NACIONALNI LABORATORIJ ZA
ZDRAVJE, OKOLJE IN HRANO

CENTER ZA OKOLJE IN ZDRAVJE



# STROKOVNE PODLAGE ZA MONITORING ORGANIZMOV
## ZAKLJUČNO POROČILO

Maribor, avgust 2020

**Oddelek za okolje in zdravje Maribor**
Prvomajska ulica 1, 2000 Maribor, **T:** (02) 45 00 260, **F:** (02) 45 00 148, **E:** mb.coz@nlzoh.si
**Nacionalni laboratorij za zdravje, okolje in hrano,** Prvomajska ulica 1, 2000 Maribor
**ID za DDV:** SI19651295, **TRR:** SI5601100-6000043285, **BIC:** BSLJSI2X, Banka Slovenije

| | |
|---|---|
| Naslov: | Strokovne podlage za monitoring organizmov |
| Izvajalec: | NACIONALNI LABORATORIJ ZA ZDRAVJE, OKOLJE IN HRANO<br>Center za okolje in zdravje<br>Oddelek za okolje in zdravje Maribor<br>Prvomajska 1, 2000 MARIBOR |
| Naročnik: | Republika Slovenija<br>Ministrstvo za okolje in prostor<br>Agencija Republike Slovenije za okolje<br>Vojkova 1b<br>1000 LJUBLJANA |
| Evidenčna oznaka: | 2111e-19/40409/1 |
| Delovni nalog: | Pogodba št. 2551-19-200003 z dne 26.02.2019 |
| Šifra dejavnosti: | 2111e – Projekti, raziskave in ekotoksikološki laboratorij |
| Izvajalci naloge: | |
| Vodja: | doc.dr. Mojca Durjava, univ.dipl.inž.kem.tehnol. |
| Sodelavci NLZOH: | Barbara Hajnžič, prof.biol.<br>Mojca Baskar, univ.dipl.inž.kem.tehnol.<br>Lovro Arnuš, prof.biol. |

MOJCA KOS DURJAVA
Digitalno podpisal MOJCA KOS DURJAVA
Datum: 2020.08.21 11:48:16 +02'00'

Maribor, 21.08.2020

ODDELEK ZA OKOLJE IN ZDRAVJE MARIBOR
Vodja:

mag. Emil Žerjal, univ.dipl.inž.kem.tehnol.

NATAŠA SOVIČ
Digitally signed by NATAŠA SOVIČ
Location: your signing location here
Date: 2020-08-21 11:55:43
Foxit Reader Version: 9.7.1

# KAZALO

STRAN

## Kazalo preglednic

## Razlaga pojmov in okrajšav

| | |
|---|---|
| EFSA | Evropska agencija za varno hrano |
| < LOQ | Označuje vrednost, ki je manjša od meje določanja |
| OSK | Okoljski standard kakovosti |
| $OSK_{organizmi}$ | Okoljski standard kakovosti za organizme |
| VD | Vodna direktiva, 2000/60/ES |
| BCF | Biokoncentracijski faktor organizmi/voda [L/kg] – upošteva izpostavljenost snovi preko obdajajočega medija (vode). |
| BAF | Bioakumulacijski faktor organizmi/sediment (tla) [-] – upošteva izpostavljenost snovi preko vseh možnih poti izpostavljenosti (zrak, voda, tla, sediment) in preko hrane. |
| BMF | Biomagnifikacijski faktor plenilec/plen [-]– upošteva izpostavljenost snovi preko hrane. |
| $DT_{50}$ | Čas potreben za razgradnjo 50% začetne koncentracije snovi v testu [dan] |
| $K_p$ | Porazdelitveni koeficient suspendirani delci/voda [L/kg] |
| $K_{ow}$ | Porazdelitveni koeficient oktanol/voda [-] |
| $K_d$ | Porazdelitveni koeficient tla/voda [L/kg] |
| $K_{oc}$ | Porazdelitveni koeficient organski ogljik/voda [L/kg] |
| $K_{psed}$ | Porazdelitveni koeficient sediment/voda [L/kg] |
| NOEC | Najnižja testna koncentracija snovi, ki ne povzroči učinka v kroničnem testu strupenosti. |
| LOEC | Najnižja testna koncentracija snovi, ki povzroči učinek v kroničnem testu strupenosti. |
| $LC_{50}$ | Testna koncentracija snovi, pri kateri pogine 50% testnih organizmov v akutnem testu strupenosti. |
| $EC_{50}$ | Testna koncentracija snovi, ki ima učinek na 50% testnih organizmov v akutnem testu strupenosti. |

# 1 Izhodišča

Izhodišče za pripravo strokovne podlage je 23. člen Zakona o varstvu okolja (Uradni list RS, št. 39/06 – uradno prečiščeno besedilo, 49/06 – ZMetD, 66/06 – Odl. US, 33/07-ZPNačrt, 57/08-ZFO-1A in 70/08), ki določa, da Vlada RS določi standarde kakovosti okolja in merila občutljivosti, ranljivosti ali obremenjenosti okolja, na podlagi katerih se deli okolja ali posamezna območja razvrščajo v razrede ali stopnje.

Pri določanju standardov kakovosti okolja je treba upoštevati tudi določbe zakonodaje Evropske skupnosti, ki zlasti na področju vrednotenja kemijskega stanja površinskih voda določa skupna merila pri vrednotenju posameznih parametrov stanja površinskih voda.

Slovenija izvaja monitoring in ocenjevanje kemijskega stanja površinskih voda v organizmih, kot to zahteva Direktiva 2013/39 EU Evropskega parlamenta in Sveta o spremembi direktiv 2000/60/ES in 2008/105/ES v zvezi s prednostnimi snovmi na področju vodne politike. Za namen optimizacije tega monitoringa je potrebno pripraviti strokovne podlage glede strokovno ustreznega časovnega obdobja spremljanja stanja v organizmih.

Projektna naloga Strokovne podlage za monitoring organizmov je predvidevala izvedbo štirih poglavij in sicer:

1. Določiti strokovno utemeljeno pogostost monitoringa za zanesljivo ugotavljanje kemijskega stanja v organizmih;
2. Pripraviti popis emisij BDE in način določitve ocene kemijskega stanja tistih vodnih teles, v katerih se monitoring BDE v organizmih ne izvaja;
3. Pripraviti popis emisij Hg in način določitve ocene kemijskega stanja tistih vodnih teles, v katerih se monitoring Hg v organizmih ne izvaja;
4. Določiti način ocenjevanja kemijskega stanja tistih vodnih teles, v katerih se monitoring organizmov ne izvaja.

Na Nacionalnem laboratoriju za zdravje, okolje in hrano smo nalogo izvedli deloma in sicer je prvo poglavje predstavljeno v tretji točki poročila. V tem poglavju smo utemeljili pogostost monitoringa organizmov. Četrto poglavje projektne naloge je izvedeno deloma in predstavljeno v četrti točki poročila. V tem delu naloge smo natančneje predstavili zbrane podatke in za vsako snov posamezno utemeljili pogostost monitoringa organizmov. Drugo in tretje poglavje projektne naloge ni bilo izvedeno.

# 2 Cilji in namen naloge

Cilj naloge je izdelati strokovno podlago za časovno ustrezno izvedbo monitoringa stanja površinskih voda (rek, jezer in morja) na podlagi analiz organizmov, ob upoštevanju zahtev Direktive 2013/39/EU.

Direktiva 2008/105/ES o okoljskih standardih na področju vodne politike, ki je bila dopolnjena z Direktivo 2013/39/EU, predpisuje okoljske standarde kakovosti v organizmih za snovi, ki so navedene v preglednici 1.

Preglednica 1: Okoljski standardi kakovosti za organizme v Direktivi 2013/39/ES

| Zap. št. | Ime snovi | CAS številka | OSK organizmi (µg/kg) |
|---|---|---|---|
| (5) | Bromirani difeniletri | 32534-91-9 | 0,0085 |
| (15) | Fluoranten | 206-44-0 | 30 |
| (16) | Heksaklorobenzen | 118-74-1 | 10 |
| (17) | Heksaklorobutadien | 87-68-3 | 55 |
| (21) | Živo srebro in njegove spojine | 7439-97-6 | 20 |
| (28) | Benzo(a)piren | 50-32-8 | 5 (1) |
| (34) | Dikofol | 115-32-3 | 33 |
| (35) | Perfluorooktansulfonska kislina in njeni derivati (PFOS) | 1763-23-1 | 9,1 |
| (37) | Dioksini in dioksinom podobne spojine | n.p. | vsota PCDD + PCDF + PCB-DL 0,0065 TEQ (2) |
| (43) | Heksabromociklododekan (HBCDD) | 25637-99-4/ 3194-55-6/ 134237-50-6/ 134237-51-7/ 134237-52-8 | 167 |
| (44) | Heptaklor in heptaklorepoksid | 76-44-8 / 1024-57-3 | 0,0067 |

*Legenda:*

n.p. = ni podatka

(1) Pri skupini prednostnih snovi poliaromatskih ogljikovodikov (PAH) (št. 28) se OSK za organizme in ustrezni LP-OSK v vodi nanašajo na koncentracijo benzo(a)pirena, saj temeljijo na njegovi toksičnosti. Benzo(a)piren se lahko šteje za kazalnik za druge PAH, zato je treba za primerjavo z OSK za organizme ali ustreznimi LP-OSK za vodo spremljati le benzo(a)piren.

