	O-G/na	4 ^f	(van Birgelen <i>et al.</i> , 1995)
PCB 156	Mouse	nr (10-13 d) <i>GRO_{bw}* , GRO_{ow}</i>	20	10, 20	O-G/na	4 ^f	(Birbaum <i>et al.</i> , 1985)
PCB 156	Rat	NOEC (90d) <i>GRO_{bw}* , GRO_{ow}* , ENZ* , HRM*</i>	≤1.2 ^h	1.2, 6, 12	O-D/nr	2	(van Birgelen <i>et al.</i> , 1994)
PCB 180	-	-	-	-	-	-	-

^a ED : Effect Dose; ED, for x% of the population; NOEC : No Observed Effect Concentration; HRM : Hormone level; BCM₁ : biochemical effect in the liver for which endpoint is vitamin A level (VITA) or certain protein level (prot); HST_{1-cell.abn.}: histological effect for which endpoint is liver cell abnormality; GRO_{bw} : growth for which endpoint criterion is body weight; GRO_{ow} : growth for which endpoint criterion is an organ weight; ENZ : Enzyme(s) induction/inhibition. *: endpoint for which value is reported (when several endpoints observed and different EC/NOEC). *Italics* : endpoints which are usually not considered as acceptable for risk assessment purposes.

^b EC/NOEC : value can be reported specifically for females (f) or for males (m).

^c Expo. Conc. : Concentration of the substance to which organisms were exposed during the test.

^d nr : information not reported; na : not applicable; O : oral exposure ; D : dietary exposure ; G : exposure *via* gavage ; N : only nominal concentrations in food are reported; M : analysis of dietary substances was carried out and measured concentrations are ≥80% of nominal concentrations.

^e RI : Reliability Index (Klimish *et al.*, 1997); 1 :Valid without restriction; 2 :Valid with restriction; 3 :Not reliable; 4 :Not assignable.

^f Information on methodology was not available (RI=4) or could not be validated according to OECD guidelines (RI=3) but test was considered as « acceptable » given that it is used in RIVM report (RIVM, 1999).

^g NOEC is in this test is the highest concentration tested.

^h NOEC is in this test is the lowest concentration tested.

Many of the tests realised on rats have been led on female and male separately. For those tests, the lowest value (most of the time data on female) has been reported so as to consider the worst case. Unfortunately, those data are not usable for comparison of differences with sex because for almost all of them, NOECs were reported as “superior to”, that is to say being the highest concentrations tested.

4.2.4. Thresholds of no effect

Thresholds of no effect for pelagic organisms

There is fairly not enough *valid* ecotoxicity data to derive any thresholds of no effect for the marine environment, considering pelagic compartment.

Thresholds of no effect for benthic organisms

Given that absolutely no valid data are available in the literature, it is not possible to derive a thresholds of no effect of PCBs for benthic organisms. Moreover, data obtained for pelagic organisms are not sufficiently reliable to be used for derivation in sediments *via* the equilibrium partitioning method.

Thresholds of no effect for marine top predators

Concerning secondary poisoning, there is neither enough data for PCB 105 nor PCB 156 to derive thresholds of no effect. On the other hand, 5 ecotoxicity data are reported in Table 4.2.3-2 for PCB 118. Therefore, a Predicted No Effect Concentration for marine top predators ($PNEC_{oral}$) can be *proposed*.

Data reported from MacLellan *et al.* (1994) does not refer to a classical ecotoxicity endpoint but to liver cell abnormality which is a histological endpoint. For this reason, it was decided not to take it into account to derive thresholds for top predators. The NOEC reported for the 13 weeks dietary exposure of male and female rats to PCB 118 is related to growth endpoint, the criteria of which is body weight. As the methodology of this test was shown to be almost validated, it seems appropriate to take it into account for the derivation of the $PNEC_{oral}$, dividing it by an assessment factor (AF) of 90, according to the procedure described in the TGD (European Commission, 2003) :

$$PNEC_{oral} = 0.1 \text{ (mg/kg}^{-1} \text{ food ww.)} / 90 = 0.0011 \text{ mg.kg}^{-1} \text{ food ww.} = 1.1 \text{ } \mu\text{g.kg}^{-1} \text{ food ww.}$$

This value shall not be taken as a reliable threshold because the dataset is poor and data are not consistent between each others: LOEC reported by MacLellan *et al.* (1994) differs from a factor of 100 compared to NOEC reported by Chu *et al.* (1995).

In the RIVM report (RIVM, 1999) an important list of available bioconcentration factors (BCF) and biomagnification factors (BMF) is indicated that could be used to have an idea of the corresponding thresholds of no effect for marine predators in water.

- BCF_{lab} for fish: 59,000 (Opperhuizen and Jongeneel, 1986), crustaceans: 26,000 (Dillon *et al.*, 1990)
- BCF_{field} for filtrating molluscs = $4 \cdot 10^6 - 1.3 \cdot 10^7$ (Delft Hydraulics, 1995)
- BMF_{lab} = 6 (Fisk *et al.*, 1998)
- BMF_{field} = 7 – 35 (Leonards *et al.*, *subm.*; Smit *et al.*, 1996)

Applying a worst case, highest BCF of $1.3 \cdot 10^7$ and highest BMF of 35 shall be used :

$$PNEC_{oral, water} = PNEC_{oral} \text{ (mg.kg}^{-1} \text{ ww.)} / [BCF \times BMF] = 0.0011 / [1.3 \cdot 10^7 \times 35] = 2.4 \cdot 10^{-3} \text{ } \mu\text{g.L}^{-1}$$

Overall threshold of no effect for marine environment

Thresholds of no effect for marine top predators are the only one that could be derived ($1.1 \text{ } \mu\text{g.kg}^{-1}$ food ww.) and it is not a reliable value. As a matter of fact, it is very different from regulatory values, e.g. 8 – 12 pg.kg^{-1} food ww. in fish and crustaceans consumed by human (Regulation 199/2006/CE^a)

On the other hand the corresponding value in water obtained according to application of the worst case is far lower than water quality criteria reported in the literature : in USA, water quality criteria for PCBs is 30 ng.L^{-1} (US-EPA, 1980) and in Canada it is 10 ng.L^{-1} (CDWR, 1995)^b.

In conclusion, toxicity data which are available in the literature nowadays are not in sufficient number and reliable enough to derive a relevant threshold of no effect for the marine environment.

Other questions are not dealt with in the present study because it is not clearly stated how to take them into account in environmental risk assessment methodology (e.g. indirect toxic effects such as mutagenicity and cancerogenicity). Those questions have to be raised and answered to reach an appropriate result and derive thresholds of ecological relevancy for PCBs.

^a Commission Regulation (EC) No 199/2006 of 3 February 2006 amending Regulation (EC) No 466/2001 setting maximum levels for certain contaminants in foodstuffs as regards dioxins and dioxin-like PCBs

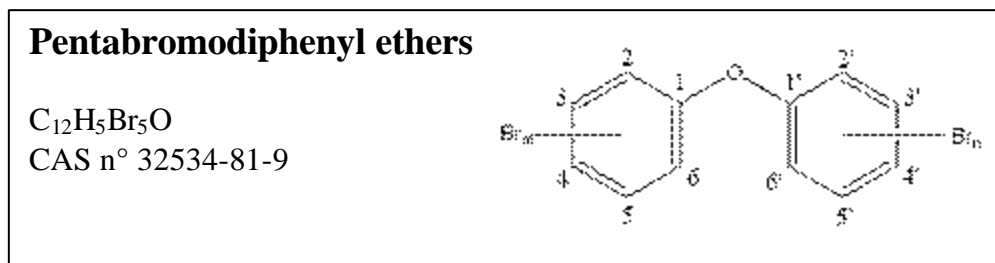
^b Guidelines was updated in 2005 and it was decided to withdraw this value. In fact, as environmental exposure is considered to occur predominantly *via* sediment, soil, and/or tissue, it was considered not relevant to keep this value in water and to refer to the respective guidelines for these media.

4.3. Pentabromodiphenyl ethers (PBDEs)

Data indicated in this report have been mostly extracted from the finalized Risk Assessment Report published of the European Union (EU-RAR) (European Commission, 2000).

4.3.1. General issues, physico-chemical characteristics and behaviour in the marine environment

Figure 4.3.1-1 : CAS number, structural features and chemical formula of PBDEs.



Chemicals considered

Brominated flame retardant available commercially are mixtures of diphenyl ethers with varying degrees of bromination. This is therefore the case of the product referred as "pentabromodiphenyl ethers" (PBDEs) and studied in this report which is not a pure substance but a mixture of congeners, (which may be grouped to homolog classes, while each class contain different isomers). The term pentabromodiphenyl ether denotes the main component of the mixture. The specification of the commercial product referred as "pentabromodiphenyl ether" may vary but is generally 50-62% w/w of pentabromodiphenyl ether (CAS No 32534-81-9), 24-38% w/w of tetrabromodiphenyl ether (CAS No 40088-47-9), 4-12% w/w of hexabromodiphenyl ether (CAS No 36483-60-0), 0-1% w/w of tribromodiphenyl ether (CAS No 49690-94-0) and traces of w/w of heptabromodiphenyl ether (CAS No 68928-80-3).

No ecotoxicity data could be found testing the pure substance. Therefore, the term "pentabromodiphenyl ethers" and the abbreviation "PBDEs" will be used in this report to refer to the commercially available product. Percentages will be specified where possible.

Table 4.3.1-1 : Physico-chemical characteristics of PBDEs influencing their behaviour in the marine environment.

Properties	Remarks	Values	References
Molecular weight (g.mol⁻¹)	with 70.8% bromine by weight	564.7	-
Water solubility (mg.L⁻¹)	commercial product, 25°C pentaBDE component, 25°C tetraBDE component, 25°C	13.3 10 ⁻³ 2.4 10 ⁻³ 10.9 10 ⁻³	(Stenzel and Markley, 1997)
log K_{OW}	commercial product, measured	6.57	(MacGregor and Nixon, 1997)
Vapour pressure (Pa)	comm. product, 21°C	4.65 10 ⁻⁵	(Stenzel and Nixon, 1997)
Henry Constant (Pa.m³.mol⁻¹)	calculated from vapour pressure	11	-
log K_{OC} (L.kg⁻¹)	calculated from logK _{OW}	5.42	-

Physico-chemical properties of the PBDEs are determined by their structural features, that is to say to some extent by the number of bromine atoms and their substitution pattern on the main ring structure.

The parameters influencing these physico-chemical properties are reported in Table 4.3.1-1. The low vapour pressure of PBDEs indicates that they are unlikely to volatilize from spillage to land whereas their low water solubility indicates that their volatilisation from solution may still be significant. However, partition coefficients between octanol and water on one hand and organic carbon and water on the other hand, permit to assume that PBDEs will not be found in great concentrations in the water column but more likely in sediments and fatty tissues of aquatic organisms where they highly bioconcentrate.

4.3.2. *Toxicological properties*

Acute toxicity

Chronic toxicity

The main effects of repeated dose exposure to PBDEs appear to be on the liver.

PBDEs have been shown to cause significant induction of EthoxyResorufin-O-Deethylase (EROD), MethoxyResorufin-O-Deethylase (MROD) and PentoxyResorufin-O-Deethylase (PROD) activities (Hallgren and Darnerud, 1998).

Effects on the thyroid hormonal system have also been shown. For example, it was demonstrated using phenobarbital induced rat liver microsomes that metabolites of certain lower brominated diphenyl ethers can undergo competitive binding with thyroxin (T₄) to transthyretin (Bergman *et al.*, 1997; Sinjari *et al.*, 1998). A similar study (Meerts *et al.*, 1998) reported that some of the lower brominated diphenyl ethers, including some PBDEs congeners, can give rise to strong (specifically 2,2',4,4',6-pentabromodiphenyl ether) or slight competitive binding to human transthyretin after incubation with phenobarbital induced rat liver microsomes.

This competitive binding with thyroxin indicates that metabolites of some of the lower brominated diphenyl ethers may have potential to cause endocrine disturbing effects in wildlife (Bergman *et al.*, 1997).

4.3.3. *Effects on organisms*

Ecotoxicity data issued from valid bioassays testing PBDEs are not so numerous.

Data reported thereafter do not represent an exhaustive list of ecotoxicity data for PBDEs but the data which could be considered as relevant for risk assessment purposes for the marine environment.

Effects on pelagic organisms

Few valid ecotoxicity data of PBDEs to pelagic organisms can be cited from the EU-Risk Assessment Report (European Commission, 2000). Actually, 5 data which are "valid" or "valid with restrictions" are reported in Table 4.3.3-1 : one reported from a chronic algae test, two reported from tests on crustacean (one acute and one chronic test) and also two reported from tests on fish (also one acute and one chronic test). Other data reported in EU-RAR are not reported in Table 4.3.3-1 because they were considered as not reliable.

Table 4.3.3-1 : Acute and chronic toxicity to pelagic organisms

Taxa	Species ^c	EC type ^d	EC/NOEC value (µg.L ⁻¹)	Expo. Conc. ^e (µg.L ⁻¹)	Expo. Type ^f	RI ^g	References
Algae	<i>Selenastrum Capricornutum</i> (FW)	EC ₁₀ (24h) GRO _b	2.7 ^h	At t ₀ : 1.7, 3.1, 5.9, 12, 26	S/M 54.6% PBDEs	2	(Palmer <i>et al.</i> , 1997a)
Invertebrates Crustaceans	<i>Daphnia magna</i> (FW)	EC ₅₀ (48h) NOEC (48h) MOR	14 ⁱ 4.9	At t ₀ : 1.2, 2.4, 4.9, 9.1, 20	C/M 54.6% PBDEs	2 ^j	(Palmer <i>et al.</i> , 1997b)
		NOEC (21d) GRO	5.3	At t ₀ : 1.4, 2.6, 5.3, 9.8, 20	C/M 54.6% PBDEs	1	(Drottar and Krueger, 1998)
Fish	<i>Oncorhynchus mykiss</i> (FW)	LC ₅₀ (96h) NOEC (96h) MOR	> 21 ⁱ	1.1, 2.3, 3.9, 7.8, 21	C/M 54.6% PBDEs	2	(Palmer <i>et al.</i> , 1997c)
		NOEC (87d) ELS	≥8.9	Over the test : 1.2, 2.5, 4.0, 8.9, 16	C/M 55.1% PBDEs	1	(Wildlife International, 2000a)

^c FW : fresh water organisms.

^d EC : Effect Concentration; LC : Lethal concentration; EC_{50/10} (LC₅₀) : EC(LC) for 50/10% of the population; NOEC : No Observed Effect Concentration; GRO : growth; MOR : mortality; ELS : diverse endpoints observed during early life stage.

^e Expo. Conc. : Concentration of the substance to which organisms were exposed during the test.

^f S : static exposition; R : renewal exposition; C : continuous/flow-through exposition; N : EC/NOEC value based on nominal concentrations; M : EC/NOEC value based on measured concentrations; O : open vessel; Cl : closed vessel.

^g RI : Reliability Index (Klimish *et al.*, 1997); 1 : Valid without restriction; 2 : Valid with restriction; 3 : Not reliable; 4 : Not assignable.

^h No effect were seen at 96h, whatever concentration.

ⁱ Values higher than solubility of commercial product in water.