(2) PCDD: poliklorirani dibenzo-p-dioksini; PCDF: poliklorirani dibenzofurani; PCB-DL: dioksinom podobni poliklorirani bifenili; TEQ: toksični ekvivalenti v skladu s faktorji toksične ekvivalentnosti Svetovne zdravstvene organizacije iz leta 2005.

Navedeni okoljski standardi se nanašajo na ribe, razen za snovi pod zaporedno št. 15 in 28, kjer se standard za organizme nanaša na rake in mehkužce in za snovi pod številko 37 (dioksini in dioksinom podobne spojine), kjer se OSK za organizme nanaša na ribe, rake in mehkužce (npr. školjke).

V nalogi smo pripravili strokovne podlage glede strokovne utemeljenosti pogostosti monitoringa za zanesljivo ugotavljanje kemijskega stanja v organizmih.

# 3 Strokovna utemeljenost pogostosti monitoringa za zanesljivo ugotavljanje kemijskega stanja v organizmih

## 3.1 Monitoring organizmov in okoljski standardi kakovosti za organizme v okviru Vodne direktive

Namen okoljskih standardov kakovosti (v nadaljevanju OSK) je zaščititi vodne ekosisteme pred škodljivimi učinki kemikalij in zaščititi zdravje človeka pred škodljivimi učinki v povezavi z uživanjem pitne vode ali hrane iz vodnega okolja (Evropska komisija, 2014a). OSK so tako določeni za več ciljev, ki jih želimo zaščititi. OSK za organizme (v nadaljevanju $OSK_{organizmi}$) imajo dva cilja zaščite:

- Zaščita pred akumulacijo kemikalij v prehranjevalni verigi, predvsem za ptice in sesalce, ki predstavlja tveganje za sekundarne zastrupitve preko uživanja onesnaženega plena. Standard označujemo z $OSK_{organizmi,sek.zastr.}$ (Evropska komisija, 2014a).
- Zaščita zdravja človeka pred škodljivimi učinki uživanja hrane, n.pr. rib, školjk, rakov, različnih olj, onesnaženih s kemikalijami. Standard označujemo z $OSK_{organizmi,čl.hrana}$ (Evropska komisija, 2014a).

OSK so vedno določeni tako, da ščitijo celoten ekosistem in ne le tistega, na katerega se OSK nanašajo. V navodilu za določanje OSK (Evropska komisija, 2011) je poudarjeno, da n.pr. $OSK_{organizmi}$ za ptice in sesalce ščitijo tudi bentoške in pelagične plenilce. V preglednici 2 so predstavljene snovi iz Direktive 2013/39/ES z $OSK_{organizmi}$ s ciljem zaščite in z vrsto organizmov, ki jih je treba preiskati v okviru monitoringa površinskih voda.

Preglednica 2: Snovi iz Direktive 2013/39/ES z $OSK_{organizmi}$, vrsto organizmov in ciljem zaščite

| Zap. št. | Ime snovi | $OSK_{organizmi}$ (µg/kg) | Vrsta organizma | Cilj zaščite | Uporabljeno tkivo |
|---|---|---|---|---|---|
| (5) | Bromirani difeniletri | 0,0085 | ribe | zdravje človeka | mišice rib |
| (15) | Fluoranten | 30 | raki ali školjke | zdravje človeka | mehko tkivo rakov ali školjk |
| (16) | Heksaklorobenzen | 10 | ribe | zdravje človeka | mišice rib |
| (17) | Heksaklorobutadien | 55 | ribe | sek. zastrupitev | celotna riba |
| (21) | Živo srebro in njegove spojine | 20 | ribe | sek. zastrupitev | celotna riba |
| (28) | Benzo(a)piren | 5 | raki ali školjke | zdravje človeka | mehko tkivo rakov ali školjk |
| (34) | Dikofol | 33 | ribe | sek. zastrupitev | celotna riba |
| (35) | Perfluorooktansulfonska kislina in njeni derivati (PFOS) | 9.1 | ribe | zdravje človeka | mišice rib |
| (37) | Dioksini in dioksinom podobne spojine | 0,0065 (vsota TEQ) | ribe ali raki ali školjke | zdravje človeka | mišice rib ali mehko tkivo rakov ali školjk |
| (43) | Heksabromociklododekan (HBCDD) | 167 | ribe | sek. zastrupitev | celotna riba |
| (44) | Heptaklor in heptaklorepoksid | 0,0067 | ribe | zdravje človeka | mišice rib |

*Legenda:*

zdravje človeka =zdravje človeka preko uživanja ribjih proizvodov

sek. zastrupitev =sekundarna zastrupitev

Vrednosti $OSK_{organizmi}$, katerih cilj zaščite je zdravje človeka, so določeni na osnovi vrednosti, ki jih je določila Evropska agencija za varno hrano, EFSA. Določene so kot dopustni tedenski vnos v mikrogramih na kilogram teže telesa in maksimalnih vrednosti v hrani. Nevarne snovi, za katere so vrednosti $OSK_{organizmi}$ določene na ta način, so predstavljene v preglednici 2 in mednje spadajo bromirani difeniletri, fluoranten, heksaklorobenzen, benzo(a)piren, perfluorooktansulfonska kislina in njeni derivati (PFOS), dioksini in dioksinom podobne spojine in heptaklor ter heptaklorepoksid. Ostale vrednosti za $OSK_{organizmi}$, katerih cilj je zaščita pred sekundarno zastrupitvijo, so določene na osnovi ekotoksikoloških podatkov v skladu z navodili Evropske komisije za določanje OSK (Evropska komisija, 2011). Mednje spadajo heksaklorobutadien, živo srebro in njegove spojine, dikofol in heksabromociklododekan (HBCDD).

Navodilo za monitoring organizmov (Evropska komisija, 2014a) ne določa, katero vrsto organizmov je treba vzorčiti, izbira rib oziroma nevretenčarjev (rakov in mehkužcev) je prepuščena državam članicam. Leta 2016 smo na NLZOH v sodelovanju z Zavodom za ribištvo in Agencijo RS za okolje v projektni nalogi določili organizme za monitoring organizmov (Kos Durjava in ost., 2016), pri čemer smo pri izbiri organizma upoštevali, da je le ta odvisna od prisotnosti določene vrste na območju vzorčenja. Ob izbiri organizma smo določili tudi vrsto tkiva, ki ga preiskujemo, v odvisnosti od cilja zaščite, na osnovi katerega je bil določen $OSK_{organizmi}$.

## 3.2 Pregled fizikalno kemijskih lastnosti, podatkov o usodi in obnašanju v okolju in podatkov o učinkih na vodno okolje za snovi, za katere so določeni $OSK_{organizmi}$ za vodno okolje

Med podatki, predstavljenimi v dosjejih za določitev OSK vrednosti, dostopnih na straneh Evropske komisije, CIRCABC, WFD CIRCA: Implementing the Water Framework Directive[1], najdemo razen različnih OSK vrednosti za posamezne snovi ali skupine snovi tudi relevantne fizikalno kemijske lastnosti snovi (topnost, porazdelitveni koeficient oktanol/voda, hlapnost, adsorpcija), podatke o usodi in obnašanju snovi v okolju (bioakumulacija, biomagnifikacija, abiotska, biotska razgradljivost), ter podatke o strupenosti snovi za vodno okolje in sekundarni zastrupitvi.

Pregleden povzetek podatkov za vse snovi je predstavljen v preglednici 3, preglednici 4 in preglednici 5. Vsi relevantni izvorni podatki so predstavljeni v prilogi 1 poročila, kot izseki iz originalnih dosjejev iz leta 2011 (v angleškem jeziku).