^j Effects seen could have been due to physical impairment rather than to direct toxic effect.

Effects on benthic organisms

Three valid long-term data are available for testing of sediment toxicity of PBDEs on benthic organisms.

Table 4.3.3-2 : Acute and chronic toxicity of PBDEs to benthic organisms

Taxa	Species ^a	EC type ^b	EC/NOEC value (mg.kg ⁻¹ dw)	Expo. Conc. ^c (mg.kg ⁻¹ dw)	Expo. Type ^d	RI ^e	References
Invertebrates Annelids	<i>Lumbriculus variegatus</i>	NOEC (28d) REP, GRO	3.1	3.1, 6.3, 13, 25, 50 (N) OM <2%	C/N (M) 55.1% PBDEs	2	(Wildlife International, 2000d)
Crustaceans	<i>Hyalella azteca</i> (FW)	NOEC (28d) MOR, GRO	6.3	3.1, 6.3, 13, 25, 50 (N) OM <2%	C/N (M) 55.1% PBDEs	2	(Wildlife International, 2000b)
Insects	<i>Chironomus riparius</i> (FW)	NOEC (28d) MOR, DVP, EMG	28	3.1, 6.3, 13, 25, 50 (N) OM <2%	C/M 55.1% PBDEs	2	(Wildlife International, 2000c)

^a FW : fresh water organisms.

^b LC₅₀ : Lethal Concentration for 50% of the population; NOEC : No Observed Effect Concentration; MOR : mortality; REP : reproduction; EMG : emergence of larvae.

^c Expo. Conc. : Concentration of the substance to which organisms were exposed during the test. Concentrations are expressed as nominal (N) concentrations. n=number of exposure concentrations apart from controls. OM : Organic Matter content.

^d M : EC/NOEC value based on measured concentrations. N (M) : Concentrations were measured during the test but LC value is based on nominal concentrations because approximately no loss of chemicals occurred in the whole system.

^e RI : Reliability Index (Klimish *et al.*, 1997); 1 : Valid without restriction; 2 : Valid with restriction; 3 : Not reliable; 4 : Not assignable.

Effects on top predators : secondary poisoning

All data reported in top predators are extracted from the Risk Assessment Report of the European Union (European Commission, 2000).

Table 4.3.3-3 : Toxicity of PBDEs to mammalian species

Species	EC type ^a	EC/NOEC value ^b (mg.kg ⁻¹ food, ww.)	Expo. Conc. ^c (mg.kg ⁻¹ food, ww.)	Expo. Type ^d	% PBDEs	RI ^e	References
Rat	LD50 (acute) MOR	> 2000 (fm)	Up to 10 000	O-DG/nr	CP, %nr	uk	(Luneval Products Ltd., 1977)
							(Great Lakes Chemical Corporation, 1975)
							(Ethyl Corporation, 1984)
							(I.S.C. Chemicals Ltd., 1977a) (I.S.C. Chemicals Ltd., 1977b)
							(von Meyerinck <i>et al.</i> , 1990)
							(Fowles <i>et al.</i> , 1994)
Rat	NOEC (28d) MOR, FDC, GRO _{bw} GRO _{ow} HST _t	≥1000 (fm) 100 (fm) < 100 (fm)	0, 100, 1000	O-D/nr	CP, %nr	1	(Great Lakes Chemical Corporation, 1976)
	NOEC (90d) MOR, GRO _{bw} GRO _{ow} BCM _{chol, prot} , HRM _{T4*, T3} HST	≥100 (fm) 2-10 (fm) 2 (fm) 2 (f), <2 (m)	0, 2, 10, 100	O-D/nr	CP, %nr	1	(Great Lakes Chemical Corporation, 1984)
	NOEC (30d) MOR, GRO _{bw} , FDC, BEH, HST, BCM	≥10 (fm)	0, 0.1, 0.5, 1, 5, 10	O-D/nr	CP, %nr	1	(Great Lakes Chemical Corporation, 1985)
Rat	NOEC (90d) ENZ	< 8.8	0, 8.8, 2000	O-nr/nr	CM	uk	(Carlson, 1980)
Mouse	ED ₆₀₋₇₀ (14d) GRO HRM, IMM	<150 ^f -600 ^g 600	0, 150, 300, 600	O-nr/nr	CP, %nr	4	(Fowles <i>et al.</i> , 1994)
Mouse	NOEC (14d) IMM	150	0, 150, 300	O-nr/nr	CP, %nr	4	(Darnerud and Thuvander, 1998)

^a LD : lethal dose ; ED : effect dose; ED_x/LD_x for x% of the population; NOEC : No Observed Effect Concentration; MOR : mortality; FDC : Feeding Consumption; GRO_{bw} : growth for which endpoint criterion is body weight; GRO_{ow} : growth for which endpoint criterion is organ weight; HST_t : Histological effect (t_h: on thyroid gland); BCM₁ : biochemical effect in the liver for which endpoint is vitamin A level (VITA) or certain protein level (prot) ; HRM : Hormone levels (T4 and/or T3); ENZ : Enzyme(s) induction/inhibition, IMM : immunological effect. *: endpoint for which value is reported (when several endpoints observed and different EC/NOEC). *Italics*: endpoints which are usually not considered as acceptable for risk assessment purposes.

^b EC/NOEC : value can be reported for both sex, or specifically for females (f) or for males (m).

^c Expo. Conc. : Concentration of the substance to which organisms were exposed during the test.

^d O : oral exposure ; D : dietary exposure ; G : exposure *via* gavage ; nr : information on analysis of dietary substances not reported.

^e RI : Reliability Index (Klimish *et al.*, 1997); 1 : Valid without restriction; 2 : Valid with restriction; 3 : Not reliable; 4 : Not assignable, uk : information given in EU-RAR was not sufficient enough to estimate RI.

^f Relative liver weight

^g Total body weight, Relative spleen weight

Overall, the results of studies cited in Table 4.3.3-3 and led on dietary toxicity in rats and mice demonstrate that the liver is the key organ affected by PBDEs. The effects observed include marked increase liver weight associated with cytoplasmic changes, together with disturbances in porphyrin and cholesterol synthesis. Indirect consequences of induction of liver enzymes are also observed: hyperplasia and decrease of thyroid hormone (T4) levels. Finally, even though sexes were differentiated most of the time in studies cited, there does not seem to be a specific trend leading to marked differences in toxicology between sexes.

4.3.4. *Thresholds of no effect*

Thresholds of no effect for pelagic organisms

Long-term NOECs are available for fish, crustaceans and algae. The lowest value NOEC issued from a 21 day reliable chronic test is $5.3 \mu\text{g}\cdot\text{L}^{-1}$ (Drottar and Krueger, 1998). Results available for the algal test are difficult to interpret but indicate that effects on green algae are likely to occur for similar concentrations of PBDEs.

According to TGD (European Commission, 2003), the recommended assessment factor to apply to this NOEC value for saltwater organisms is 100.

$$\text{PNEC}_{\text{seawater}} = 5.3 (\mu\text{g}/\text{L}^{-1}) / 100 = 0.053 \mu\text{g}\cdot\text{L}^{-1}$$



Threshold of no effect for marine pelagic organisms = $53 \text{ ng}\cdot\text{L}^{-1}$

Thresholds of no effect for benthic organisms

Three chronic freshwater values are available for derivation of PNEC for marine benthic organisms ($\text{PNEC}_{\text{marine sediment}}$), issued from tests carried out on species which represent different living and feeding conditions. According to the TGD, an assessment factor of 50 can thus be chosen for the derivation of the PNEC for benthic organisms. Moreover, *‘for soil organisms, the NOEC should be normalised to the standard organic matter of soil [...]. This normalisation is not suggested in the TGD for NOEC from sediment tests, but, in principle, it seems sensible to carry out such a normalisation assumes that the toxicity seen is due to the chemical present in porewater of the soil and sediment.[...]. The actual organic carbon contents of the sediments used in the tests are unknown. [...] The test reports indicates that the organic carbon contents of the sediments used was <2% in each test. Since organic matter content are usually very approximately two times higher than the organic carbon contents, this would imply that the organic contents of the sediment used were very low at <1%. Assuming this value and the standard organic carbon content of sediment to be 5%’* according to the TGD, the lowest $\text{NOEC}_{\text{standard}}$ should then be 5 times the NOEC reported in Table 4.3.3-2.

Among them, the 28 day NOEC of $3.1 \text{ mg}\cdot\text{kg}^{-1} \text{ dw}$ obtained for *Lumbriculus variegatus* is the lowest one. Therefore, the equivalent $\text{NOEC}_{\text{standard}}$ is considered to be $15.5 \text{ mg}\cdot\text{kg}^{-1} \text{ dw}$:

$$\text{PNEC}_{\text{marine sediment}} = 15.5 (\text{mg}/\text{kg}^{-1} \text{ dw}) / 50 = 0.31 \text{ mg}/\text{kg}^{-1} \text{ dw}$$



Threshold of no effect for marine benthic organisms = $310 \mu\text{g}\cdot\text{kg}^{-1} \text{ dw}$

Thresholds of no effect for marine top predators

It has clearly been demonstrated that the main effects of repeated dose exposure to PBDEs appear to be on liver. Based on mammalian toxicity data, the NOEC determined as the more relevant one for secondary poisoning is thus issued from the 30 day reliable study run on male and female rats by Great Lakes Chemical Corporation (1985), that is to say 10 mg.kg⁻¹ of food. The PNEC_{oral} will therefore be estimated from this NOEC.

As it is not very clear why an assessment factor of 10 was chosen in the Risk Assessment Report of the European Union (European Commission, 2000), it was decided not to follow this decision but to consider as appropriate to apply an assessment factor of 300 – as recommended in the TGD (European Commission, 2000) for the derivation of a PNEC from a result of a 28 day (*ca.* 30 day) repeated dose study – and to divided it by 10, given that the NOEC chosen for the derivation represents the most sensitive toxicological endpoint seen in a range or repeated dose studies. Finally, it seems that an assessment factor of 30 may then be the most appropriate :

$$\text{PNEC}_{\text{oral}} = 10 \text{ (mg/kg}^{-1} \text{ food ww.)} / 30 = 0.333 \text{ mg.kg}^{-1} \text{ food ww.}$$



Threshold of no effect for marine top predators = 333 μg.kg⁻¹ food ww.

Overall threshold of no effect for the marine environment

Thresholds of no effect are available for the three compartments considered: pelagic and benthic organisms as well as marine top predators.

The **PNEC_{seawater} is 53 ng.L⁻¹**.

To compare them, values have to be derived in the same unity.

- Derivation of **PNEC_{marine sediment}** in water :

Taking into account a K_{OC} of approximately 26327 L.kg⁻¹, the corresponding value of the PNEC_{marine sediment} of 0.31 mg.kg⁻¹ permits to calculate a corresponding value in water of **61.3 ng.L⁻¹**.

- Derivation of **PNEC_{oral} in water** :

Several studies led on the accumulation of PBDEs in aquatic species have shown that bioaccumulation of this chemical is important (European Commission, 2000). The value retained for calculations was a BCF for fish of approximately 27400 L.kg⁻¹. Dividing the PNEC_{oral} of 333 μg.kg⁻¹ ww by this factor, the corresponding value obtained in water (PNEC_{oral, water}) is **12.2 ng.L⁻¹**.

Comparing those three data all together, it seems that the most protective threshold is the one obtained with marine top predators. Therefore, it is decided to consider this threshold as the overall threshold for the marine environment.



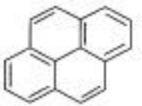
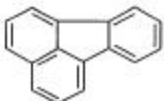
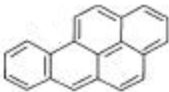
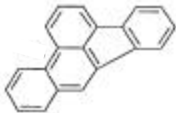
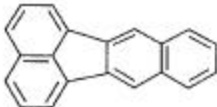

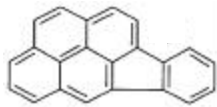
Overall threshold of no effect for marine environment for PeBDE :

- 333 μg.kg⁻¹ in marine organisms (wet weight)
- ~ 12.2 ng.L⁻¹ in water

4.4. Properties common to PAHs

4.4.1. General issues, physico-chemical characteristics and behaviour in the marine environment

Figure 4.4.1-1 : CAS numbers, structural features, chemical formula and physico-chemical characteristics of PAHs influencing their behaviour in the marine environment

		Sol.W. (25°C) ($\mu\text{g.L}^{-1}$)	logK _{ow}	V _p (25°C) (mPa)	H (Pa.m ³ .mol ⁻¹)	logK _{oc} (L.kg ⁻¹)
Pyrene C ₁₆ H ₁₀ CAS n° 129-00-0 MW = 202.3 g.mol ⁻¹		105-150	4.80-5.20	0.2-4.9	0.9-2	4.22-5.65
Fluoranthene C ₁₆ H ₁₀ CAS n° 206-44-0 MW = 202.3 g.mol ⁻¹		166-283	4.70-5.33	0.2-8.6	0.1-1.1	4.62-5.40
Benzo[a]pyrene C ₂₀ H ₁₂ CAS n° 50-32-8 MW = 252.3 g.mol ⁻¹		1.2-4.7	5.78-6.57	~ 0.0007	0.009-0.056	5.48-6.74
Benzo[b]fluoranthene C ₂₀ H ₁₂ CAS n° 205-99-2 MW = 252.3 g.mol ⁻¹		1.5	6.06-6.57	0.021-0.067	1.2	5.70-5.74
Benzo[k]fluoranthene C ₂₀ H ₁₂ CAS n° 207-08-9 MW = 252.3 g.mol ⁻¹		0.7-0.8	6.06-6.85	0.0129-0.00128	0.016-0.043	5.74-6.89
Benzo[g,h,i]perylene C ₂₂ H ₁₂ CAS n° 191-24-2 MW = 276.3 g.mol ⁻¹		0.22-0.29	6.22-7.23	~ 0.00001	0.015-0.027	6.20-6.26
Indeno[1,2,3-c,d]pyrene C ₂₂ H ₁₂ CAS n° 193-39-5 MW = 276.3 g.mol ⁻¹		0.05	6.58-7.66	< 0.00001	0.029	6.20-7.40

Due to their concern for adverse effects to human health and the environment, PAHs are widely studied contaminant. Thus, reliable sources of information describing chemical properties of PAHs are numerous. For this reason, for easiness, and also because describing physico-chemical properties of contaminant is not the main aim of this report, it was decided not to cite all original references as usually done but to refer to MacKay *et al.* Handbook (Mackay *et al.*, 2000) as a unique source of information.

Physico-chemical properties are mainly determined by the conjugated alpha-electron systems, which vary fairly regularly with the number of rings and molecular mass, giving rise to a more or less wide range of values for each parameter.

All PAHs have very low solubility in water whereas PAHs are soluble in many organic solvents (IARC, 1983; Lide, 1991). Solubility in water tends to decrease with increasing molecular mass as does their vapour pressure (varying by more than 10 orders of magnitude), but they are considered to be low anyway. Therefore, it can be considered that PAHs will not be found in great concentrations in the water column and it could be expected that they will highly bioconcentrate in sediments and in fatty tissues of aquatic organisms. However, it is not so clear whether these substances bioaccumulate or not. Indeed, PAHs have been reported to bioaccumulate in invertebrates (Cid Montañes *et al.*, 1995; van Hattum *et al.*, 1998), while they undergo biotransformation and/or excretion in birds and mammals.

4.4.2. *Toxicological properties*

Acute toxicity

PAH are expected to have low acute toxicity (Kalf *et al.*, 1995).

Chronic toxicity

It is known that many possible processes can lead to the formation of reactive PAHs metabolites and/or intermediates, that may be highly toxic, mutagenic or carcinogenic (Neff, 1985).

For example, PAHs can be transformed by light induced (photo)oxidation. Polycyclic aromatic hydrocarbons phototoxicity is caused by the absorbance and transfer of UV radiation energy from the excited state of the PAH compound to molecular oxygen, thereby forming excited single state molecules that may damage tissues directly or cause redox cycling and subsequent cell death (Ankley *et al.*, 1994; Ankley *et al.*, 1995; Landrum *et al.*, 1986; Newsted and Giesy, 1987; Oris *et al.*, 1984). Therefore, this process of phototoxicity is a function of the chemical, but is also dependent of the capacity of organisms to bioaccumulate it.

The existence of such phenomenon has led RIVM to establish criteria of how to deal with literature concerning phototoxic effects in their report dealing with Integrated Environmental Quality Objectives for PAHs (Kalf *et al.*, 1995). In this report, it is stated that "*most toxicity studies found in the literature are performed under standard laboratory conditions*" where "*animals are exposed to light regimes of 12h:12h or 16h:8h light:dark and light sources like bulbs or fluorescent lamps*". As phototoxicity phenomenon are very likely to happen also in the actual environment, it was decided in this report to validate tests for which:

- light regime used in the test is as much as possible comparable with natural conditions (duration of light:dark exposure, intensity of light)
- light source used in the test provides visible light, UV-A and/or UV-B as close as possible as natural conditions
- incubation of PAH during a pre-incubation period in the dark is allowed but incubation time has to be mentioned.

In the present report, it was decided to stick as close as possible to these criteria established by RIVM in their report for validation of study.

PAHs are also known to be subject of biological transformations, *via* the cytochrome P-450 Mixed Function Oxidase System (MFO system). These transformations may also lead to generate highly toxic metabolites, sometimes more toxic than parent compounds.

Carcinogenicity and mutagenicity

Some report have demonstrated that action of the MFO system may lead to transformation of PAHs to metabolites which may bind to cellular macromolecules such as DNA, RNA and protein (Neff, 1985) possibly causing mutagenic and/or carcinogenic effects.

Benzo[a]pyrene is classified in **Group 2A** by IARC, as ‘*probably carcinogenic to humans*’ (IARC, 1983). In fact, IARC reports that there is “*limited evidence of carcinogenicity*” in humans and “*sufficient evidence of carcinogenicity*” in experimental animals.

Benzo[b]fluoranthene, Benzo[k]fluoranthene and Indeno[1,2,3-cd]pyrene are classified in **Group 2B** by IARC, as “*possibly carcinogenic to humans*” (IARC, 1983). In fact, IARC reports that there is “*inadequate evidence of carcinogenicity*” in humans but there is “*sufficient evidence of carcinogenicity*” in experimental animals.

Benzo[g,h,i]perylene, Fluoranthene, Pyrene **Group 3** are classified as “*not classifiable as to its carcinogenicity to humans*” (IARC, 1983) because the evidence of carcinogenicity is “*inadequate*” in humans and “*inadequate*” or “*limited*” in experimental animals.

Carcinogenic effects are observed at the individual levels but there occurrence and possible consequences on populations are not well known for the moment. This is the reason why such effects are not taken into account in datasets and derivation of thresholds for the marine environment.

4.5. Pyrene

4.5.1. Effects on organisms

Effects on pelagic organisms

Acute and chronic ecotoxicity data are available for freshwater and marine algae and crustaceans but absolutely no valid data is reported for fish.

Table 4.5.1-1 : Acute toxicity of Pyrene to pelagic organisms

Taxa	Species ^a	EC type ^b	EC/NOEC value ^c ($\mu\text{g.L}^{-1}$)	Expo.Conc. ^d ($\mu\text{g.L}^{-1}$)	Expo. Type ^e	RI ^f	References
Invertebrates Molluscs	<i>Mulinia lateralis</i> (SW) (embryos)	LC ₅₀ (96h) MOR	1.09 (UV) 58.8	0, 1, 3, 10, 30, 100 (UV) (N) 0, 10, 100, 1000, 10000, 20000 (N)	S/M	1	(Pelletier <i>et al.</i> , 1997)
	<i>Utterbackia imbecillis</i> (FW)	LC ₅₀ (24h) MOR	2.63 (UV) > 28.2	5.3, 8.0, 12.6, 19.3 (M)	R/M	1	(Weinstein and Polk, 2001)
Crustaceans	<i>Daphnia magna</i> (FW)	LC ₅₀ (48h) MOR	24.6	nr (n>4)	S/M	1	(Bisson <i>et al.</i> , 2000)
		EC ₅₀ (24h) IMM	> 1024 5.7 (UV)	nr	nr	4	(Wernersson and Dave, 1997)
		EC ₅₀ (48h) IMM	3–30 (UV) 29.2–54.8 (D)	0.01 – 41.7 (n=7) 0.1 – 99.0 (n=6)	S/N	2	(Nikkila <i>et al.</i> , 1999)
	<i>Mysidopsis bahia</i> (SW)	LC ₅₀ (48h) MOR	5.32 (UV) 63.8	0, 1, 3, 10, 30, 100 (UV) (N) 0, 10, 100, 1000, 10000, 20000 (N)	S/M	1	(Pelletier <i>et al.</i> , 1997)

^a FW : fresh water organisms.

^b EC : Effect Concentration; LC : Lethal concentration; EC_{50/10} (LC₅₀) : EC(LC) for 50/10% of the population; NOEC : No Observed Effect Concentration; GRO : growth; MOR : mortality; ELS : diverse endpoints observed during early life stage.

^c UV : exposure carried out under UV radiations ; D : exposure carried out in the dark.

^d Expo.Conc. : Concentration of the substance to which organisms were exposed during the test. Concentrations can be expressed as nominal (N) or measured (M) concentrations. n=number of exposure concentrations apart from controls.

^e S : static exposition; R : renewal exposition; C : continuous/flow-through exposition; N : EC/NOEC value based on nominal concentrations; M : EC/NOEC value based on measured concentrations; O : open vessel; Cl : closed vessel.

^f RI : Reliability Index (Klimish *et al.*, 1997); 1 :Valid without restriction; 2 :Valid with restriction; 3 :Not reliable; 4 :Not assignable.

Table 4.5.1-2 : Chronic toxicity of Pyrene to pelagic organisms

Taxa	Species ^a	EC type ^b	EC/NOEC value ($\mu\text{g.L}^{-1}$)	Expo. Conc. ^c ($\mu\text{g.L}^{-1}$)	Expo. Type ^d	RI ^e	References
Algae	<i>Pseudokirchneriella subcapitata</i> (FW)	EC ₁₀ (72h) GRO _b	1.2	nr (n>4)	S/M	1	(Bisson <i>et al.</i> , 2000)
Invertebrates Crustaceans	<i>Ceriodaphnia dubia</i> (FW)	EC ₁₀ (7d) REP	2.1	nr (n>4)	R/M	1	(Bisson <i>et al.</i> , 2000)

^a FW : fresh water organisms.

^b EC : Effect Concentration; LC : Lethal concentration; EC_{50/10} (LC₅₀) : EC(LC) for 50/10% of the population; NOEC : No Observed Effect Concentration; GRO : growth; MOR : mortality; ELS : diverse endpoints observed during early life stage.

^c Expo. Conc. : Concentration of the substance to which organisms were exposed during the test.

^d S : static exposition; R : renewal exposition; C : continuous/flow-through exposition; N : EC/NOEC value based on nominal concentrations; M : EC/NOEC value based on measured concentrations; O : open vessel; Cl : closed vessel.

^e RI : Reliability Index (Klimish *et al.*, 1997); 1 :Valid without restriction; 2 :Valid with restriction; 3 :Not reliable; 4 :Not assignable.

Effects on benthic organisms

There is no data available in the literature issued from valid water sediment toxicity tests, reporting toxicity of sediment spiked with pyrene to benthic organisms.

Effects on top predators: secondary poisoning

Only one study is available for repeated dose-exposure of mammalian species to pyrene. This 90 day study carried out by US-EPA lead to a LOAEL of $125 \text{ mg.kg}^{-1}.\text{j}^{-1}$ and a NOAEL of $75 \text{ mg.kg}^{-1}.\text{j}^{-1}$ corresponding to a NOEC of 622.5 mg.kg^{-1} food according to conversion factors indicated in the TGD (European Commission, 2003) for mice.

Table 4.5.1-3 : Toxicity of Pyrene to mammalian species

Species	EC type ^a	EC/NOEC value ^b (mg.kg^{-1} food, ww.)	Expo. Conc. ^c (mg.kg^{-1} food, ww.)	Expo. Type ^d	RI ^e	References
Mouse	NOEC (90d) DYS ₂	622.5 (fm)	0, 622.5, 1037.5, 2075	O-G	4	(US-EPA, 1989)

^a LOEC : Low Observed Effect Concentration; NOEC : No Observed Effect Concentration; DYS₂ : renal dysfunctioning.

^b (fm) : value reported for both sex: females (f) and males (m).

^c Expo. Conc. : Concentration of the substance to which organisms were exposed during the test.

^d O : oral exposure ; G : exposure *via* gavage.

^e RI : Reliability Index (Klimish et al., 1997); 1 :Valid without restriction; 2 :Valid with restriction; 3 :Not reliable; 4 :Not assignable.

4.5.2. *Thresholds of no effect*

Thresholds of no effect for pelagic organisms

Acute toxicity data to pelagic organisms are solely available for one marine mollusc, marine and freshwater crustaceans (see Table 4.5.1-1) and long-term data are available for freshwater crustaceans and algae (see Table 4.5.1-2). As the taxa of fish is not represented at all in these datasets, it is not possible to state if the more sensitive species would be taken into account in the derivation of a threshold from such datasets.

Therefore, it is not reliable to derive a threshold of no effect of Pyrene based on data available at present.

Thresholds of no effect for benthic organisms

Given that absolutely no valid data are available in the literature, it is not possible to derive a threshold of no effect of pyrene for benthic organisms.

Thresholds of no effect for marine top predators

As only one data is available (see Table 4.5.1-3), lack of data is obvious and it is not possible to derive any threshold of no effect of Pyrene for top predators.

Overall threshold of no effect for the marine environment

Due to important lack of data, no reliable threshold of no effect can be derived.

4.6. Fluoranthene

4.6.1. Effects on organisms

Looking at short term data, no significant difference of sensitivity can be demonstrated between marine and freshwater organisms. Phototoxicity to UV radiation was observed in many of the tests reported above. Boese *et al.* (1997) have shown that this phenomenon can also be influenced by other parameters, such adaptation to high UV radiation. Therefore, in order to take this parameter into account correctly, species studied have to be chosen carefully.

Results issued from long term toxicity data reported in Table 4.6.1-1 are consistent between each other. Although marine data are lacking, it seems that no significant difference can be seen between marine and freshwater crustaceans. Occurrence of phototoxicity is still obvious for long term data.

Table 4.6.1-1 : Acute toxicity of Fluoranthene to pelagic organisms

Taxa	Species ^a	EC type ^b	EC/NOEC Value ^c (µg.L ⁻¹)	Expo. Conc. ^d (µg.L ⁻¹)	Expo. Type ^e	RI ^f	References
Algae	<i>Scenedesmus subspicatus</i> (FW)	EC ₅₀ (96h) GRO	12	nr	S/N	4	(Kördel <i>et al.</i> , 1981)
	<i>Selenastrum capricornutum</i> (FW)	EC ₅₀ (96h) GRO	54 400 ^g	nr	nr	4	(US-EPA, 1978)
	<i>Skeletonema costatum</i> (SW)	EC ₅₀ (96h) GRO	45 600 ^g	nr	nr	4	(US-EPA, 1978)
Invertebrates Hydrozoans	<i>Hydra americana</i> (FW)	LC ₅₀ (96h) MOR	2.2 (UV) 70	nr (n=5)	C/M	2	(Spehar <i>et al.</i> , 1999)
Annelids	<i>Stylaria lacustris</i> (FW)	LC ₅₀ (48h) MOR	> 220	nr (n=5)	S/M	2	(Suedel and Rodgers, 1996)
	<i>Neanthes arenaceodentata</i> (SW)	LC ₅₀ (96h) MOR	500 ^g	0,10,50,100,500,1000, 2500,5000	S/M	1	(Rossi and Neff, 1978)
Molluscs	<i>Mulinia lateralis</i> (SW) (embryos)	LC ₅₀ (96h) MOR	1.09 (UV) 58.8	0,1,3,10,30,100 (UV) (N) 0,10,10 ² , 10 ³ , 10 ⁴ , 2. 10 ⁴ (N)	S/M	1	(Pelletier <i>et al.</i> , 1997)
	<i>Mytilus edulis</i> (SW)	EC ₅₀ (9d) FIL	80	nr (n>4)	S/M	1	(Donkin <i>et al.</i> , 1989)
Crustaceans	<i>Ampelisca abdita</i> (SW)	LC ₅₀ (24h) MOR	>100	0,0.035,0.35,3.5,35,100 (N)	S/N	2	(Werner and Nagel, 1997)
		LC ₅₀ (96h) MOR	67	nr (n=5)	R/M	1	(Spehar <i>et al.</i> , 1999)
	<i>Corophium insidiosum</i> (SW, b)	EC ₅₀ (4d) BUR	20 (UV) 54	nr	R/M	2	(Boese <i>et al.</i> , 1997)
	<i>Daphnia magna</i> (FW)	LC ₅₀ (48h) MOR	1.6 (UV) 117	nr (n=5)	C/M	2	(Spehar <i>et al.</i> , 1999)
		LC ₅₀ (10d) MOR	102.6	nr (n=6)	S/M	2	(Suedel and Rodgers, 1996)
		EC ₅₀ (48h) nr	45	nr	nr/M	4	(Oris <i>et al.</i> , 1991)
	<i>Emerita analoga</i> (SW)	EC ₅₀ (96h) BUR	74 (UV) 73	nr	R/M	2	(Boese <i>et al.</i> , 1997)
<i>Eohaustorius estuarius</i> (SW)	EC ₅₀ (96h) BUR	7 (UV) >70	nr	R/M	2	(Boese <i>et al.</i> , 1997)	

^a FW : fresh water organisms; SW : marine and estuarine organisms; b : benthic organisms.

^b EC : Effect Concentration; LC : Lethal concentration; EC_{50/10} (LC₅₀) : EC(LC) for 50/10% of the population; NOEC : No Observed Effect Concentration; GRO : growth; MOR : mortality; FIL : inhibition of filtration capacity; BUR : inhibition of burrowing capacity.

^c UV : exposure carried out under UV radiations.

^d Expo.Conc. : Concentration of the substance to which organisms were exposed during the test. Concentrations can be expressed as nominal (N) or measured (M) concentrations. n=number of exposure concentrations apart from controls.

^e S : static exposition; R : renewal exposition; C : continuous/flow-through exposition; N : EC/NOEC value based on nominal concentrations; M : EC/NOEC value based on measured concentrations.