### *Fizikalno kemijske lastnosti snovi*

Pregleden povzetek fizikalno kemijskih lastnosti snovi, za katere so določeni $OSK_{organizmi,}$ je predstavljen v preglednici 3.

Iz predstavljenih podatkov je razvidno, da so vse obravnavane snovi slabo oziroma zelo slabo topne v vodi, izjema je PFOS, ki je v vodi srednje topen. Vse snovi so hidrofobne oziroma zelo hidrofobne z logaritmom porazdelitvenega koeficienta oktanol/voda najmanj 4 pa vse do več kot 8 v primeru dioksinov. Izjema so živo srebro, ki ni organska snov in zato $logK_{OW}$ ni relevanten podatek in PFOS, kjer podatka ni na razpolago. Parni tlak vseh snovi kaže na to, da je večina snovi slabo ali zelo slabo hlapnih, z izjemo heksaklorobutadiena, ki je hlapen, živega srebra, ki je srednje hlapna snov in PFOS, ki so od zelo slabo do srednje hlapni. Iz Henrijeve konstante je razvidno, da so vse snovi srednje ali zelo hlapne iz vode, znova z izjemo PFOS, ki je slabo hlapna iz vode. Iz predstavljenih podatkov o adsorpciji snovi je razvidno, da imajo

[1] Podatki iz dosjejev Evropske komisije za določitev OSK za prednostne snovi, objavljenih na straneh CIRCABC WFD, v knjižnici delovne skupine WG Chemicals (https://circabc.europa.eu/ui/group/9ab5926d-bed4-4322-9aa7-9964bbe8312d/library/dfcfb52e-48f1-4431-bff7-0c14919738fc?p=1&n=10&sort=modified_DESC).

vse snovi logaritem porazdelitvenega koeficienta organski ogljik/voda višji od 3 in porazdelitveni koeficient sediment/voda kaže na to, da se vežejo na sediment. Izjema je PFOS, kjer lahko iz vrednosti porazdelitvenih koeficientov sklepamo, da se snovi slabo vežejo na sediment in da so dobro mobilne v sedimentu.
V poglavju 4 je predstavljena opisna razlaga numeričnih vrednosti zbranih v preglednici 3.

***Usoda in obnašanje snovi v okolju***

Pregleden povzetek podatkov o usodi in obnašanju snovi v okolju, za snovi za katere so določeni $OSK_{organizmim}$ je predstavljen v preglednici 4.
Iz podatkov o razgradnji je razvidno, da so vse snovi slabo ali sploh niso biorazgradljive. Hidrolitična razgradnja v glavnem ne poteka, razen deloma v primeru dikofola in heptaklora. Fotolitična razgradnja pri nekaterih snoveh do neke mere poteče. Iz bioakumulacijskih faktorjev (BCF), ki so v glavnem višji od 2000, je razvidno, da se snovi kopičijo v organizmih. Izjema so benzo(a)piren ter oktaBDE in nonaBDE, ki imajo nižje BCF in se ne kopičijo v organizmih. Kopičenje snovi v prehranjevalni verigi in posledično sekundarno zastrupitev ocenjujemo z velikostjo biomagnifikacijskega faktorja, BMF. V kolikor je 1, se snov ne kopiči v prehranjevalni verigi, vrednosti večje od 1 pa nakazujejo da se snov kopiči v prehranjevalni verigi in da obstaja možnost sekundarne zastrupitve. Od snovi za katere so določeni $OSK_{organizmi}$, se v prehranjevalni verigi kopičijo živo srebro, dikofol, dioksini, HBCDD ter heptaklor in heptaklorepoksid. Fluoranten, heksaklorobutadien in benzo(a)piren se glede na predstavljene podatke ne kopičijo v prehranjevalni verigi. Vendar lahko glede na zelo visoke vrednosti BCF za heksaklorbutadien vseeno sklepamo, da se tudi kopiči v prehranjevalni verigi, našo oceno smo tudi potrdili s podatki iz literature (Moermon in Verbruggen, 2011). Za bromirane difeniletre, heksaklorobenzen in PFOS podatkov o biomagnifikaciji ni na razpolago.
V poglavju 4 je predstavljena opisna razlaga numeričnih vrednosti zbranih v preglednici 4.

***Učinek snovi na vodno okolje in sekundarna zastrupitev***

Pregleden povzetek podatkov o učinkih na vodno okolje, za snovi za katere so določeni $OSK_{organizmi}$ je predstavljen v preglednici 5.
Na osnovi predstavljenih končnih točk iz podatkov testiranja strupenosti (EC50, LC50, LOEC in NOEC vrednostih) vidimo, da so vse snovi akutno in kronično zelo strupene za vodno okolje. Iz preglednice 2 je tudi razvidno, da se je Evropska komisija odločila, da zaradi kopičenja heksaklorobutadiena, živega srebra, dikofola in HBCDD v prehranjevalni verigi cilj zaščite za te snovi ni vodno okolje, temveč sekundarna zastrupitev.
V poglavju 4 je predstavljena opisna razlaga numeričnih vrednosti zbranih v preglednici 5.

Preglednica 3: Fizikalno kemijske lastnosti snovi, za katere so določeni $OSK_{organizmi}$[2]

| Zap. št. | Ime snovi | CAS številka | Topnost (mg/L) | Log $K_{OW}$ (-) | Hlapnost Parni tlak (Pa) Henryjeva konstanta ($Pa*m^3*mol^{-1}$) | Adsorpcija Log $K_{OC}$ Log $K_{sed}$ |
|---|---|---|---|---|---|---|
| (5) | Bromirani difeniletri | 32534-91-9 | 0,011 | 5.87-6.16 | 0,00025-0,00033 Pa<br>10,6 $Pa*m^3*mol^{-1}$ | 5,75<br>4,15 |
| (15) | Fluoranten | 206-44-0 | 0,2 | 5,2 | 0,00012 Pa<br>1,1 $Pa*m^3*mol^{-1}$ | 4,99<br>2,444 |
| (16) | Heksaklorobenzen | 118-74-1 | 0,005-0,006 | 3,93-6,53 | 0,0011-0,0025 Pa<br>131 $Pa*m^3*mol^{-1}$ | 3,48-5,26<br>4,00-7,08 |
| (17) | Heksaklorobutadien | 87-68-3 | 2-4 | 4,78-4,9 | 20-36 Pa<br>1630 $Pa*m^3*mol^{-1}$ | 3,95-4,51<br>4,40-6,10 |
| (21) | Živo srebro in njegove spojine | 7439-97-6 | 20-30 ng/L | Ni relevanten podatek. | 0,25 Pa | Log $K_d$ = 5,50<br>Log $K_p$ = 5,00 |
| (28) | Benzo(a)piren | 50-32-8 | 0,00154 | 6,11 | $7,3*10^{-7}$ Pa<br>0,034 $Pa*m^3*mol^{-1}$ | 5,92<br>4,32 |
| (34) | Dikofol | 115-32-3 | 0,8 | p,p'-dikofol 4,08<br>o,p'-dikofol 4,32 | $5,3*10^{-7}$ Pa<br>0,015 $Pa*m^3*mol^{-1}$ | p,p'-dikofol 3,70; o,p'-dikofol 4,23 |

[2] V preglednici so predstavljeni podatki iz dosjejev Evropske komisije za določitev OSK za prednostne snovi, objavljenih na straneh CIRCABC WFD, v knjižnici delovne skupine WG Chemicals (https://circabc.europa.eu/ui/group/9ab5926d-bed4-4322-9aa7-9964bbe8312d/library/dfcfb52e-48f1-4431-bff7-0c14919738fc?p=1&n=10&sort=modified_DESC). Predstavljen je pregled podatkov, za katere ocenjujemo da so zanesljivi in reprezentativni za določeno snov ali skupino snovi.

| Zap. št. | Ime snovi | CAS številka | Topnost (mg/L) | Log $K_{OW}$ (-) | Hlapnost Parni tlak (Pa) Henryjeva konstanta ($Pa*m^3*mol^{-1}$) | Adsorpcija Log $K_{OC}$ Log $K_{sed}$ |
|---|---|---|---|---|---|---|
| | | | | | | p,p'-dikofol 2,10; o,p'-dikofol 2,63 |
| (35) | Perfluorooktansulfonska kislina in njeni derivati (PFOS) | 1763-23-1 | 370-570 | Ni podatka | $3,1*10^{-11}$-0,85 Pa<br>0,000319 $Pa*m^3*mol^{-1}$ | 1,81<br>0,71 |
| (37) | Dioksini in dioksinom podobne spojine | n.p. | $10^{-10}<S<10^{-2}$ | 6,0-8,20 | <0,000117 Pa<br>0,19-88,2 $Pa*m^3*mol^{-1}$ | 3,06-7,5<br>1,48-6,89 |
| (43) | Heksabromociklododekan (HBCDD) | 25637-99-4/ 3194-55-6/ 134237-50-6/ 134237-51-7/ 134237-52-8 | 0,0021-0,066 | 5,07-5,62 | $6,3*10^{-5}$ Pa<br>0,75 $Pa*m^3*mol^{-1}$ | 4,66<br>3,06 |
| (44) | Heptaklor in heptaklorepoksid | 76-44-8 / 1024-57-3 | 0,06-0,3 | 5,40-6,10 | $3,5*10^{-5}$-0,053 Pa<br>3,2-29,8 $Pa*m^3*mol^{-1}$ | 4,00-5,82<br>2,40-4,22 |