^f RI : Reliability Index (Klimish *et al.*, 1997); 1 : Valid without restriction; 2 : Valid with restriction; 3 : Not reliable; 4 : Not assignable.

^g Effect concentration above chemical solubility.

Taxa	Species ^a	EC type ^b	EC/NOEC Value ^c (µg.L ⁻¹)	Expo. Conc. ^d (µg.L ⁻¹)	Expo. Type ^e	RI ^f	References
	<i>Excirrolana</i> (SW)	EC ₅₀ (96h) BUR	>70 (UV) >70	nr	R/M	2	(Boese <i>et al.</i> , 1997)
	<i>Gammarus minus</i> (FW)	EC ₅₀ (96h) nr	32	nr	nr/M	4	(Horne <i>et al.</i> , 1983)
	<i>Grandidierella japonica</i> (SW, b)	EC ₅₀ (96h) BUR	19 (UV) 27	nr	R/M	2	(Boese <i>et al.</i> , 1997)
	<i>Hyalella azteca</i> (FW)	LC ₅₀ (10d) MOR	30.3	nr (n=6)	S/M	2	(Suedel and Rodgers, 1996)
		LC ₅₀ (10d) MOR	> 500 ^g	0, 1, 10, 100, 500	S/N	2	(Werner and Nagel, 1997)
	<i>Leptocheirus plumulosus</i> (SW, b)	EC ₅₀ (96h) BUR	20 (UV) 51	nr	R/M	2	(Boese <i>et al.</i> , 1997)
	<i>Mysidopsis bahia</i> (SW)	LC ₅₀ (48h) MOR	5.32 (UV) 63.8	0,1,3,10,30,100 (UV) (N) 0,10,10 ² , 10 ³ , 10 ⁴ , 2. 10 ⁴ (N)	S/M	1	(Pelletier <i>et al.</i> , 1997)
		LC ₅₀ (96h) MOR	40	nr	-	4	(US-EPA, 1978)
		LC ₅₀ (96h) MOR	1.4-1.7(UV) 31	nr (n=5)	C/M	1	(Spehar <i>et al.</i> , 1999)
	<i>Rhepoxynius abronius</i> (SW)	LC ₅₀ (24h) MOR	> 100	0, 0.35, 3.5, 35, 70, 100	S/N	2	(Werner and Nagel, 1997)
		EC ₅₀ (96h) BUR	<5 (UV) 63	nr	R/M	2	(Boese <i>et al.</i> , 1997)
Insects	<i>Aedes aegypti</i> (FW)	LC ₅₀ (24h) MOR	10	nr	nr	4	(Borovsky <i>et al.</i> , 1987)
	<i>Chironomus tentans</i> (FW)	LC ₅₀ (10d) MOR	37.8	nr (n=6)	S/M	2	(Suedel and Rodgers, 1996)
Fish	<i>Cyprinodon variegatus</i> (SW)	LC ₅₀ (96h) MOR	>560000 ^h	nr (n>1)	S/N	3	(Heitmuller <i>et al.</i> , 1981)
	<i>Ictalurus punctatus</i> (FW)	LC ₅₀ (96h) MOR	36	nr	nr/M	4	(Gendusa, 1990)
	<i>Onchorhynchus mykiss</i> (FW)	LC ₅₀ (96h) MOR	187	nr	nr/M	4	(Horne <i>et al.</i> , 1983)
	<i>Pimephales promelas</i> (FW)	LC ₅₀ (96h) MOR	14-18	nr	nr/M	4	(Diamond, 1995)

^h Effect concentration above solubility of the chemical in water

Table 4.6.1-2 : Chronic toxicity of Fluoranthene to pelagic organisms

Taxa	Species ^a	EC type ^b	EC/NOEC Value (µg.L ⁻¹)	Expo. Conc. ^c (µg.L ⁻¹)	Expo. Type ^d	RI ^e	References
Algae	<i>Pseudokirchneriella subcapitata</i> (FW)	EC ₁₀ (72h) GRO _b	8.6	nr (n>4)	M	1	(Bisson <i>et al.</i> , 2000)
	<i>Scenedesmus subspicatus</i> (FW)	EC ₁₀ (96h) GRO	1.6	nr	S/N	4	(Kördel <i>et al.</i> , 1981)
Invertebrates Crustacean	<i>Ceriodaphnia dubia</i> (FW)	EC ₁₀ (7d) REP	1	nr (n>4)	M	1	(Bisson <i>et al.</i> , 2000)
	<i>Daphnia magna</i> (FW)	NOEC (21d) MOR	1.4 (UV) 17	nr (n=5)	R/M	2	(Spehar <i>et al.</i> , 1999)
	<i>Mysidopsis bahia</i> (SW)	NOEC (31d) MOR	0.6 (UV) 11.1	nr (n=5)	C/M	1	(Spehar <i>et al.</i> , 1999)
Fish	<i>Brachydanio rerio</i> (FW)	NOEC(41d) MOR/GRO	6.9/22-69	nr	R/M	1	(Hooftman and Evers-de Ruyter, 1992)
	<i>Pimephales promelas</i> (FW)	NOEC (28d) MOR	1.4 (UV) 10.4	nr (n=5)	C/M	1	(Spehar <i>et al.</i> , 1999)

^a FW : fresh water organisms.

^b LC₅₀ : Lethal Concentration for 50% of the population; NOEC : No Observed Effect Concentration; MOR : mortality.

^c Expo. Conc. : Concentration of the substance to which organisms were exposed during the test. n=number of exposure concentrations apart from controls.

^d S : static exposition; R : renewal exposition; C : continuous/flow-through exposition; N : EC/NOEC value based on nominal concentrations; M : EC/NOEC value based on measured concentrations.

^e RI : Reliability Index (Klimish *et al.*, 1997); 1 : Valid without restriction; 2 : Valid with restriction; 3 : Not reliable; 4 : Not assignable.

Effects on benthic organisms

Toxicity data of sediment spiked with fluoranthene to marine crustaceans and some marine and freshwater insects are quite consistent all together (see Table 4.6.1-3). It is rather surprising however to see that some studies show quite important differences in values, i.e. high LC₅₀ of 99.4 mg.kg⁻¹dw for the marine amphipod *R.abronius* (Swartz *et al.*, 1997) and even including high values of chronic values: NOEC of 31 mg.kg⁻¹dw for *C.riparius* (Stewart and Thompson, 1995) and a NOEC of 61 mg.kg⁻¹dw for *S.knabeni* (Lotufo, 1997). These differences may be explained by the nature of sediments used in each study, the contents of organic carbon being much higher in those studies compared to others.

Table 4.6.1-3 : Acute and chronic toxicity of Fluoranthene to benthic organisms

Taxa	Species ^a	EC type ^b	EC/NOEC Value (mg.kg ⁻¹ dw)	Expo.Conc. ^c (mg.kg ⁻¹ dw)	Expo. Type ^d	RI ^e	References
Invertebrates Crustaceans	<i>Hyalella azteca</i> (FW)	LC ₅₀ (10d) MOR	2.3-7.4	nr (n=6) TOC : 0.44-0.5%	M	1	(Suedel <i>et al.</i> , 1993)
	<i>Rhepoxynius abronius</i> (SW)	LC ₅₀ (10d) MOR	3.4-10.7	0, 0.9, 1.5, 3, 6.5, 13.6 (M) OC : 0.18-0.48%	M	2	(Swartz <i>et al.</i> , 1990)
		LC ₅₀ (10d) MOR	11.1-19.1	0,4,5,7,8,2,11.7,16.7,23.8 (N) OC : 0.3%	M	2	(DeWitt <i>et al.</i> , 1992)
		LC ₅₀ (10d) MOR	99.4	0.7, 1.4, 3.3, 6.4 mg.g ⁻¹ OC (M) CO : 3%	M	2	(Swartz <i>et al.</i> , 1997)
Insects	<i>Chironomus tentans</i> (FW)	LC ₅₀ (10d) MOR	3-8.7	nr (n=6) TOC : 0.44-0.5%	M	1	(Suedel <i>et al.</i> , 1993)
	<i>Chironomus riparius</i> (FW)	NOEC (28d) EMG	31	5.2 - 170 (n=nr) TOC : 1.1%	M	1	(Stewart and Thompson, 1995)
	<i>Schizopera knabeni</i> (SW)	NOEC (14d) REP	61	61, 137, 249 TOC : 1.5%	M	3	(Lotufo, 1997)

^a FW : fresh water organisms.

^b LC₅₀ : LC for 50% of the population; NOEC : No Observed Effect Concentration; MOR : mortality; REP : reproduction; EMG : emergence of larvae.

^c Expo.Conc. : Concentration of the substance to which organisms were exposed during the test. Concentrations can be expressed as nominal (N) or measured (M) concentrations. n=number of exposure concentrations apart from controls. (T)OC : (Total) Organic Carbon.

^d N : EC/NOEC value based on nominal concentrations; M : EC/NOEC value based on measured concentrations.

^e RI : Reliability Index (Klimish *et al.*, 1997); 1 :Valid without restriction; 2 :Valid with restriction; 3 :Not reliable; 4 :Not assignable.

Effects on top predators : secondary poisoning

Only one study is available for repeated dose-exposure of mammalian species to fluoranthene. This 90d study carried out by US-EPA lead to a NOAEL of 125 mg.kg⁻¹.j⁻¹ corresponding to a NOEC of 1037.5 mg.kg⁻¹ food according to conversion factors indicated in the TGD (European Commission, 2003) for mice.

Table 4.6.1-4 : Toxicity of Fluoranthene to mammalian species

Species	EC type ^a	EC/NOEC value ^b (mg.kg ⁻¹ food, ww.)	Expo. Conc. ^c (mg.kg ⁻¹ food, ww.)	Expo. Type ^d	RI ^e	References
Mouse	NOEC (90d) DYS _r	1037.5 (fm)	0, 622.5, 1037.5, 2075	O-G	4	(US-EPA, 1988)

^a LOEC : Low Observed Effect Concentration; NOEC : No Observed Effect Concentration; DYS_r : renal dysfunctioning.

^b (fm) : value reported for both sex: females (f) and males (m).

^c Expo. Conc. : Concentration of the substance to which organisms were exposed during the test.

^d O : oral exposure ; G : exposure *via* gavage.

^e RI : Reliability Index (Klimish *et al.*, 1997); 1 :Valid without restriction; 2 :Valid with restriction; 3 :Not reliable; 4 :Not assignable.

4.6.2. *Thresholds of no effect*

Thresholds of no effect for pelagic organisms

Acute toxicity data are available for the three main trophic levels (algae, crustaceans and fish) for both freshwater and saltwater. Moreover, short term data are also available for additional freshwater taxa (hydrozoans, annelids, and insects) and one additional saltwater taxa, i.e. molluscs. Results of long term tests are available for the three main trophic levels in freshwater but only one long term data for marine organisms is available for crustaceans taxa.

From this data set, there does not seem to be any significant difference of sensitivity between freshwater and saltwater species. Therefore, $PNEC_{\text{seawater}}$ can be determined from both saltwater and freshwater dataset. The lowest chronic value issued from exposure under fluorescent light is obtained by Bisson *et al.* (2000) for *Ceriodaphnia dubia*. This is an EC_{10} (7 day), taken as a $NOEC(7d) = 1 \mu\text{g/l}$. This value is not far from the ones reported by Spehar *et al.* (1999) for other crustaceans (marine and freshwater) and a fish after UV exposure.

As a first approach, an assessment factor of 10 can be applied to the $NOEC$ for *Ceriodaphnia dubia* :

$$PNEC_{\text{seawater}} = 1 (\mu\text{g/L}^{-1}) / 10 = 0.1 \mu\text{g.L}^{-1}$$



Threshold of no effect for marine pelagic organisms = 100 ng.L^{-1}
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Thresholds of no effect for benthic organisms

Data issued from water-sediment toxicity tests are available but only one valid chronic data is reported. This chronic available value is the one reported by Stewart and Thompson (1995) for *Chironomus riparius* after a 28d exposure : $31 \text{ mg.kg}^{-1} \text{ dw}$. According to the TGD (European Commission, 2003), taking into account that only one chronic value is available; an assessment factor of 1000 shall be applied. Moreover, as said in the Risk Assessment Report of PBDEs already cited above (European Commission, 2000) “*for soil organisms, the NOEC should be normalised to the standard organic matter of soil [...]. This normalisation is not suggested in the TGD for NOEC from sediment tests, but, in principle, it seems sensible to carry out such a normalisation assumes that the toxicity seen is due to the chemical present in porewater of the soil and sediment.*” In the case of Stewart and Thompson (1995), the test reports indicate that the organic carbon contents of the sediments used is 1.1%. “*Assuming the standard organic carbon content of sediment to be 5%*” according to the TGD (European Commission, 2003), the lowest $NOEC_{\text{standard}}$ should then be about 5 times the $NOEC$ of Stewart and Thompson (1995), i.e. 155 mg.kg^{-1} :

$$PNEC_{\text{marine sediment}} = 155 (\text{mg/kg}^{-1} \text{ dw}) / 1000 = 0.155 \text{ mg/kg}^{-1} \text{ dw}$$



Threshold of no effect for marine benthic organisms = 155 $\mu\text{g.kg}^{-1} \text{ dw}$
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Thresholds of no effect for marine top predators

Only one 90 day toxicity data on mammals is available. Therefore, an assessment factor of 90 is applied according to TGD (European Commission, 2003) :

$$\text{PNEC}_{\text{oral}} = 1037.5 \text{ (mg/kg}^{-1} \text{ food ww.)} / 90 = 11.5 \text{ mg.kg}^{-1} \text{ food ww.}$$



Threshold of no effect for marine top predators = 11.5 mg.kg⁻¹ food ww.

Overall threshold of no effect for the marine environment

Thresholds of no effect are available for the three compartment considered: pelagic and benthic organisms as well as marine top predators.

The **PNEC_{seawater} is 100 ng.L⁻¹**.

To compare them between each other, values have to be derived in the same unity.

- Derivation of **PNEC_{marine sediment}** in water :

Taking into account a K_{OC} range of 41,687 – 251,189 L.kg⁻¹, the value of the PNEC_{marine sediment} of 155 µg.kg⁻¹ permit to calculate a corresponding value in water PNEC_{marine sediment,water} of **32 – 193 ng.L⁻¹**.

- Derivation of **PNEC_{oral}** in water :

Several studies led on the accumulation of fluoranthene in aquatic species have shown that bioaccumulation of this chemical is not negligible. Among these, two BCF values were retained : a value of 378 L.kg⁻¹ for fish (Gerhart and Carlson, 1978), and a value of 5920 L.kg⁻¹ for molluscs (McLeese and Burrige, 1987). Dividing the PNEC_{oral} of 11.5 mg.kg⁻¹ ww by these factors, the corresponding values obtained in water (PNEC_{oral,water}) are **1.9 µg.L⁻¹** and **30.4 µg.L⁻¹**.

Comparing those three data all together, it seems that the most protective threshold is the one obtained for benthic organisms. Therefore, it is decided to consider this threshold as the overall threshold for the marine environment.