*Legenda:*

$K_p$ = Porazdelitveni koeficient suspendirani delci/voda [L/kg]

$K_{ow}$ = Porazdelitveni koeficient oktanol/voda [-]

$K_d$ = Porazdelitveni koeficient tla/voda [L/kg]

$K_{oc}$ = Porazdelitveni koeficient organski ogljik/voda [L/kg]

$K_{psed}$ = Porazdelitveni koeficient sediment/voda [L/kg]

Preglednica 4: Usoda in obnašanje snovi, za katere so določeni $OSK_{organizmi}$, v okolju[3]

| | | | Abiotska in biotska razgradnja | | | Bioakumulacija | |
|---|---|---|---|---|---|---|---|
| **Zap. št.** | **Ime snovi** | **CAS številka** | **Hidroliza** | **Fotoliza** | **Biorazgradljivost** | **BCF (L/kg)** | **BMF (-)** |
| (5) | Bromirani difeniletri | 32534-91-9 | Ni podatkov, vendar se na osnovi strukture predvideva, da je ta skupina snovi hidrolitično stabilna v okoljskih pogojih. | PBDE imajo potencial za fotolizo v vodi. | PentaBDE je obstojen in ni biorazgradljiv. | $BCF_{RIBE}$ nižjih BDE (tetra, penta; hepta) je med 1.440 do 35.100.<br>Okta in nonaBDE se ne kopičijo v organizmih. | Ni podatkov |
| (15) | Fluoranten | 206-44-0 | Ne poteka hidrolitična razgradnja. | Poteka fotokemijska razgradnja. | Hitrost biorazgradljivosti PAH upada s številom aromatskih obročev. | $BCF_{RIBE}$ = 2.439 | Se ne kopiči v prehranjevalni verigi. |
| (16) | Heksaklorobenzen | 118-74-1 | Ni podatka | Ni podatka | Ni podatka | $BAF_{RIBE}$ = 42.000 | Ni podatkov |
| (17) | Heksaklorobutadien | 87-68-3 | Ne poteka hidrolitična razgradnja. | Ni podatka | $DT_{50}$ (naravne vode) = 4-52 tednov | $BCF_{RIBE}$ (šarenka) = 2.000-19.000 | Se ne kopiči v prehranjevalni verigi. |

[3] V preglednici so predstavljeni podatki iz dosjejev Evropske komisije za določitev OSK za prednostne snovi, objavljenih na straneh CIRCABC WFD, v knjižnici delovne skupine WG Chemicals (https://circabc.europa.eu/ui/group/9ab5926d-bed4-4322-9aa7-9964bbe8312d/library/dfcfb52e-48f1-4431-bff7-0c14919738fc?p=1&n=10&sort=modified_DESC). Predstavljen je pregled podatkov, za katere ocenjujemo da so zanesljivi in reprezentativni za določeno snov ali skupino snovi.

| | | | Abiotska in biotska razgradnja | | | Bioakumulacija | |
|---|---|---|---|---|---|---|---|
| **Zap. št.** | **Ime snovi** | **CAS številka** | **Hidroliza** | **Fotoliza** | **Biorazgradljivost** | **BCF (L/kg)** | **BMF (-)** |
| (21) | Živo srebro in njegove spojine | 7439-97-6 | Ni podatka | Ni podatka | Ni podatka | $BAF_{RIBE}$ 21.000 - 78.000.000 | Se kopiči v prehranjevalni verigi. |
| (28) | Benzo(a)piren | 50-32-8 | Ne poteka hidrolitična razgradnja. | Poteka fotokemijska razgradnja. | Hitrost biorazgradljivosti PAH upada s številom aromatskih obročev. | $BCF_{RIBE}$ = 135 | Ni podatka, predvidevamo, da se ne kopiči v prehranjevalni verigi. |
| (34) | Dikofol | 115-32-3 | Poteka hidrolitična razgradnja v nevtralnem in alkalnem mediju. | p,p'-dikofol $DT_{50}$ = 93 dni<br>o,p'-dikofol $DT_{50}$ = 15 dni | Počasi biorazgradljiv v sistemu sediment/voda<br>$DT_{50}$ = 70-84 dni | Se kopiči v organizmih.<br>BCF = 25.000 | Se kopiči v prehranjevalni verigi.<br>BMF1=BMF2=42 |
| (35) | Perfluorooktansulfonska kislina in njeni derivati (PFOS) | 1763-23-1 | Ne poteka hidrolitična razgradnja. | Ne poteka fotorazgradnja. | Ne poteka biorazgradnja. | $BCF_{RIBE}$ = 2796 | Ni podatka. |
| (37) | Dioksini in dioksinom podobne spojine | n.p. | Ne poteka hidrolitična razgradnja. | $DT_{50}$<br>0,19-1,2 dni | Poteka počasna delna biorazgradnja v vodi in v sedimentu. | $BCF_{RIBE}$ = 41.540 | BMF1 = BMF2 = 10 |

| | | | Abiotska in biotska razgradnja | | | Bioakumulacija | |
|---|---|---|---|---|---|---|---|
| **Zap. št.** | **Ime snovi** | **CAS številka** | **Hidroliza** | **Fotoliza** | **Biorazgradljivost** | **BCF (L/kg)** | **BMF (-)** |
| (43) | Heksabromociklododekan (HBCDD) | 25637-99-4/ 3194-55-6/ 134237-50-6/ 134237-51-7/ 134237-52-8 | Ne poteka hidrolitična razgradnja. | $DT_{50}$ 12,2 tedna | Počasi razgradljiv v sedimentu $DT_{50}$ = 1,5 – 101 dni | $BCF_{RIBE}$ (šarenka) = 8.974-21.940 | BMF (šarenka) = 4,3 - 9,2 |
| (4L4) | Heptaklor in heptaklorepoksid | 76-44-8 / 1024-57-3 | Heptaklor - poteka hidrolitična razgradnja. Heptaklorepoksid – ne poteka hidrolitična zgradnja. | Poteka fotorazgradnja (za heptaklorepoksidele v površinski vodi). | Heptaklor – ni hitro biorazgradljiv. Heptaklorepoksid – zelo obstojna snov, ni biorazgradljiv. | $BCF_{RIBE}$ (tolstoglavi pisanec) = 14.400 | BMF1 = 2,26 BMF2 = 19,8 |

*Legenda:*

BCF = Biokoncentracijski faktor organizmi/voda [L/kg]

BAF = Bioakumulacijski faktor organizmi/sediment (tla) [-]

BMF = Biomagnifikacijski faktor plenilec/plen [-]

$DT_{50}$ = Čas potreben za razgradnjo 50% začetne koncentracije snovi v testu [dan]