Overall threshold of no effect for marine environment for Fluoranthene :

- 155 µg.kg⁻¹ in sediment (dry weight)
- ~ 32 ng.L⁻¹ in water

4.7. Benzo[a]pyrene

4.7.1. Effects on organisms

Effects on pelagic organisms

According to the dataset available presented in Table 4.7.1-1, there does not seem to be a significant difference of sensitivity between marine and freshwater crustaceans. Data available are rather consistent between each other and lower values are observed for the two tests realised with measurement of concentration in the media during the test (Newsted and Giesy, 1987; Bisson *et al.*, 2000), suggesting that loss of chemicals occurs in tests and that toxicity may be underestimated where effect concentrations are expressed in terms of nominal concentrations.

Table 4.7.1-1 : Acute toxicity of Benzo[a]pyrene to pelagic organisms

Taxa	Species ^a	EC type ^b	EC/NOEC Value (µg.L ⁻¹)	Expo.Conc. ^c (µg.L ⁻¹)	Expo. Type ^d	RI ^e	References
Algae	<i>Scenedesmus acutus</i> (FW)	EC ₅₀ (72h) GRO	5 ^f	Nr	nr/N	4	(Schoeny <i>et al.</i> , 1988)
Invertebrates Crustacean	<i>Daphnia magna</i> (FW)	LC ₅₀ (29h) MOR	1.5		R/M	2	(Newsted and Giesy, 1987)
		LC ₅₀ (48h) MOR	>2.7	nr (n>4)	S/M	1	(Bisson <i>et al.</i> , 2000)
	<i>Daphnia pulex</i> (FW)	LC ₅₀ (96h) MOR	5 ^f	0-10 (n=nr)	S/N/CI	2	(Trucco <i>et al.</i> , 1983)
	<i>Eurytemora affinis</i> (SW)	LC ₅₀ (96h) MOR	58 ^f	Nr	R/nr	4	(Forget <i>et al.</i> , 2001)
	<i>Gammarus duebeni</i> (SW)	LC ₅₀ (48h) MOR	11 ^f	0-1000 (n=nr)	S/N	3 ^g	(Lawrence and Poulter, 1998)
NOEC (134h) LOEC (134h) SWM		8 ^f 12 ^f	0, 4, 8, 12 (n=3)	S/N	3		

^a FW : fresh water organisms.

^b EC : Effect Concentration; LC : Lethal concentration; EC_{50/10} (LC₅₀) : EC(LC) for 50/10% of the population; NOEC : No Observed Effect Concentration; GRO : growth; MOR : mortality; ELS : diverse endpoints observed during early life stage.

^c Expo.Conc. : Concentration of the substance to which organisms were exposed during the test. Concentrations can be expressed as nominal (N) or measured (M) concentrations. n=number of exposure concentrations apart from controls.

^d S : static exposition; R : renewal exposition; C : continuous/flow-through exposition; N : EC/NOEC value based on nominal concentrations; M : EC/NOEC value based on measured concentrations; CI : Closed vessels to limit loss by volatilisation.

^e RI : Reliability Index (Klimish *et al.*, 1997); 1 :Valid without restriction; 2 :Valid with restriction; 3 :Not reliable; 4 :Not assignable.

^f Effect concentration above solubility of the chemical in water

^g Benzo[a]pyrene diluted in presence of benzene.

Most chronic data are issued from tests where concentrations were measured during the bioassay. Results are rather consistent between each others, even if many of the values are higher than water solubility as chemical was diluted with solvent in the test media.

There is an obvious lack of marine data. No clear difference can be shown between marine and freshwater crustaceans.

Table 4.7.1-2 : Chronic toxicity of Benzo[a]pyrene to pelagic organisms

Taxa	Species ^a	EC type ^b	EC/NOEC Value (µg.L ⁻¹)	Expo. Conc. ^c (µg.L ⁻¹)	Expo. Type ^d	RI ^e	References
Algae	<i>Pseudokirchneriella subcapitata</i> (FW)	EC ₁₀ (72h) GRO _b	0.78	nr (n>4)	S/M	1	(Bisson <i>et al.</i> , 2000)
Invertebrates Crustacean	<i>Ceriodaphnia dubia</i> (FW)	EC ₁₀ (7d) REP	0.5	nr (n>4)	R/M	1	(Bisson <i>et al.</i> , 2000)
	<i>Eurytemora affinis</i> (SW)	NOEC (10d) MOR	12 ^f	nr	R/nr	4	(Forget <i>et al.</i> , 2001)
Fish	<i>Brachydanio rerio</i> (FW)	NOEC (28d) ELS	>4 ^f	nr	nr/M	1	(Hooftman and Evers-de Ruiter, 1992)
		NOEC (42d) nr	6.3 ^f	nr	nr/M	4	TNO (1993) ^g
	<i>Oncorhynchus mykiss</i> (FW)	NOEC (36d) ELS	2.4	nr	nr/M	4	(Hannah <i>et al.</i> , 1982)
	<i>Leuresthes tenuis</i> (FW) (embryos)	NOEC (14d) nr	7 ^f	nr	nr	4	(Winkler <i>et al.</i> , 1983)

^a FW : fresh water organisms.

^b EC : Effect Concentration; LC : Lethal concentration; EC_{50/10} (LC₅₀) : EC(LC) for 50/10% of the population; NOEC : No Observed Effect Concentration; GRO : growth; MOR : mortality; ELS : diverse endpoints observed during early life stage.

^c Expo.Conc. : Concentration of the substance to which organisms were exposed during the test. Concentrations can be expressed as nominal (N) or measured (M) concentrations. n=number of exposure concentrations apart from controls.

^d S : static exposition; R : renewal exposition; C : continuous/flow-through exposition; N : EC/NOEC value based on nominal concentrations; M : EC/NOEC value based on measured concentrations.

^e RI : Reliability Index (Klimish *et al.*, 1997); 1 :Valid without restriction; 2 :Valid with restriction; 3 :Not reliable; 4 :Not assignable.

^f Effect concentration above solubility of the chemical in water

^g Whole reference is no cited in this report (6. References) because it could not be found.

Effects on benthic organisms

There is no data available in the literature issued from valid water-sediment toxicity tests, reporting toxicity to benthic organisms of sediment spiked with benzo[a]pyrene.

Effects on top predators: secondary poisoning

Two acute toxicity data on mammals are available but no value could be found issued from tests carried out with repeated dose long term exposure.

Table 4.7.1-3 : Toxicity of Benzo[a]pyrene to mammalian species

Species	EC type ^a	EC/NOEC value ^b (mg.kg ⁻¹ food, ww.)	Expo. Conc. ^c (mg.kg ⁻¹ food, ww.)	Expo. Type ^d	RI ^e	References
Mouse	LD ₅₀ (acute) nr	> 1600	Up to 1600	O-nr	4	(Awogi and Sato, 1989)
Rat	NOEC (4d) ^f DYS _{GHR}	1500	0, 500, 1500	O-nr	1	(Nousiainen <i>et al.</i> , 1984)

^a LD₅₀: Lethal Dose for 50% of the population ; NOEC : No Observed Effect Concentration; DYS_{GHR} : Gastric, Hepatic and Renal Dysfunctioning.

^b (fm): value reported for both sex: females (f) and males (m).

^c Expo. Conc. : Concentration of the substance to which organisms were exposed during the test.

^d O : oral exposure ; G : exposure *via* gavage.

^e RI : Reliability Index (Klimish *et al.*, 1997); 1 :Valid without restriction; 2 :Valid with restriction; 3 :Not reliable; 4 :Not assignable.

^f Not acceptable as a NOEC because exposure duration is too short

4.7.2. *Thresholds of no effect*

Threshold of no effect for pelagic organisms

Given the consistent dataset available, no difference between marine and freshwater organisms can be stressed. Therefore, both marine and freshwater data are usable to derive the threshold of no effect. Chronic values are available for the three main trophic levels (algae, crustaceans, fish) in freshwater, and for one estuarine crustacean. The lowest data is an EC₁₀ obtained by Bisson *et al.* (2000) for their 7 day test on reproduction of *Ceriodaphnia dubia*. According to the TGD (European Commission, 2003), this value can be assimilated to a NOEC and an assessment factor of 100 can be applied to it to derive a PNEC for marine organisms :

$$\text{PNEC}_{\text{seawater}} = 0.5 (\mu\text{g/L}^{-1}) / 100 = 0.005 \mu\text{g.L}^{-1}$$



Threshold of no effect for marine pelagic organisms = 5 ng.L⁻¹

Thresholds of no effect for benthic organisms

Given that absolutely no valid data are available in the literature, it is not possible to derive a threshold of no effect of benzo[a]pyrene for benthic organisms.

Threshold of no effect for marine top predators

According to the TGD (European Commission, 2003), secondary poisoning effects on bird and mammal populations rarely become manifest in short-term studies. Therefore, results from long-term studies are strongly preferred, such as NOECs for mortality, reproduction or growth.

In the case of Benzo[a]pyrene, as no adequate toxicity data for mammals or birds are available, an assessment of secondary poisoning cannot be made.

Overall threshold of no effect for the marine environment

The threshold of no effect for pelagic organisms is the only one that could be derived.

As a first approach, this threshold will be considered for the protection of the whole marine environment :



Overall threshold of no effect for marine environment for Benzo[a]pyrene :

- 5 ng.L⁻¹ of water

4.8. Benzo[b]fluoranthene

4.8.1. Effects on organisms

Effects on pelagic organisms

Very few data are available for exposition of pelagic organisms to benzo[b]fluoranthene. At least, all these data reported in Table 4.8.1-1 and Table 4.8.1-2 are of good reliability and very consistent between each other because issued from the same study of Bisson *et al.* (2000).

Table 4.8.1-1 : Acute toxicity of Benzo[b]fluoranthene to pelagic organisms

Taxa	Species ^a	EC type ^b	EC/NOEC Value ($\mu\text{g.L}^{-1}$)	Expo.Conc. ^c ($\mu\text{g.L}^{-1}$)	Expo. Type ^d	RI ^e	References
Invertebrates Crustacean	<i>Daphnia magna</i> (FW)	LC ₅₀ (48h) MOR	>1.1	nr (n>4)	S/M	1	(Bisson <i>et al.</i> , 2000)

^a FW : fresh water organisms.

^b EC : Effect Concentration; LC : Lethal concentration; EC_{50/10} (LC₅₀) : EC(LC) for 50/10% of the population; NOEC : No Observed Effect Concentration; GRO : growth; MOR : mortality; ELS : diverse endpoints observed during early life stage.

^c Expo.Conc. : Concentration of the substance to which organisms were exposed during the test. Concentrations can be expressed as nominal (N) or measured (M) concentrations. n=number of exposure concentrations apart from controls.

^d S : static exposition; R : renewal exposition; C : continuous/flow-through exposition; N : EC/NOEC value based on nominal concentrations; M : EC/NOEC value based on measured concentrations; CI : Closed vessels to limit loss by volatilisation.

^e RI : Reliability Index (Klimish *et al.*, 1997); 1 :Valid without restriction; 2 :Valid with restriction; 3 :Not reliable; 4 :Not assignable.

Table 4.8.1-2 : Chronic toxicity of Benzo[b]fluoranthene to pelagic organisms

Taxa	Species ^a	EC type ^b	EC/NOEC value ($\mu\text{g.L}^{-1}$)	Expo. Conc. ^c ($\mu\text{g.L}^{-1}$)	Expo. Type ^d	RI ^e	References
Algae	<i>Pseudokirchneriella subcapitata</i> (FW)	EC ₁₀ (72h) GRO _b	>1	nr (n>4)	S/M	1	(Bisson <i>et al.</i> , 2000)
Invertebrates Crustacean	<i>Ceriodaphnia dubia</i> (FW)	EC ₁₀ (7d) REP	>1.1	nr (n>4)	R/M	1	(Bisson <i>et al.</i> , 2000)

^a FW : fresh water organisms.

^b EC : Effect Concentration; LC : Lethal concentration; EC_{50/10} (LC₅₀) : EC(LC) for 50/10% of the population; NOEC : No Observed Effect Concentration; GRO : growth; MOR : mortality; ELS : diverse endpoints observed during early life stage.

^c Expo.Conc. : Concentration of the substance to which organisms were exposed during the test. Concentrations can be expressed as nominal (N) or measured (M) concentrations. n=number of exposure concentrations apart from controls.

^d S : static exposition; R : renewal exposition; C : continuous/flow-through exposition; N : EC/NOEC value based on nominal concentrations; M : EC/NOEC value based on measured concentrations.

^e RI : Reliability Index (Klimish *et al.*, 1997); 1 :Valid without restriction; 2 :Valid with restriction; 3 :Not reliable; 4 :Not assignable.

Effects on benthic organisms

There is no data available in the literature issued from valid water-sediment toxicity tests, reporting toxicity of sediment spiked with benzo[b]fluoranthene to benthic organisms.

Effects on top predators : secondary poisoning

One toxicity data on mammals is available but it could not be validated and it is reported in Table 4.8.1-3 only as an indicative value.

Table 4.8.1-3 : Toxicity of Benzo[b]fluoranthene to mammalian species

Species	EC type ^a	EC/NOEC value ^b (mg.kg ⁻¹ food, ww.)	Expo. Conc. ^c (mg.kg ⁻¹ food, ww.)	Expo. Type ^d	RI ^e	References
Mouse	NOEC (56d) IMM	<0.5	0, 0.5, 5	O-nr	4	(Lee and Strickland, 1993)

^a NOEC : No Observed Effect Concentration; IMM : immunologic effects for which endpoint is levels of antibodies.

^b (fm) : value reported for both sex: females (f) and males (m).

^c Expo. Conc. : Concentration of the substance to which organisms were exposed during the test.

^d O : oral exposure ; G : exposure *via* gavage.

^e RI : Reliability Index (Klimish et al., 1997); 1 :Valid without restriction; 2 :Valid with restriction; 3 :Not reliable; 4 :Not assignable.

4.8.2. *Thresholds of no effect*

Threshold of no effect for pelagic organisms

Ecotoxicity data to pelagic organisms are solely available for freshwater organisms : one acute data for *Daphnia magna* (see Table 4.8.1-1) and two chronic data for a green algae and *Ceriodaphnia dubia* (see Table 4.8.1-2). As the taxa of fish is absolutely not represented in these datasets, it is not possible to state if the more sensitive species would be taken into account in the derivation of a threshold from such datasets.

Therefore, it is not relevant to derive a threshold of no effect of benzo[b]fluoranthene based on data available at present.

Thresholds of no effect for benthic organisms

Given that absolutely no valid data are available in the literature, it is not possible to derive a threshold of no effect of benzo[b]fluoranthene for benthic organisms.

Threshold of no effect for marine top predators

Given that only one data is available and that this data could not be validate, it is not possible to derive a threshold of no effect for top predators.

Overall threshold of no effect for the marine environment

Given that derivation of thresholds can be done for none of the three compartment (pelagic, benthic, top predators), it is not possible to evaluate a threshold of no effect for the marine environment.

4.9. Benzo[k]fluoranthene

4.9.1. Effects on organisms

Effects on pelagic organisms

Few data are available for exposition of pelagic organisms to benzo[k]fluoranthene. They are reported in Table 4.9.1-1 and Table 4.9.1-2.

Table 4.9.1-1 : Acute toxicity of Benzo[k]fluoranthene to pelagic organisms

Taxa	Species ^a	EC type ^b	EC/NOEC Value ($\mu\text{g}\cdot\text{L}^{-1}$)	Expo.Conc. ^c ($\mu\text{g}\cdot\text{L}^{-1}$)	Expo. Type ^d	RI ^e	References
Invertebrates Crustacean	<i>Daphnia magna</i> (FW)	LC ₅₀ (37h) MOR	1.4 ^f		R/M	2	(Newsted and Giesy, 1987)
		LC ₅₀ (48h) MOR	>1.1 ^f	nr (n>4)	S/M	2	(Bisson <i>et al.</i> , 2000)

^a FW : fresh water organisms.

^b LC₅₀ : Lethal concentration for 50% of the population; MOR : mortality.

^c Expo.Conc. : Concentration of the substance to which organisms were exposed during the test. n=number of exposure concentrations apart from controls; nr : information not reported.

^d S : static exposition; R : renewal exposition; N : EC/NOEC value based on nominal concentrations; M : EC/NOEC value based on measured concentrations; Cl : Closed vessels to limit loss by volatilisation.

^e RI : Reliability Index (Klimish *et al.*, 1997); 1 :Valid without restriction; 2 :Valid with restriction; 3 :Not reliable; 4 :Not assignable.

^f Effect concentration above solubility of the chemical in water.

Table 4.9.1-2 : Chronic toxicity of Benzo[k]fluoranthene to pelagic organisms

Taxa	Species ^a	EC type ^b	EC/NOEC value ($\mu\text{g}\cdot\text{L}^{-1}$)	Expo. Conc. ^c ($\mu\text{g}\cdot\text{L}^{-1}$)	Expo. Type ^d	RI ^e	References
Algae	<i>Pseudokirchneriella subcapitata</i> (FW)	EC ₁₀ (72h) GRO _b	>1 ^f	nr (n>4)	S/M	2	(Bisson <i>et al.</i> , 2000)
Invertebrates Crustacean	<i>Ceriodaphnia dubia</i> (FW)	EC ₁₀ (7d) REP	>1.1 ^f	nr (n>4)	R/M	2	(Bisson <i>et al.</i> , 2000)
Fish	<i>Brachydanio rerio</i> (FW)	NOEC (42d) GRO	0.36	nr	R/M	1	(Hooftman and Evers-de Rooter, 1992)

^a FW : fresh water organisms.

^b EC₁₀ : Effect Concentration for 10% of the population; NOEC : No Observed Effect Concentration; GRO : growth; MOR : mortality; ELS : diverse endpoints observed during early life stage.

^c Expo.Conc. : Concentration of the substance to which organisms were exposed during the test. Concentrations can be expressed as nominal (N) or measured (M) concentrations. n=number of exposure concentrations apart from controls.

^d S : static exposition; R : renewal exposition; C : continuous/flow-through exposition; N : EC/NOEC value based on nominal concentrations; M : EC/NOEC value based on measured concentrations.

^e RI : Reliability Index (Klimish *et al.*, 1997); 1 :Valid without restriction; 2 :Valid with restriction; 3 :Not reliable; 4 :Not assignable.

^f Effect concentration above solubility of the chemical in water.

Effects on benthic organisms

Only one study is available for effects of benzo[k]fluoranthene on benthic organisms. This water-sediment test led by Verrhiest *et al.* (2001) was carried out with spiked sediment on two freshwater invertebrates : the crustacean *Hyaella azteca* and the insect *Chironomus riparius*. Lethal concentration for 50% of the population could not be determined but 45% of *Hyaella* died at the highest concentration tested, indicating that LC₅₀ for this species was not much higher than the value of 300 mg.kg⁻¹ dw. No more information is given for *Chironomus riparius*.

Table 4.9.1-3 : Acute toxicity of benzo[k]fluoranthene to benthic organisms

Taxa	Species ^a	EC type ^b	EC/NOEC value (mg.kg ⁻¹ dw)	Expo.Conc. ^c (mg.kg ⁻¹ dw)	Expo. Type ^d	RI ^e	References
Invertebrates Crustaceans	<i>Hyaella azteca</i> (FW)	LC ₅₀ (48h)	>300	0-300 (n=nr)	N (M)	2	(Verrhiest <i>et al.</i> , 2001)
		LC ₄₅ (48h)	300				
MOR							
Insects	<i>Chironomus riparius</i> (FW)	LC ₅₀ (14d)	>300				
		MOR					

^a FW : fresh water organisms.

^b LC₅₀ : Lethal Concentration for 50% of the population; MOR : mortality.

^c Expo.Conc. : Concentration of the substance to which organisms were exposed during the test. n=number of exposure concentrations apart from controls; nr : information not reported.

^d N (M) : Concentrations were measured during the test but LC values are based on nominal concentrations because no loss of chemicals occurred.

^e RI : Reliability Index (Klimish *et al.*, 1997); 1 :Valid without restriction; 2 :Valid with restriction; 3 :Not reliable; 4 :Not assignable.

Effects on top predators: secondary poisoning

Many toxicity data on mammals have been carried out with cutaneous exposition but no oral toxicity data was found.

4.9.2. Thresholds of no effect

Threshold of no effect for pelagic organisms

Given the available dataset, it can not be stated if differences of sensitivity exist between marine and freshwater organisms. Freshwater data will be used by default to derive PNEC_{seawater}.

Chronic values are available for the three main trophic levels (algae, crustaceans, fish) in freshwater. The lowest data is a NOEC obtained by Hooftman and Evers de Ruiten (1992) for a 42 day test on growth of *Brachydanio rerio*. According to the TGD (European Commission, 2003), an assessment factor of 100 can be applied to this value to derive a PNEC for marine organisms :

$$\text{PNEC}_{\text{seawater}} = 0.36 \text{ (}\mu\text{g/L}^{-1}\text{)} / 100 = 0.0036 \text{ }\mu\text{g.L}^{-1}$$



Threshold of no effect for marine pelagic organisms = 3.6 ng.L ⁻¹
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However, this value has to be considered with precaution given that it is derived from freshwater data only.

Thresholds of no effect for benthic organisms

Two acute sediment toxicity data are reported in Table 4.9.1-3 for freshwater invertebrates. It was decided to apply the worst case and consider the LC₄₅ for *Hyaella azteca* as a LC₅₀, given that difference between both must be very little.

According to the TGD (European Commission, 2003), when only acute data are available PNEC_{sediment} should be derived using both assessment factor and Equilibrium Partitioning methods.

- Assessment factor method

Following the recommended methodology of TGD (European Commission, 2003), an assessment factor of 10,000 should be applied if only one acute freshwater or marine test is available, while an assessment factor of 1000 should be applied if two acute tests including a minimum of one marine test with an organism of a sensitive taxa. In the case of benzo[k]fluoranthene, the dataset is borderline, presenting two acute toxicity data but no result on marine organisms. Moreover, the taxa of fish is not represented in the dataset while it seems to be the most sensitive taxa (see Table 4.9.1-2). Therefore, it seems appropriate to apply an assessment factor of 5000 to the LC₄₅₋₅₀ of 300 :

$$\text{PNEC}_{\text{marine sediment}} = 300 \text{ (mg/kg}^{-1} \text{ dw)} / 5000 = 0.06 \text{ mg/kg}^{-1} \text{ dw}$$



Threshold of no effect for marine benthic organisms = 60 µg.kg⁻¹ dw

- Equilibrium partitioning method

Following the recommended methodology of TGD (European Commission, 2003), marine PNEC for benthic organisms can also be derived using the following equation :

$$\text{PNEC}_{\text{marine sediment}} \text{ (mg/kg}^{-1} \text{ dw)} = (\text{K}_{\text{sed-water}} / \text{RHO}_{\text{sed}}) \times \text{PNEC}_{\text{seawater}} \times 1000$$

with $\text{K}_{\text{sed-water}}$ = water/sediment partition coefficient = $F_{\text{water}_{\text{sed}}} + F_{\text{solid}_{\text{sed}}} \times \text{Kp}_{\text{sed}} \times \text{RHO}_{\text{solid}}$

$F_{\text{water}_{\text{sed}}}$ = fraction of water in suspension matter = 0.8 m³.m⁻³ (default value)

$F_{\text{solid}_{\text{sed}}}$ = fraction of solid in suspension matter = 0.2 m³.m⁻³ (default value)

Kp_{sed} = solid/water partition coefficient in the sediment = $F_{\text{OC}} \times \text{K}_{\text{OC}}$

F_{OC} = weight fraction of Organic Carbon in the sediment = 0.05 (default value)

K_{OC} = Organic Carbon/water partition coefficient = 550,000 – 7,760,000 L.kg⁻¹

$\text{RHO}_{\text{solid}}$ = solid phase density = 2.5 kg.L⁻¹ (default value)

RHO_{sed} = humid sediment density = 1300 kg.m⁻³ (default value)

$\text{PNEC}_{\text{seawater}} = 3.6 \cdot 10^{-6} \text{ mg.L}^{-1}$

$$\text{PNEC}_{\text{marine sediment}} = [(0.8 + 0.2 \times 0.05 \times 550,000 \times 2.5) / 1300] \times 3.6 \cdot 10^{-6} \times 1000 \quad (\text{min})$$

$$\text{PNEC}_{\text{marine sediment}} = [(0.8 + 0.2 \times 0.05 \times 7,760,000 \times 2.5) / 1300] \times 3.6 \cdot 10^{-6} \times 1000 \quad (\text{max})$$



Threshold of no effect for marine benthic organisms = 38 - 537 µg.kg⁻¹ dw

Threshold of no effect for marine top predators

Given that absolutely no valid data are available in the literature, it is not possible to derive a threshold of no effect of benzo[k]fluoranthene related to secondary poisoning.

Overall threshold of no effect for the marine environment

Thresholds of no effect are available for two of the compartments considered : pelagic and benthic organisms.

The **PNEC_{seawater} is 3.6 ng.L⁻¹**.

To compare them between each other, values have to be derived in the same unity.

- Derivation of **PNEC_{marine sediment}** in water :

Taking into account a K_{OC} range of 550,000 – 7,760,000 L.kg⁻¹, the value of the PNEC_{marine sediment} of 60 µg.kg⁻¹ based on sediment toxicity tests permits to calculate a corresponding value in water (PNEC_{marine sediment, water}) of **0.4 – 5.7 ng.L⁻¹**.

Comparing both pelagic and benthic data, it seems that the thresholds are quite consistent between each other. However, it was decided to apply the worst case and to consider the lowest PNEC_{marine sediment, water} of 0.4 ng.L⁻¹, obtained when taking into account the highest K_{OC} value of 7,760,000 L.kg⁻¹.



Overall threshold of no effect for marine environment for Benzo[k]fluoranthene :

- 60 µg.kg⁻¹ of sediment (dry weight)
- ~ 0.4 ng.L⁻¹ of water

4.10. Benzo[g,h,i]perylene

4.10.1. Effects on organisms

Effects on pelagic organisms

Few data are available for exposition of pelagic organisms to benzo[g,h,i]perylene. They are reported in Table 4.10.1-1 and Table 4.10.1-2.

Table 4.10.1-1 : Acute toxicity of Benzo[g,h,i]perylene to pelagic organisms

Taxa	Species ^a	EC type ^b	EC/NOEC Value ($\mu\text{g}\cdot\text{L}^{-1}$)	Expo.Conc. ^c ($\mu\text{g}\cdot\text{L}^{-1}$)	Expo. Type ^d	RI ^e	References
Invertebrates Crustacean	<i>Daphnia magna</i> (FW)	LC ₅₀ (38h) MOR	0.2		R/M	2	(Newsted and Giesy, 1987)
		LC ₅₀ (48h) MOR	>0.2	nr (n>4)	S/M	2	(Bisson <i>et al.</i> , 2000)

^a FW : fresh water organisms.

^b LC₅₀ : Lethal concentration for 50% of the population; MOR : mortality.

^c Expo.Conc. : Concentration of the substance to which organisms were exposed during the test. n=number of exposure concentrations apart from controls; nr : information not reported.

^d S : static exposition; R : renewal exposition; M : EC/NOEC value based on measured concentrations.

^e RI : Reliability Index (Klimish *et al.*, 1997); 1 :Valid without restriction; 2 :Valid with restriction; 3 :Not reliable; 4 :Not assignable.

Table 4.10.1-2 : Chronic toxicity of Benzo[g,h,i]perylene to pelagic organisms

Taxa	Species ^a	EC type ^b	EC/NOEC value ($\mu\text{g}\cdot\text{L}^{-1}$)	Expo. Conc. ^c ($\mu\text{g}\cdot\text{L}^{-1}$)	Expo. Type ^d	RI ^e	References
Algae	<i>Pseudokirchneriella subcapitata</i> (FW)	EC ₁₀ (72h) GRO _b	>0.16	nr (n>4)	S/M	2	(Bisson <i>et al.</i> , 2000)
Invertebrates Crustacean	<i>Ceriodaphnia dubia</i> (FW)	EC ₁₀ (7d) REP	0.08	nr (n>4)	R/M	2	(Bisson <i>et al.</i> , 2000)
Fish	<i>Brachydanio rerio</i> (FW)	NOEC (28d) MOR, GRO	>0.16	nr	R/M	4	(Hooftman and Evers-de Ruyter, 1992)

^a FW : fresh water organisms.

^b EC₁₀ : Effect Concentration for 10% of the population; NOEC : No Observed Effect Concentration; GRO : growth; MOR : mortality; ELS : diverse endpoints observed during early life stage.

^c Expo.Conc. : Concentration of the substance to which organisms were exposed during the test. n=number of exposure concentrations apart from controls; nr : information not reported.

^d S : static exposition; R : renewal exposition; M : EC/NOEC value based on measured concentrations.

^e RI : Reliability Index (Klimish *et al.*, 1997); 1 :Valid without restriction; 2 :Valid with restriction; 3 :Not reliable; 4 :Not assignable.

Effects on benthic organisms

There is no data available in the literature issued from valid water sediment toxicity tests, reporting toxicity of sediment spiked with benzo[g,h,i]perylene to benthic organisms.

Effects on top predators: secondary poisoning

Many toxicity data on mammals have been carried out with cutaneous exposition but no oral toxicity data was found.

4.10.2. *Thresholds of no effect*

Threshold of no effect for pelagic organisms

Given the dataset available, it can not be stated if differences of sensitivity exist between marine and freshwater organisms. Freshwater data will be used by default to derive marine PNEC.

Chronic values are available for the three main trophic levels (algae, crustaceans, fish) in freshwater. The lowest data is an EC₁₀ obtained by Bisson *et al.* (2000) for their 7 day test on reproduction of *Ceriodaphnia dubia*. According to the TGD (European Commission, 2003), this value can be assimilated to a NOEC and an assessment factor of 100 can be applied to it to derive a PNEC for marine organisms:

$$\text{PNEC}_{\text{seawater}} = 0.08 \text{ (}\mu\text{g/L}^{-1}\text{)} / 100 = 0.0008 \text{ }\mu\text{g.L}^{-1}$$



Threshold of no effect for marine pelagic organisms = 0.8 ng.L⁻¹

Thresholds of no effect for benthic organisms

Given that absolutely no valid data are available in the literature, it is not possible to derive a threshold of no effect of benzo[g,h,i]perylene for benthic organisms.

Threshold of no effect for marine top predators

Given that absolutely no valid data are available in the literature, it is not possible to derive a threshold of no effect of benzo[g,h,i]perylene for top predators.