Preglednica 5: Učinki snovi, za katere so določeni $OSK_{organizmi}$, na vodno okolje[4]

| Zap. št. | Ime snovi | CAS številka | Akutna strupenost za vodno okolje (najnižja vrednost) | Kronična strupenost za vodno okolje (najnižja vrednost) | Sekundarna zastrupitev (NOEC za izračun $OSK_{organizmi}$) |
|---|---|---|---|---|---|
| (5) | Bromirani difeniletri | 32534-91-9 | pentaBDE<br>*Daphnia magna*<br>48h $EC_{50}$ = 0,014 mg/L | pentaBDE<br>*Psetta maxima*<br>*4d* NOEC = 0,00049 mg/L | Oralna strupenost sesalci<br>Miš; 30d NOEC = 4 mg/kg |
| (15) | Fluoranten | 206-44-0 | *Pleuronectus americanus;*<br>96h $EC_{50}$ = 0,0001 mg/L | Mulinea lateraliz<br>48h NOEC > 0,0011 mg/kg | Oralna strupenost sesalci<br>Miš; 90d NOEC = 1037 mg/kg |
| (16) | Heksaklorobenzen | 118-74-1 | *Daphnia magna*<br>48h $EC_{50}$ = 0,00473 mg/L | *Daphnia magna*<br>21d NOEC = 0,00013 mg/L | Oralna strupenost sesalci<br>Kuna; ena generacija<br>NOEC = 0,5 mg/kg |
| (17) | Heksaklorobutadien | 87-68-3 | *Mysidopsis bahia*<br>48h $EC_{50}$ = 0,059 mg/L | *Daphnia magna*<br>21d NOEC = 0,0044 mg/L | Oralna strupenost sesalci<br>Miš; ena generacija<br>NOEC = 1,66 mg/kg |
| (21) | Živo srebro in njegove spojine | 7439-97-6 | *Carascius auratus*<br>8d $LC_{50}$ = 0,0007 mg/L | *Clavopsella michaeli*<br>9d NOEC = 0,0001 mg/L | Oralna strupenost sesalci - metil Hg *Mamaca spec*; 365 d<br>NOEC = 0,22 mg/kg |
| (28) | Benzo(a)piren | 50-32-8 | *Daphnia pulex*<br>48h $EC_{50}$ = 0,005 mg/L | *Crassotrea gigas*<br>48h $EC_{10}$ = 0,00022 mg/L | Oralna strupenost sesalci<br>Miš; 90d<br>LOEC = 10 mg/kg |

[4] V preglednici so predstavljeni podatki iz dosjejev Evropske komisije za določitev OSK za prednostne snovi, objavljenih na straneh CIRCABC WFD, v knjižnici delovne skupine WG Chemicals (https://circabc.europa.eu/ui/group/9ab5926d-bed4-4322-9aa7-9964bbe8312d/library/dfcfb52e-48f1-4431-bff7-0c14919738fc?p=1&n=10&sort=modified_DESC). Predstavljen je pregled podatkov, za katere ocenjujemo da so zanesljivi in reprezentativni za določeno snov ali skupino snovi.

| Zap. št. | Ime snovi | CAS številka | Akutna strupenost za vodno okolje (najnižja vrednost) | Kronična strupenost za vodno okolje (najnižja vrednost) | Sekundarna zastrupitev (NOEC za izračun $OSK_{organizmi}$) |
|---|---|---|---|---|---|
| (34) | Dikofol | 115-32-3 | *Onchorhynchus clarki* *96*h $EC_{50}$ = 0,012 mg/L | *Onchorhynchus mykiss* 45d NOEC = 0,00395 mg/L | Oralna strupenost ptice *Falco sparverius* NOEC = 1,0 mg/kg |
| (35) | Perfluorooktansulfonska kislina in njeni derivati (PFOS) | 1763-23-1 | *Daphnia magna* 48h $EC_{50}$ = 4,0 mg/L | *Chironomus tentans* 36d NOEC < 0,0023 mg/L | Oralna strupenost sesalci Zajec; 20d NOEC = 2 mg/kg |
| (37) | Dioksini in dioksinom podobne spojine | n.p. | *Onchorhynchus mykiss* 56 $EC_{50}$ = $4,6*10^{-8}$ mg/L | *Onchorhynchus mykiss* 28d NOEC $1,1*10^{-9}$ mg/L | Oralna strupenost sesalci Podgana; 90d NOEC = 0,00011 mg/kg |
| (43) | Heksabromociklododekan (HBCDD) | 25637-99-4/ 3194-55-6/ 134237-50-6/ 134237-51-7/ 134237-52-8 | *Sceletonemu scotatum* 72h $EC_{50}$ = 0,052 mg/L | *Daphnia magna* 21d NOEC = 0,0031 mg/L | Oralna strupenost ptice Prepelica; 42d NOEC = 5,0 mg/kg |
| (44) | Heptaklor in heptaklorepoksid | 76-44-8 / 1024-57-3 | *Penaeus duorarum* 96h $LC_{50}$ = 0,00003 mg/L | *Cyprinodon variegatus* 28d NOEC = 0,00079 mg/L | Oralna strupenost sesalci Pes; 2 leti NOEC = 1 mg/kg |

*Legenda:*

$EC_{50}$ = Testna koncentracija snovi, ki ima učinek na 50% testnih organizmov.

$LC_{50}$ = Testna koncentracija snovi, pri kateri pogine 50% testnih organizmov.

LOEC = Najnižja testna koncentracija snovi, ki povzroči učinek.

NOEC = Najnižja testna koncentracija snovi, ki ne povzroči učinka.

Po pregledu podatkov za snovi, za katere so določeni $OSK_{organizmi}$, lahko povzamemo, da ima večina vseh snovi podobne fizikalno kemijske lastnosti in sicer so slabo ali zelo slabo topne v vodi, so hidrofobne ali zelo hidrofobne, so slabo ali zelo slabo hlapne in srednje ali zelo hlapne iz vode ter se vežejo na sediment. Izjema je PFOS, ki se razlikuje v praktično vseh lastnostih in glede hlapnosti živo srebro, saj je srednje hlapna snov. Večina snovi se tudi obnaša zelo podobno v vodnem okolju, vse snovi so slabo ali sploh niso biorazgradljive, hidrolitična razgradnja v glavnem ne poteka, fotolitična razgradnja pa v nekaterih primerih deloma poteče. Vse snovi, z izjemo benzo(a)pirena ter okta in nonaBDE so visoko bioakumulativne in se kopičijo v organizmih, šest od enajstih snovi pa se tudi kopiči v prehranjevalni verigi. Iz podatkov o strupenosti za vodno okolje pa vidimo, da so vse snovi akutno in kronično zelo strupene za vodno okolje.

## 3.3 Predlagana pogostost monitoringa za ugotavljanje kemijskega stanja v organizmih

### Zakonodajne zahteve

Pravilnik o monitoringu stanja površinskih voda, ki vsebinsko povzema zahteve Direktive 2013/39/EU, v 14. členu predpisuje, da je potrebno meritve parametrov kemijskega stanja v organizmih izvajati vsaj enkrat letno za snovi, za katere so s predpisom, ki ureja stanje površinskih voda, določeni okoljski standardi kakovosti, izraženi kot vrednost parametra kemijskega stanja v tkivu organizmov. V skladu s 5. alinejo istega člena Pravilnika pa je za meritve parametrov kemijskega stanja v organizmih možno določiti pogostost meritev, ki odstopa od predpisane pogostosti, če je na podlagi tehničnega znanja in strokovne presoje upravičeno izvajanje meritev v drugačnih časovnih presledkih.

Pravilnik še posebej navaja, da se za snovi bromirani difeniletri, živo srebro in njegove spojine, poliaromatski ogljikovodiki (PAH), perfluorooktansulfonska kislina in njeni derivati (PFOS), dioksini in dioksinom podobne spojine, heksabromociklododekan (HBCDD), heptaklor in heptaklorepoksid monitoring v organizmih lahko izvaja manj pogosto kot enkrat letno, če je na podlagi tehničnega znanja in strokovne ocene upravičeno izvajanje monitoringa v drugačnih časovnih presledkih.

### *Snovi, za katere so določeni $OSK_{organizmi}$*

Če povzamemo ugotovitve poglavja 3.2, ugotavljamo, da so snovi, za katere je potrebno izvajati monitoring organizmov za ugotavljanje kemijskega stanja, v glavnem slabo topne v vodi, hidrofobne, slabo hlapne, večinoma so hlapne iz vode in se vežejo na sediment. So obstojne, se vežejo na organizme in se lahko kopičijo v prehranjevalni verigi. Kljub temu, da se vežejo na sediment in je s tem njihova mobilnost zmanjšana, se v površinski vodi prenašajo na velike razdalje z vezavo na raztopljene organske snovi in tudi z vezavo na lipofilne snovi v živih organizmih, kjer se kopičijo v daljšem časovnem obdobju. Analize v ribah je zato zaradi ugotavljanja vplivov biomagnifikacije potrebno izvajati v organizmih starosti od 3 do 5 let, v kolikor je stanje na terenu takšno, da to omogoča. Snovi, za katere so določeni $OSK_{organizmi}$, so torej v vodnem ekosistemu obstojne, se kopičijo v organizmih v daljšem časovnem obdobju, se tudi vežejo na sediment. V

glavnem niso hlapne, so pa srednje hlapne iz vode, kar pomeni, da se lahko prenašajo na daljše razdalje tudi preko atmosfere, deloma se nekatere snovi pri tem tudi fotolitsko razgradijo.

Obravnavane snovi so v glavnem globalno prisotne v okolju, kjer zelo počasi ali sploh ne razpadajo in njihovo prisotnost v vodnem okolju lahko pričakujemo še desetletja (Fliedner in ostali, 2016). Razpoložljivi podatki monitoringa organizmov v površinskih vodah (ARSO, 2019) kažejo na to, da so koncentracije bromiranih difeniletrov in živega srebra v organizmih višje od $OSK_{organizmi}$ praktično v vseh celinskih površinskih vodah po Sloveniji in koncentracije z leti ne upadajo. V morju je v zadnjih letih koncentracija živega srebra v organizmih višja od $OSK_{organizmi}$ na vseh merilnih mestih, v letu 2016 je bila vrednost $OSK_{organizmi}$ presežena tudi za bromirane difeniletre na merilnem mestu na morju in v letu 2017 na dveh merilnih mestih in sicer na merilnem mestu na teritorialnem morju in na Lazaret-Ankaranu.

Za PFOS ter za dioksine in dioksinom podobne spojine vrednosti $OSK_{organizmi}$ v celinskih površinskih vodah in v morju glavnem niso presežene, izjema je PFOS, ki presega $OSK_{organizmi}$ v Savi v Prebačevem ter dioksini, za katere je $OSK_{organizmi}$ presežena pri 7 meritvah, med drugim v Krupi in v Lahinji. Za fluoranten in benzo(a)piren vrednosti $OSK_{organizmi}$ niso presežene, v glavnem so vse izmerjene vrednosti pod mejo določanja. Tudi fluoranten v organizmih morja je v zadnjih letih večkrat kvantificiran, vendar so najvišje vrednosti okoli tretjino vrednosti $OSK_{organizmi}$. Heksaklorobenzen, heksaklorobutadien, dikofol in HBCDD po podatkih monitoringa organizmov v celinskih površinskih vodah niso prisotni v organizmih, vse njihove izmerjene vrednosti so manjše od meje določanja in pod vrednostjo $OSK_{organizmi}$, enako velja za merilna mesta na morju. Izjema sta heptaklor in heptaklorepoksid, za katera ni na razpolago ustrezno občutljive analizne metode, o čemer smo se prepričali tudi v literaturi (Fliedner in sod.). Vse vrednosti za ti dve snovi so nižje od meje določanja (2 μg/kg), vendar znaša $OSK_{organizmi}$ 0,0067 μg/kg. Ker je meja določanja za heptaklor in heptaklorepoksid višja od $OSK_{organizmi}$, parameter sicer ni ocenjen. Izmerjene, kvantificirane vrednosti snovi kažejo na to, da koncentracija snovi v organizmih z leti ne upada. Za snovi, ki so pod mejo določanja, pa ostaja koncentracija pod mejo določanja vsa leta merjenja.

**Predlagana pogostost monitoringa**

Ob upoštevanju fizikalno kemijskih lastnosti snovi, usode in obnašanja snovi v okolju, za katere je potrebno izvajati monitoring organizmov za ugotavljanje kemijskega stanja, zakonodajnih zahtev, dosedanjih izmerjenih vrednosti in na podlagi strokovnih raziskav trendov pojavljanja teh snovi v ribah (Arle in sod, 2016; Eljarrat in Barceló, 2018; Fliedner in ost., 2016) ocenjujemo, da se pogostost monitoringa organizmov lahko zmanjša. Glavni razlogi za zmanjšanje pogostosti monitoringa so globalna prisotnost obravnavanih snovi (Arle in sod.), lastnosti snovi ter dejstvo, da izmerjene, kvantificirane vrednosti snovi v izvedenih monitoringih organizmov v RS kažejo na to, da koncentracija snovi v organizmih z leti ne upada in tudi ne narašča. Za snovi, ki so pod mejo določanja, pa ostaja koncentracija pod mejo določanja vsa leta merjenja ali pa so kvantificirane le redko.

Na osnovi navedenega predlagamo, da se monitoring organizmov za vse vodne kategorije (vodotoki, jezera, morje) izvaja pregledno enkrat letno na 6 let na nadzornih merilnih mestih na celinskih površinskih vodah in na mestih na morju za vse snovi, za katere so določeni $OSK_{organizmi}$ in so predstavljene v preglednici 1. Tekom izvajanja monitoringa je potrebno posebno pozornost nameniti snovem, katerih vrednosti $OSK_{organizmi}$ so presežene. V kolikor bi za posamezno snov izmerjena koncentracija na merilnem mestu naraščala, je potrebno monitoring te snovi začeti izvajati enkrat letno. V primeru upadanja vrednosti se pregledno spremljanje ohrani.

Na operativnih merilnih mestih na celinskih površinskih vodah se odločitev za monitoring organizmov za snovi iz preglednice 1 sprejme od primera do primera, glede na obstoječo problematiko. Monitoring organizmov se na teh mestih izvede enkrat letno na mestih, kjer so vrednosti OSK za celinske površinske vode presežene in kadar so hkrati v bližini evidentirane emisije merjene snovi.

Natančnejši pregled podatkov za vse snovi in merila za odločitev o pogostosti izvajanja monitoringa organizmov so podana v 4. poglavju.

# 4 Natančnejši pregled podatkov in predlog za odločitev o pogostosti izvajanja monitoringa organizmov za izbrane snovi

Snovi predstavljene v preglednici 1, ki jih je potrebno spremljati v organizmih, veljajo za obstojne, bioakumulativne in strupene. Nekatere od njih veljajo za vsesplošno prisotne snovi v okolju in jih je možno najti v okolju še desetletja po sprejetju ukrepov za zmanjšanje oziroma odpravo emisij teh snovi in se prenašajo tudi na velike razdalje.

V spodnjih preglednicah so za vse snovi pregledno opisane njene lastnosti, učinki na vodno okolje, ocena kemijskega stanja na merilnih mestih, tveganje na merilnih mestih in predlog izvedbe monitoringa organizmov.

| | |
|---|---|
| **Zap. št.** | (5) |
| **Ime snovi** | Bromirani difeniletri |
| **CAS številka** | 32534-91-9 |
| **Fizikalno kemijske lastnosti** | Zelo slabo topni, zelo hidrofobni, slabo hlapni, srednje hlapni iz vode, se močno vežejo na sediment. |
| **Usoda in obnašanje v okolju** | Hidrolitično stabilni, možna fotolitična razgradnja, niso biorazgradljivi, se kopičijo v organizmih, razen višjih BDE, okta in nona. |
| **Učinki na vodno okolje** | Akutno in kronično zelo strupeni za vodno okolje. |
| **Ocena kemijskega stanja na merilnih mestih** | Na celinskih površinskih vodah je bilo izvedenih 48 vzorčenj in laboratorijskih meritev. Na vseh merilnih mestih v letih 2016, 2017 in 2018 je vrednost $OSK_{organizmi}$ presežena, ocenjeno kemijsko stanje je za vse meritve slabo. Na merilnih mestih na morju je bila v letu 2016 presežena vrednost $OSK_{organizmi}$ za eno merilno mesto v letu 2016 in v letu 2017 na dveh merilnih mestih in sicer na merilnem mestu na teritorialnem morju in na Lazaret-Ankaranu. |
| **Prisotno tveganje na merilnih mestih** | Da |

| | |
|---|---|
| **Predlog izvedbe monitoringa organizmov bromiranih difeniletrov** | Iz ocene kemijskega stanja vidimo, da je za bromirane difeniletre na merilnih mestih prisotno tveganje za vodno okolje in ocenjujemo, da so vsesplošno prisotni v vodnem okolju v Sloveniji. Izmerjene koncentracije ne upadajo in ne naraščajo.<br><br>Iz fizikalno kemijskih lastnosti ter iz usode in obnašanja v okolju vidimo, da se lahko preko vezave na raztopljene organske snovi in deloma preko atmosfere prenašajo na velike razdalje, so tudi obstojni in se kopičijo v organizmih.<br><br>Glede na navedeno predlagamo, da monitoring organizmov za bromirane difeniletre izvedemo na nadzornih merilnih mestih na celinskih površinskih vodah in na mestih na morju enkrat letno na 6 let. V primeru, da je (1) zadnja izmerjena vrednost višja od $OSK_{organizmi}$, (2) glede na predhodno analizo narašča in (3) za več kot 20 % presega geometrijsko povprečje zadnjih vsaj dveh do takrat izmerjenih vrednosti, se pogostost monitoringa spremeni. Od takrat dalje se snov v organizmih spremlja vsako leto. Analize se začne znova izvajati na 6 let takoj, ko eden od navedenih pogojev (1), (2), (3) ni izpolnjen.<br><br>Na operativnih merilnih mestih na celinskih površinskih vodah se odločitev za monitoring organizmov za bromirane difeniletre sprejme od primera do primera glede na obstoječo problematiko. Monitoring organizmov se na teh mestih izvede enkrat letno na mestih, kjer so vrednosti OSK za celinske površinske vode presežene in kadar so hkrati v bližini evidentirane emisije bromiranih difeniletrov. |