Overall threshold of no effect for the marine environment

The threshold of no effect for pelagic organisms is the only one that could be derived.

As a first approach, this threshold will be considered for the protection of the whole marine environment:



Overall threshold of no effect for marine environment for Benzo[g,h,i]perylene :

- 0.8 ng.L⁻¹ of water

4.11. Indeno[1,2,3-cd]pyrene

4.11.1. *Effects on organisms*

Effects on pelagic organisms

Few data are available for exposition of pelagic organisms to indeno[1,2,3-cd]pyrene. They are reported in Table 4.11.1-1 and Table 4.11.1-2.

Table 4.11.1-1 : Acute toxicity of Indeno[1,2,3-cd]pyrene to pelagic organisms

Taxa	Species ^a	EC type ^b	EC/NOEC Value ($\mu\text{g.L}^{-1}$)	Expo.Conc. ^c ($\mu\text{g.L}^{-1}$)	Expo. Type ^d	RI ^e	References
Invertebrates Crustacean	<i>Daphnia magna</i> (FW)	LC ₅₀ (48h) MOR	>397	nr (n>4)	S/M	2	(Bisson <i>et al.</i> , 2000)

^a FW : fresh water organisms.

^b LC₅₀ : Lethal concentration for 50% of the population; MOR : mortality.

^c Expo.Conc. : Concentration of the substance to which organisms were exposed during the test. n=number of exposure concentrations apart from controls; nr : information not reported.

^d S : static exposition; M : EC/NOEC value based on measured concentrations.

^e RI : Reliability Index (Klimish *et al.*, 1997); 1 :Valid without restriction; 2 :Valid with restriction; 3 :Not reliable; 4 :Not assignable.

Table 4.11.1-2 : Chronic toxicity of Indeno[1,2,3-cd]pyrene to pelagic organisms

Taxa	Species ^a	EC type ^b	EC/NOEC value ($\mu\text{g.L}^{-1}$)	Expo. Conc. ^c ($\mu\text{g.L}^{-1}$)	Expo. Type ^d	RI ^e	References
Algae	<i>Pseudokirchneriella subcapitata</i> (FW)	EC ₁₀ (72h) GRO _b	1.5	nr (n>4)	S/M	2	(Bisson <i>et al.</i> , 2000)
Invertebrates Crustacean	<i>Ceriodaphnia dubia</i> (FW)	EC ₁₀ (7d) REP	0.27	nr (n>4)	R/M	2	(Bisson <i>et al.</i> , 2000)

^a FW : fresh water organisms.

^b EC₁₀ : Effect Concentration for 10% of the population; NOEC : No Observed Effect Concentration; GRO : growth; MOR : mortality; ELS : diverse endpoints observed during early life stage.

^c Expo.Conc. : Concentration of the substance to which organisms were exposed during the test. n=number of exposure concentrations apart from controls; nr : information not reported.

^d S : static exposition; R : renewal exposition; M : EC/NOEC value based on measured concentrations.

^e RI : Reliability Index (Klimish *et al.*, 1997); 1 :Valid without restriction; 2 :Valid with restriction; 3 :Not reliable; 4 :Not assignable.

Effects on benthic organisms

There is no data available in the literature issued from valid water-sediment toxicity tests, reporting toxicity of sediment spiked with indeno[1,2,3-cd]pyrene to benthic organisms.

Effects on top predators: secondary poisoning

Many toxicity data on mammals have been carried out with cutaneous exposition but no oral toxicity data was found.

4.11.2. *Thresholds of no effect*

Threshold of no effect for pelagic organisms

Given the dataset available, it can not be stated if most sensitive species are represented as no data could be found for marine and freshwater fish. Therefore, it is not possible to derive a threshold of no effect of indeno[1,2,3-cd]pyrene for pelagic organisms.

Thresholds of no effect for benthic organisms

Given that absolutely no valid data are available in the literature, it is not possible to derive a threshold of no effect of indeno[1,2,3-cd]pyrene for benthic organisms.

Threshold of no effect for marine top predators

Given that absolutely no valid data are available in the literature, it is not possible to derive a threshold of no effect of indeno[1,2,3-cd]pyrene for top predators.

Overall threshold of no effect for the marine environment

Given that derivation of thresholds can be done for none of the three compartment (pelagic, benthic, top predators), it is not possible to evaluate a threshold of no effect for the marine environment.

4.12. Cadmium

4.12.1. General issues, physico-chemical characteristics and behaviour in the marine environment

Cadmium (Cd) is a trace metal that naturally occurs in the environment. It is not considered to be essential to life but its role for carbon assimilation by phytoplankton has been recognized (Lane *et al.*, 2005).

Figure 4.12.1-1 : CAS numbers, structural features, chemical formula and physico-chemical characteristics of cadmium forms influencing their behaviour in the marine environment (INRS, 1997)

	Sol.W. (25°C) (mg.L ⁻¹)	Vp (Pa)
Cadmium metal : Cd CAS n° 7440-43-9 MW = 112.41 g.mol ⁻¹	insoluble	0.0028 (157°C) 184 (400°C) 2,130 (500°C)
Cadmium oxyde : CdO CAS n° 1306-19-0 MW = 128.41 g.mol ⁻¹	insoluble	130 (1000°C)
Cadmium chloride : CdCl ₂ CAS n° 10108-64-2 MW = 183.32 g.mol ⁻¹	1.4 10 ⁶	400 (400°C) 82,400 (952°C)
Cadmium nitrate, hydrated : Cd(NO ₃) ₂ , H ₂ O CAS n° 10325-94-7 MW = 308.48 g.mol ⁻¹	1.5 10 ⁶	
Cadmium sulfate, hydrated : 3 (CdSO ₄), 8 H ₂ O CAS n° 10124-36-4 MW = 769.53 g.mol ⁻¹	1.13 10 ⁰	
Cadmium sulfide : CdS CAS n° 1306-23-6 MW = 144.47 g.mol ⁻¹	1.3	

Fate of cadmium in the environment (Cossa and Lassus, 1989)

Cadmium enters seawater mainly *via* atmospheric deposition, rain and sewage treatments or other anthropic releases. It can be found in the marine environment in different forms : dissolved, particulate or colloidal. Partition between dissolved and particulate phasis controlled by pH, redox potential, ionic strength of water, occurrence of dissolved/particulate organic matter, inorganic material and living organisms activities.

In freshwater, cadmium is mainly found in particular and colloidal forms and more precisely as organic or inorganic complexes ($\text{Cd}(\text{OH})_2$ and $\text{Cd}(\text{HCO}_3)_2$). In estuarine areas, dissolved forms and chlorocomplex (CdCl_2 , CdCl^+) are predominant as salinity rises. Finally, in marine waters strong adsorption of cadmium (very high $K_{p_{\text{sed}}}$ of 85,000 and $K_{p_{\text{MES}}}$ of 120,000) occurs on biogenic particles and their subsequent sedimentation leading to an important decrease of dissolved cadmium concentration in surface seawater. When settled with sediment, cadmium is strongly bound to sulfur in the anoxic area.

According to different studies, cadmium does not undergo biomagnification.

4.12.2. *Toxicological properties*

Acute toxicity

Cadmium is considered to have high acute toxicity, based on short-term animal tests (U.S. Department of Health and Human Services, 1993).

Chronic toxicity

Chronic inhalation or oral exposure of animals to cadmium results in effects on the kidney, liver, lung, bone, immune system, blood, and nervous system (ATSDR, 2006; Calabrese and Kenyon, 1991).

This metal is embryotoxic, causing different kinds of malformations and lethality in mammals (Belmonte *et al.*, 1989; Fein *et al.*, 1997) as well as amphibians (Herkovits and Pérez-Coll, 1990; Pérez-Coll *et al.*, 1986).

Animal studies provide evidence that cadmium has developmental effects, such as low fetal weight, skeletal malformations, interference with fetal metabolism, and impaired neurological development, *via* inhalation and oral exposure (ATSDR, 2006; Calabrese and Kenyon, 1991; HSDB, 1993). Limited mammalian data are available, although some reproductive effects, such as decreased reproduction and testicular damage, have been noted following oral exposures (ATSDR, 2006).

4.12.3. *Sources of information of effects data and thresholds determination*

A Risk Assessment Report is currently in progress in the European Union (European Commission, unpublished-1). At present, this report does not address risk assessment for the marine environment but solely for freshwater. A Substance Data Sheet written in the context of the Water Framework Directive (European Commission, unpublished-2) is moreover available, dealing with *both* freshwaters *and* saltwaters.

In order to be consistent with decision taken at the european level, it was decided to use this work lead in the context of European Union and all information provided below have been extracted from those two reports.

4.12.4. *Thresholds of no effect*

Thresholds of no effect for pelagic organisms

There is a wealth of data assessing toxicity of cadmium to freshwater and seawater organisms. These data are evaluated for reliability in the Revised Draft Risk Assessment Report for Cadmium metal and Cadmium oxide and it outcomes from the Revised Draft RAR that even after this selection there is still a lot of data available.

Therefore, both methods for derivation of PNEC are available and will be reported thereafter.

- **Derivation of PNEC by the assessment factor method**

Data are available for all three trophic levels to calculate the $PNEC_{water}$ by the assessment factor method. Therefore, according to TGD (European Commission, 2003), it seems appropriate to divide the lowest reliable NOEC of $0.16 \mu\text{g.L}^{-1}$ by the lowest assessment factor of 100 to derive $PNEC_{saltwater}$:

$$PNEC_{seawater} = 0.16 (\mu\text{g/L}^{-1}) / 100 = 0.0016 \mu\text{g.L}^{-1}$$



Threshold of no effect for marine pelagic organisms = 1.6 ng.L^{-1}

However, the dataset used contains only freshwater results therefore it was not possible to observe if significant differences appear between freshwater and saltwater data and **this $PNEC_{seawater}$ has to be considered with precaution**

- **Derivation of PNEC by the statistical extrapolation method**

HC_{5-freshwater} (European Commission, unpublished-1)

In the Revised Draft RAR, different species sensitivity distributions (SSD) have been calculated from the freshwater data available and different pool of reliable data are used to apply the statistical extrapolation method of (Aldenberg and Slob, 1993) to determine the hazardous concentration fifth percentile (HC₅), with 50% confidence, of these species sensitivity distribution.

The two SSD approaches are the following:

- log-logistic SSD
- log-normal SSD

The four different approaches of data selection are the following:

- approach using all reliable data
- approach calculating a geometric mean of the NOEC values for each species (resulting in one NOEC per species)
- approach on a case-by-case basis calculating a geometric mean of NOEC for the same species and endpoint, tested in similar media (not resulting in one NOEC per species)
- approach using lowest NOEC for each species (resulting in one NOEC per species)

Results indicate that the choice of SSD (log-logistic or log-normal) does not affect the HC₅.

On the other hand, the choice of data selection (geometric mean calculation or not, lowest NOEC selection or not) influences the HC_5 by a factor up to two. The decision is taken, based on expert judgement, to use the third approach with geometric means of each NOEC for the same species, endpoint and media (for details, see (European Commission, unpublished-1)).

This approach results in a $HC_5 = 0.38 \text{ mg L}^{-1}$ and the frequency distribution reported in Figure 4.12.4-1.

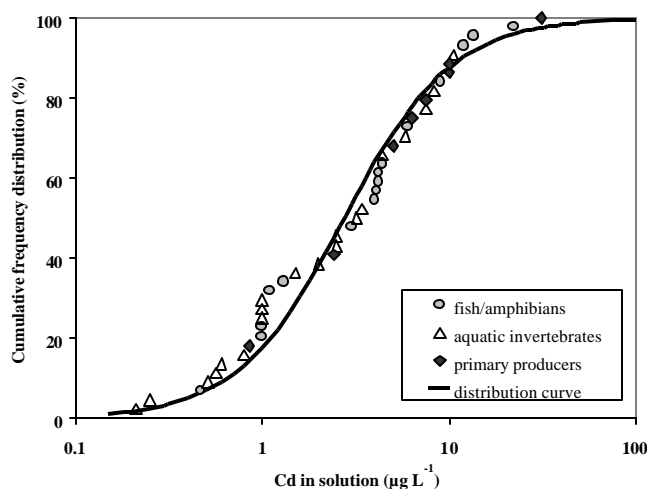


Figure 4.12.4-1: Frequency distribution and HC_5 . Cumulative frequency distribution of the reliable NOEC values of Cd toxicity tests of data used to calculate the HC_5 (case-by-case geometric mean calculation; $n = 44$) (European Commission, unpublished-1)

$PNEC_{\text{seawater}}$ (European Commission, unpublished-2)

Marine effects data of cadmium have been provided in the context of the Expert Group on Quality Standards. These data come from appendix 2 of the report from the RIVM (Crommentuijn *et al.*, 1997). Long-term NOECs for marine organisms are available for many taxa, i.e. marine fish, crustaceans, several groups of algae, shellfish, annelids, nematoda, and cyanobacteria. The species requirements for using the SSD approach as given in the TGD is nevertheless not entirely fulfilled as NOECs of insects and higher plants are not included in the database (see 2.3.2). *However, the recommendation of the TGD is focused on freshwater environments and insects and higher plants are taxonomic groups that are normally not of particular relevance in saltwater or transitional waters (with the exception of higher plants in mangrove or seagrass ecosystems).*

The fifth percentile cut-off value was calculated with the same method as the one for freshwater data (Aldenberg and Jaworska, 2000). The approach followed is in line with the approach used to derive the HC_5 for freshwater. The different taxonomic groups have been given similar weight (i.e. nearly the same number of toxicity tests per taxonomic group were included in the SSD if enough data were available, only one endpoint - the most sensitive - per species). If more than one test result for the same species, endpoint and exposure time was available the geometric mean of the individual NOECs was calculated.

The selected log-transformed data fit well to the expected distribution curve (see Figure 4.12.4-2), the probability that they fit the normal distribution is 90,7% according to the Kolmogoroff-Smirnoff goodness of fit test."

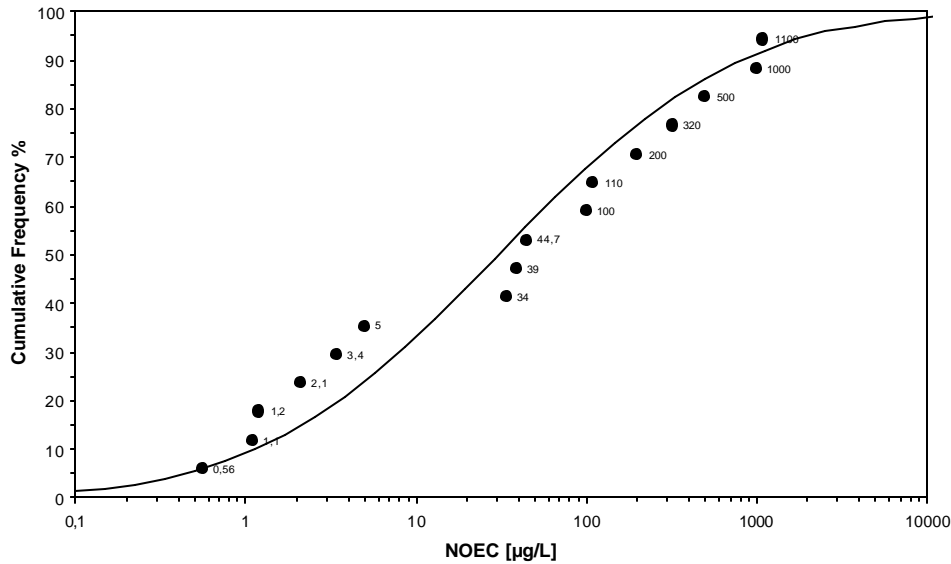


Figure 4.12.4-2 : Cumulative frequency distribution of the saltwater data set used for the derivation of the HC₅ by the method of Aldenberg and Jaworska (2000) (European Commission, unpublished-1)

This approach for seawater data results in a **HC₅ = 0.42 µg.L⁻¹** (IC95% = 0.048 – 1.779 µg.L⁻¹) (n=16)

"In order to account for further uncertainties it is foreseen in the TGD to divide the HC₅ by an appropriate assessment factor between 1 and 5. Lowering the assessment factor below 5 on the basis of increased confidence needs to be fully justified. The exact value of the assessment factor must depend on an evaluation of the uncertainties around the derivation of the 5th percentile.