| | |
|---|---|
| **Zap. št.** | (15) |
| **Ime snovi** | Fluoranten |
| **CAS številka** | 206-44-0 |
| **Fizikalno kemijske lastnosti** | Slabo topen, zelo hidrofoben, slabo hlapen, srednje hlapen iz vode, se veže na sediment. |
| **Usoda in obnašanje v okolju** | Hidrolitično stabilen, možna fotolitična razgradnja, slabo biorazgradljiv, se kopiči v organizmih, se ne kopiči v prehranjevalni verigi. |
| **Učinki na vodno okolje** | Akutno in kronično zelo strupen za vodno okolje. |
| **Ocena kemijskega stanja na merilnih mestih** | Na celinskih površinskih vodah je bilo izvedenih 39 vzorčenj in laboratorijskih meritev. Na nobenem merilnem mestu v letih 2015, 2016, 2017 in 2018 vrednost $OSK_{organizmi}$ ni presežena, ocenjeno kemijsko stanje je za vse meritve dobro. V organizmih morja je fluoranten v zadnjih letih večkrat kvantificiran, vendar so najvišje vrednosti okoli tretjino vrednosti $OSK_{organizmi,}$ ocenjeno kemijsko stanje je dobro. |
| **Prisotno tveganje na merilnih mestih** | Ne |

| | |
|---|---|
| **Predlog izvedbe monitoringa organizmov fluorantena** | Iz ocene kemijskega stanja vidimo, da za fluoranten na merilnih mestih ni prisotno tveganje za vodno okolje. Vse izmerjene koncentracije so nižje od meje določanja, pri kvantificiranih vrednostih pod mejo določanja pa lahko opazimo, da vrednosti z leti ne upadajo in ne naraščajo.<br><br>Iz fizikalno kemijskih lastnosti ter iz usode in obnašanja v okolju vidimo, da se lahko preko vezave na raztopljene organske snovi in deloma preko atmosfere prenaša na velike razdalje, je tudi obstojen in se kopiči v organizmih.<br><br>Glede na navedeno predlagamo, da monitoring organizmov za fluoranten izvedemo na nadzornih merilnih mestih na celinskih površinskih vodah in na mestih na morju enkrat letno na 6 let. V primeru, da je (1) zadnja izmerjena vrednost višja od $OSK_{organizmi}$, (2) glede na predhodno analizo narašča in (3) za več kot 20 % presega geometrijsko povprečje zadnjih vsaj dveh do takrat izmerjenih vrednosti, se pogostost monitoringa spremeni. Od takrat dalje se snov v organizmih spremlja vsako leto. Analize se začne znova izvajati na 6 let takoj, ko eden od navedenih pogojev (1), (2), (3) ni izpolnjen.<br><br>Na operativnih merilnih mestih na celinskih površinskih vodah se odločitev za monitoring organizmov za fluoranten sprejme od primera do primera glede na obstoječo problematiko. Monitoring organizmov se na teh mestih izvede enkrat letno na mestih, kjer so vrednosti OSK za celinske površinske vode presežene in kadar so hkrati v bližini evidentirane emisije fluorantena. |

| | |
|---|---|
| **Zap. št.** | (16) |
| **Ime snovi** | Heksaklorobenzen |
| **CAS številka** | 118-74-1 |
| **Fizikalno kemijske lastnosti** | Zelo slabo topen, zelo hidrofoben, slabo hlapen, zelo hlapen iz vode, se močno veže na sediment. |
| **Usoda in obnašanje v okolju** | Se kopiči v organizmih. |
| **Učinki na vodno okolje** | Akutno in kronično zelo strupen za vodno okolje. |
| **Ocena kemijskega stanja na merilnih mestih** | Na celinskih površinskih vodah je bilo izvedenih 37 vzorčenj in laboratorijskih meritev. Na nobenem merilnem mestu v letih 2014, 2015, 2016, 2017 in 2018 vrednost $OSK_{organizmi}$ ni presežena, ocenjeno kemijsko stanje je za vse meritve dobro. V organizmih morja je za heksaklorobenzen zadnja leta za vse meritve ocenjeno kemijsko stanje dobro. |
| **Prisotno tveganje na merilnih mestih** | Ne |

| | |
|---|---|
| **Predlog izvedbe monitoringa organizmov heksaklorobenzena** | Iz ocene kemijskega stanja vidimo, da za heksaklorobenzen na merilnih mestih ni prisotno tveganje za vodno okolje in vse izmerjene koncentracije so pod mejo določanja.<br><br>Iz fizikalno kemijskih lastnosti ter iz usode in obnašanja v okolju vidimo, da se lahko preko vezave na raztopljene organske snovi in preko atmosfere prenaša na velike razdalje, je tudi obstojen in se kopiči v organizmih.<br><br>Glede na navedeno predlagamo, da monitoring organizmov za heksaklorobenzen izvedemo na nadzornih merilnih mestih na celinskih površinskih vodah in na mestih na morju enkrat letno na 6 let. V primeru, da je (1) zadnja izmerjena vrednost višja od $OSK_{organizmi}$, (2) glede na predhodno analizo narašča in (3) za več kot 20 % presega geometrijsko povprečje zadnjih vsaj dveh do takrat izmerjenih vrednosti, se pogostost monitoringa spremeni. Od takrat dalje se snov v organizmih spremlja vsako leto. Analize se začne znova izvajati na 6 let takoj, ko eden od navedenih pogojev (1), (2), (3) ni izpolnjen.<br><br>Na operativnih merilnih mestih na celinskih površinskih vodah se odločitev za monitoring organizmov za heksaklorobenzen sprejme od primera do primera glede na obstoječo problematiko. Monitoring organizmov se na teh mestih izvede enkrat letno na mestih, kjer so vrednosti OSK za celinske površinske vode presežene in kadar so hkrati v bližini evidentirane emisije heksaklorobenzena. |

| | |
|---|---|
| **Zap. št.** | (17) |
| **Ime snovi** | Heksaklorobutadien |
| **CAS številka** | 87-68-3 |
| **Fizikalno kemijske lastnosti** | Slabo topen, zelo hidrofoben, srednje hlapen, zelo hlapen iz vode, se močno veže na sediment. |
| **Usoda in obnašanje v okolju** | Hidrolitično stabilen, slabo biorazgradljiv, se kopiči v organizmih, se ne kopiči v prehranjevalni verigi. |
| **Učinki na vodno okolje** | Akutno in kronično zelo strupen za vodno okolje. |
| **Ocena kemijskega stanja na merilnih mestih** | Na celinskih površinskih vodah je bilo izvedenih 37 vzorčenj in laboratorijskih meritev. Na nobenem merilnem mestu v letih 2014, 2015, 2016, 2017 in 2018 vrednost $OSK_{organizmi}$ ni presežena, ocenjeno kemijsko stanje je za vse meritve dobro. V organizmih morja je za heksaklorobutadien zadnja leta za vse meritve ocenjeno kemijsko stanje dobro. |
| **Prisotno tveganje na merilnih mestih** | Ne |

| | |
|---|---|
| **Predlog izvedbe monitoringa organizmov heksaklorobutadiena** | Iz ocene kemijskega stanja vidimo, da za heksaklorobutadien na merilnih mestih ni prisotno tveganje za vodno okolje in vse izmerjene koncentracije so pod mejo določanja.<br><br>Iz fizikalno kemijskih lastnosti ter iz usode in obnašanja v okolju vidimo, da se lahko preko vezave na raztopljene organske snovi in preko atmosfere prenaša na velike razdalje, je tudi obstojen in se kopiči v organizmih.<br><br>Glede na navedeno predlagamo, da monitoring organizmov za heksaklorobutadien izvedemo na nadzornih merilnih mestih na celinskih površinskih vodah in na mestih na morju enkrat letno na 6 let. V primeru, da je (1) zadnja izmerjena vrednost višja od $OSK_{organizmi}$, (2) glede na predhodno analizo narašča in (3) za več kot 20 % presega geometrijsko povprečje zadnjih vsaj dveh do takrat izmerjenih vrednosti, se pogostost monitoringa spremeni. Od takrat dalje se snov v organizmih spremlja vsako leto. Analize se začne znova izvajati na 6 let takoj, ko eden od navedenih pogojev (1), (2), (3) ni izpolnjen.<br><br>Na operativnih merilnih mestih na celinskih površinskih vodah se odločitev za monitoring organizmov za heksaklorobutadien sprejme od primera do primera glede na obstoječo problematiko. Monitoring organizmov se na teh mestih izvede enkrat letno na mestih, kjer so vrednosti OSK za celinske površinske vode presežene in kadar so hkrati v bližini evidentirane emisije heksaklorobutadiena. |