The data base used for the calculation of the HC₅ covers less than the 8 normally recommended different taxonomic groups. Toxicity data on relevant marine taxonomic groups such as echinodermata, coelenterata and porifera are lacking. Further the ratio between the 50% and 95% confidence levels of the 5%-cut-off-value is quite high (8.75). However, on the other hand the lowest reported NOECs for saltwater organisms are in the same range as for freshwater organisms and none of the NOECs of the saltwater database is below the calculated HC₅. It is therefore proposed to use the same assessment factor used in the risk assessment report for the result of the SSD with freshwater data, i.e. 2.", as a lot of reliable data are available and as very few reliable LOECs are below the HC₅ obtained :

$$\text{PNEC}_{\text{seawater.stat.}} = 0.42 (\mu\text{g/L}^{-1}) / 2 = 0.21 \mu\text{g.L}^{-1}$$

Threshold of no effect for marine pelagic organisms = 0.21 µg.L⁻¹

Thresholds of no effect for benthic organisms

For freshwater, *the assessment factor method yields a PNEC_{sediment} for freshwater that is almost identical as the PNEC_{sediment} derived with the equilibrium partitioning method. The assessment factor method however predicts a PNEC_{sediment} which is even below the background value of the freshwater sediment in which the lowest chronic NOEC was found (2.8 mg Cd kg⁻¹_{dw}). The separation between the PNEC and effect concentrations (n=15) is higher than 100-fold, and this is large for natural elements. Additional chronic toxicity data (currently not found) could remove this concern by reducing the assessment factor to 10 or below. However, it should be recalled that sediment toxicity tests spiked with Cd have little field relevance because Cd availability can remain low as long as the capacity of free sulphides (AVS) in the sediment is not exceeded. Mixed metal pollution is the rule rather than the exception in the field and the Cd availability in metal polluted sediment is larger than in clean sediment."*

There is currently no data available for sediment toxicity testing of cadmium. Given this lack of data and the uncertainties stressed above, it does not seem appropriate to derive a PNEC_{marine sediment} without experimental data.

Thresholds for marine top predators

For freshwater, a PNEC_{oral} of 16 mg.kg⁻¹ (ww) was determined in the Revised Draft RAR of cadmium but it is stated in this report that this derivation of PNEC_{oral} is *"made for freshwater systems and not for marine environments. Nephrotoxic lesions ascribed to Cd have been found in sea birds from areas that are relatively uncontaminated and where natural Cd may be the source. It is therefore proposed in that the PNEC_{oral} should not be used for the marine environment where the bioaccumulation of Cd differs from that in freshwater dominated systems."*

4.13. Mercury

4.13.1. General issues, physico-chemical characteristics and behaviour in the marine environment

Mercury (Hg) is a trace metal that naturally occurs in the environment but is not essential to life.

Figure 4.13.1-1 : CAS numbers, structural features, chemical formula and physico-chemical characteristics of mercury forms influencing their behaviour in the marine environment (INERIS, 2005)

	Sol.W. (20°C) (mg.L ⁻¹)	Vp (20°C) (Pa)
Mercury metal : Hg CAS n°7439-97-6 MW = 200.59 g.mol ⁻¹	0.0567	0.17
Inorganic mercury : HgCl ₂ CAS n° 7487-94-7 MW = 271.52 g.mol ⁻¹	69,000	0.009
Methylmercury chloride: CH ₃ HgCl CAS n° 115-09-3 MW = 251.1 g.mol ⁻¹	6,000 (25°C)	1.8 (25°C)

Fate of mercury in the environment (Fitzgerald and Lamborg, 2003; UNEP, 2002)

Mercury enters seawater mainly *via* atmospheric deposition and sewage treatments or other anthropic releases *via* rivers input.

In both freshwater and saltwater, adsorption of mercury on suspended matter and sediments is very high (Kp *ca.* 100,000). Biogeochemical processes involving mercury in the marine environment are very complex, involving particularly air-seawater and particle-water exchanges, but their precise description is not the aim of this study.

The main information that must be kept in mind for the study of mercury effects to marine organisms is that this metal undergo processes of methylation in the aquatic environment leading to the formation of organic forms of mercury (methylmercury CH₃Hg and dimethylmercury (CH₃)₂Hg). These organic forms of mercury present fairly variable bioconcentration and biomagnification factors for diverse aquatic organisms but they can be very high (up to 10⁷), leading to important adverse effects.

4.13.2. Toxicological properties

Toxicological effects of mercury have been known for a very long time.

Human and wildlife health effects of mercury exposure have been the subjects of a number of investigations (Meyers *et al.*, 2000), but sublethal effects to aquatic species from chronic exposure, have been less studied (Wiener and Spry, 1996).

The effects described depend upon different parameters like dose and exposure route. They include organ lesions (kidney, liver, lung), haematological alterations (Iliopoulou-Georgudakis and Kotsanis, 2001; Kotsanis *et al.*, 2000), as well as immunological effects (MacDougal *et al.*, 1996; Voccia *et al.*, 1994).

Neurological effects also occurs when species are exposed to mercury. Indeed, mercury can affect the synthesis, release, and metabolism of neurotransmitters and receptors as demonstrated in mammals (Bondy *et al.*, 1979; Castoldi *et al.*, 1996; Kobayashi *et al.*, 1979) and fish (Huang *et al.*, 1997; Zhou *et al.*, 1999).

Finally, some behavioural changes have also been demonstrated in birds (Bouton *et al.*, 1999), and in fish (Weir and Hine, 1970; Zhou *et al.*, 1996). This type of effect can be of importance because modification of the ability of fish to forage, mate, compete or avoid predators can in turn affect the survival of their populations.

4.13.3. Sources of information of effects data and thresholds determination

A Substance Data Sheet is currently in progress in the context of the Water Framework Directive (European Commission, unpublished-3).

In order to be consistent with decision taken at the European level, it was decided to use this work lead in the context of European Union and all information provided below have been extracted from this report.

4.13.4. Thresholds of no effect

Thresholds of no effect for pelagic organisms

"There are many long-term no effect and short-term acute toxicity data for a broad range of species from different taxonomic groups available. With regard to long-term/chronic exposure algae, fish and crustaceans appear to be the most sensitive groups in freshwater whereas in saltwater molluscs and coelenterata (e.g. jellyfish) appear to be even more sensitive as the before mentioned groups." However, as there is no significant difference between the lower limit of the sensitivity ranges of freshwater and saltwater species, it seems appropriate to derive the thresholds for marine environment from the both freshwater and seawater datasets.

As many long-term no effect data are available, both assessment factor method and statistical extrapolation method are used for derivation of PNEC and will be reported thereafter.

▪ **Derivation of PNEC by the assessment factor method**

The lowest NOEC of $0.1 \mu\text{g.L}^{-1}$ has been obtained for the marine coelenterate *Clavopsella michaeli*. Long-term freshwater toxicity data as well as short-term acute data are available for many species of 9 different taxonomic groups. Moreover, a "comprehensive data base on marine species" is available. Therefore, it seems appropriate, "as suggested in the section on marine risk assessment in the TGD (European Commission, 2003), to apply a safety factor of 10 on the lowest reported NOEC" :

$$\text{PNEC}_{\text{seawater}} = 0.01 (\mu\text{g.L}^{-1}) / 10 = 0.001 \mu\text{g.L}^{-1}$$



Threshold of no effect for marine pelagic organisms = 1 ng.L^{-1}

▪ **Derivation of PNEC by the statistical extrapolation method**

Among the species required by TGD methodology for the use of statistical extrapolation method, the only missing taxa is higher plant species. "Since it is known that higher plants are not the group most sensitive to mercury it was deemed reasonable to apply a statistical extrapolation method."

In the Substance Data Sheet for cadmium (European Commission, unpublished-2), the 5th percentile cut-off value is calculated with the method of Aldenberg & Jaworska (2000). As far as possible the different taxonomic groups have been given equal weight (i.e. the same numbers of toxicity tests per taxonomic group have been included if enough data were available, only one test result per species was used). If more than one test result for a species was available the lowest result has been used.

Different pool of reliable data are used to apply the statistical extrapolation method to determine the HC₅ of the species sensitivity distribution:

- approach using both freshwater and seawater dataset
- approach using only freshwater dataset
- approach using only seawater dataset

Results indicate that the choice of dataset does not affect much the HC₅. Therefore, both datasets are chosen to be used for threshold derivation.

The selected log-transformed data fit well to the expected distribution curve (see Figure 4.13.4-1) and SSD calculation results in a **HC₅ = 0.142 $\mu\text{g.L}^{-1}$** (IC95% = 0.056 – 0.281 $\mu\text{g.L}^{-1}$).

"As the data base used for the calculation of the HC₅ covers 9 different taxonomic groups (but not all groups that should be covered according to the TGD) and since the confidence interval of the HC₅ is not very large (factor 2.5 between 50% certainty and 95% certainty) it is suggested to use 4 as assessment factor" for the derivation of the $\text{PNEC}_{\text{seawater}}$:

$$\text{PNEC}_{\text{seawater}} = 0.142 (\mu\text{g.L}^{-1}) / 4 = 0.036 \mu\text{g.L}^{-1}$$



Threshold of no effect for marine pelagic organisms = 36 ng.L^{-1}

Thresholds of no effect for marine top predators

Secondary poisoning is the main concern for protection of ecosystems from mercury contamination. Indeed, the most toxic form of mercury is the organic form (e.g. methylmercury) which is found in marine birds and marine mammal preys at levels as high as 70-90% of total mercury (EURO CHLOR, 1999) and for which bioaccumulation factors in top predator fish can be as high as 10^7 (Bowles *et al.*, 2001).

Therefore, in no way those parameters can be forgotten in the evaluation of effects of mercury to marine organisms and in derivation of thresholds of no effect for marine top predators.

Oral toxicity data reported in the Substance Data Sheet of mercury (European Commission, unpublished-3) all refer to inorganic mercury and the lowest reliable oral toxicity data found for birds is 0.25 mg inorganic mercury.kg⁻¹ food ww.

Applying strictly the TGD methodology would lead to the application of an assessment factor of 30 and a derivation of PNEC_{oral} for inorganic mercury of 8.3 µg.kg⁻¹ food ww. However, as toxicity data are solely referring to inorganic mercury, such threshold can not be considered relevant to protect marine top predators.

Work on derivation of PNEC_{oral} is still in progress and proposals have been made by industry and contracting parties trying to take into account bioconcentration and biomagnification processes, as well as proportion of inorganic mercury to organic mercury in organisms, but none of these proposals have yet been officially selected as more reliable than another.

To our mind, no threshold should be derived as long as no reliable test are reported that give a NOEC expressed as µg of organic mercury per kg of food administered.

Overall threshold of no effect for the marine environment

"Values calculated for the pelagic communities are presumably not low enough for the protection of predators from secondary poisoning."

Given the knowledge on bioaccumulation and toxicity of organic mercury and the considerable uncertainties cited above, no reliable overall threshold of no effect can be derived for the marine environment.

5. Conclusions

All thresholds of no effect that were reported in this report are summarized in Table 4.13.4-1. This overview makes it possible to underline the great lack of data. As a matter of fact, only 6 of the 14 substances have been attributed a minimum of one reliable and relevant threshold. The pelagic compartment is the one for which most data were available with 6 thresholds, while there are poor datasets for sediments and secondary poisoning.

A full set of thresholds is indicated in this report for Pentabromodiphenyl Ethers. The toxicity dataset is not that important but thresholds could be derived more easily than for PAH even when raw data were not available because a great amount of work had already been assessed by experts in the context of the European Union Risk Assessment Report. In the case of PCBs, it has to be stressed that very poor reliable toxicity information could be found on these chemicals although they are considered persistent organic pollutants of concern and encountered all over the world. The same remark could be done for some PAH, e.g. pyrene, benzo[b]fluoranthene and indeno[1,2,3-cd]pyrene where no thresholds could be derived. On the contrary, quite a lot of data are available for fluoranthene and benzo[g,h,i]perylene.

Table 4.13.4-1 : Overview of thresholds of no effect reported in the present study. AFM: Assessment Factor Method; SEM: Statistical Extrapolation Method; EqPM: Equilibrium Partitioning Method.

Chemicals	Thresholds of no effect for			Overall threshold of no effect for the marine environment ng.L ⁻¹
	Pelagic organisms	benthic organisms	marine top predators	
	ng.L ⁻¹	µg.kg ⁻¹ dw	µg.kg ⁻¹ ww	
PCB 105	-	-	-	-
PCB 118	-	-	1.1 (low reliability)	-
PCB 156	-	-	-	-
PCB 180	-	-	-	-
Pentabromodiphenyl Ethers	53	310	333	12.2 (←top predators)
Pyrene	-	-	-	-
Fluoranthene	100	155	11,500	32 (←sediment)
Benzo[a]pyrene	5	-	-	0.005 (←seawater)
Benzo[b]fluoranthene	-	-	-	-
Benzo[k]fluoranthene	3.6	60 (AFM) 38-537 (EqPM)	-	0.4 (←sediment)
Benzo[g,h,i]perylene	0.8	-	-	0.8 (←seawater)
Indeno[1,2,3-cd]pyrene	-	-	-	-
Cadmium	1.6 (AFM) 210 (SEM)	-	-	210 (←seawater)
Mercury	1 (not relevant)	-	-	-

Cadmium is a very well known metal for which a wealth of data is available. Therefore, the existence of the revised draft of the Risk Assessment Report made it possible to report thresholds for this substance while selection of reliable data and relevant methods is sometimes a difficult thing when a great amount of data is available. Finally, thresholds could not be derived for mercury, because so much reliable testing that refers to organic mercury is missing. Therefore, it was deemed more appropriate to wait until a decision is taken at the European Commission level in the context of the Framework Directive so as to be consistent.

Application of TGD methodology allows derivation of thresholds for marine compartments when seawater datasets are not so important. However, the work carried out during this study also permits to stress limits of the application of strict TGD methodology, when studies reveal complicated issues such as the one of toxicity of mercury. In such cases, it has to be kept in mind that methodology given in the TGD has to be used as a guidance, but never forgetting the idea that logic and expert judgement are the basis of chemical effects assessment.

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