| | |
|---|---|
| **Zap. št.** | (21) |
| **Ime snovi** | Živo srebro in njegove spojine |
| **CAS številka** | 7439-97-6 |
| **Fizikalno kemijske lastnosti** | Zelo slabo topno, srednje hlapno, se močno veže na sediment |
| **Usoda in obnašanje v okolju** | Se kopiči v organizmih, se kopiči v prehranjevalni verigi. |
| **Učinki na vodno okolje** | Akutno in kronično zelo strupeno za vodno okolje. |
| **Ocena kemijskega stanja na merilnih mestih** | Na celinskih površinskih vodah je bilo izvedenih 60 vzorčenj in laboratorijskih meritev. Na vseh merilnih mestih v letih 2014, 2015, 2016, 2017 in 2018 je vrednost $OSK_{organizmi}$ presežena, ocenjeno kemijsko stanje je za vse meritve slabo. Izjema sta 2 meritvi na merilnem mestu s šifro 8012, Soča, spodnja Trenta, za leti 2016 in 2017 in 1 meritev na merilnem mestu s šifro 2240, Meža, Podklanc, za leto 2016, kjer vrednost $OSK_{organizmi}$ ni bila presežena in je ocenjeno kemijsko stanje dobro. V morju je v zadnjih letih koncentracija živega srebra v organizmih višja od $OSK_{organizmi}$ na vseh merilnih mestih in ocenjeno kemijsko stanje slabo. |
| **Prisotno tveganje na merilnih mestih** | Da[1] |

| | |
|---|---|
| **Predlog izvedbe monitoringa organizmov živega srebra** | Iz ocene kemijskega stanja vidimo, da je za živo srebro in njegove spojine na izbranih merilnih mestih v 95 % prisotno tveganje za vodno okolje in ocenjujemo, da so vsesplošno prisotne v vodnem okolju v Sloveniji. Izmerjene koncentracije ne upadajo in ne naraščajo.<br><br>Iz fizikalno kemijskih lastnosti ter iz usode in obnašanja v okolju vidimo, da se lahko preko vezave na raztopljene organske snovi in preko atmosfere prenašajo na velike razdalje, so tudi obstojne in se kopičijo v organizmih.<br><br>Glede na navedeno predlagamo, da monitoring organizmov za živo srebro izvedemo na nadzornih merilnih mestih na celinskih površinskih vodah in na mestih na morju enkrat letno na 6 let. V primeru, da je (1) zadnja izmerjena vrednost višja od $OSK_{organizmi}$, (2) glede na predhodno analizo narašča in (3) za več kot 20 % presega geometrijsko povprečje zadnjih vsaj dveh do takrat izmerjenih vrednosti, se pogostost monitoringa spremeni. Od takrat dalje se snov v organizmih spremlja vsako leto. Analize se začne znova izvajati na 6 let takoj, ko eden od navedenih pogojev (1), (2), (3) ni izpolnjen.<br><br>Na operativnih merilnih mestih na celinskih površinskih vodah se odločitev za monitoring organizmov za živo srebro sprejme od primera do primera glede na obstoječo problematiko. Monitoring organizmov se na teh mestih izvede enkrat letno na mestih, kjer so vrednosti OSK za celinske površinske vode presežene in kadar so hkrati v bližini evidentirane emisije živega srebra. |

[1] 57 od 60 meritev presega vrednost $OSK_{organizmi}$ (95,0 %).

| | |
|---|---|
| **Zap. št.** | (28) |
| **Ime snovi** | Benzo(a)piren |
| **CAS številka** | 50-32-8 |
| **Fizikalno kemijske lastnosti** | Zelo slabo topen, zelo hidrofoben, zelo slabo hlapen, srednje hlapen iz vode, se močno veže na sediment |
| **Usoda in obnašanje v okolju** | Hidrolitično stabilen, možna fotolitična razgradnja, slabo biorazgradljiv, se ne kopiči v organizmih, se ne kopiči v prehranjevalni verigi. |
| **Učinki na vodno okolje** | Akutno in kronično zelo strupen za vodno okolje. |
| **Ocena kemijskega stanja na merilnih mestih** | Na celinskih površinskih vodah je bilo izvedenih 39 vzorčenj in laboratorijskih meritev. Na nobenem merilnem mestu v letih 2015, 2016, 2017 in 2018 vrednost $OSK_{organizmi}$ ni presežena, ocenjeno kemijsko stanje je za vse meritve dobro. V organizmih morja je za benzo(a)piren zadnja leta za vse meritve ocenjeno kemijsko stanje dobro. |
| **Prisotno tveganje na merilnih mestih** | Ne |

| | |
|---|---|
| **Predlog izvedbe monitoringa organizmov benzo(a)pirena** | Iz ocene kemijskega stanja vidimo, da za benzo(a)piren na izbranih merilnih mestih ni prisotno tveganje za vodno okolje. V glavnem so vse izmerjene koncentracije nižje od meje določanja, pri kvantificiranih vrednostih pa lahko opazimo, da vrednosti z leti ne upadajo in ne naraščajo.<br><br>Iz fizikalno kemijskih lastnosti ter iz usode in obnašanja v okolju vidimo, da se lahko preko vezave na raztopljene organske snovi in preko atmosfere prenaša na velike razdalje, je tudi obstojen in se ne kopiči v organizmih.<br><br>Glede na navedeno predlagamo, da monitoring organizmov za benzo(a)piren izvedemo na nadzornih merilnih mestih na celinskih površinskih vodah in na mestih na morju enkrat letno na 6 let. V primeru, da je (1) zadnja izmerjena vrednost višja od $OSK_{organizmi}$, (2) glede na predhodno analizo narašča in (3) za več kot 20 % presega geometrijsko povprečje zadnjih vsaj dveh do takrat izmerjenih vrednosti, se pogostost monitoringa spremeni. Od takrat dalje se snov v organizmih spremlja vsako leto. Analize se začne znova izvajati na 6 let takoj, ko eden od navedenih pogojev (1), (2), (3) ni izpolnjen.<br><br>Na operativnih merilnih mestih na celinskih površinskih vodah se odločitev za monitoring organizmov za benzo(a)piren sprejme od primera do primera glede na obstoječo problematiko. Monitoring organizmov se na teh mestih izvede enkrat letno na mestih, kjer so vrednosti OSK za celinske površinske vode presežene in kadar so hkrati v bližini evidentirane emisije benzo(a)pirena. |

| | |
|---|---|
| **Zap. št.** | (34) |
| **Ime snovi** | Dikofol |
| **CAS številka** | 115-32-3 |
| **Fizikalno kemijske lastnosti** | Slabo topen, hidrofoben, zelo slabo hlapen, slabo hlapen iz vode, se veže na sediment |
| **Usoda in obnašanje v okolju** | Možna hidrolitična in fotolitična razgradnja, slabo biorazgradljiv, se kopiči v organizmih, se kopiči v prehranjevalni verigi. |
| **Učinki na vodno okolje** | Akutno in kronično zelo strupen za vodno okolje. |
| **Ocena kemijskega stanja na merilnih mestih** | Na celinskih površinskih vodah je bilo izvedenih 43 vzorčenj in laboratorijskih meritev. Na nobenem merilnem mestu v letih 2015, 2016, 2017 in 2018 vrednost $OSK_{organizmi}$ ni presežena, ocenjeno kemijsko stanje je za vse meritve dobro. V organizmih morja je za dikofol zadnja leta za vse meritve ocenjeno kemijsko stanje dobro. |
| **Prisotno tveganje na merilnih mestih** | Ne |

| | |
|---|---|
| **Predlog izvedbe monitoringa organizmov dikofola** | Iz ocene kemijskega stanja vidimo, da za dikofol na merilnih mestih ni prisotno tveganje za vodno okolje in vse izmerjene koncentracije so pod mejo določanja.<br><br>Iz fizikalno kemijskih lastnosti ter iz usode in obnašanja v okolju vidimo, da se lahko preko vezave na raztopljene organske snovi prenaša na velike razdalje, je tudi obstojen in se kopiči v organizmih.<br><br>Glede na navedeno predlagamo, da monitoring organizmov za dikofol izvedemo na nadzornih merilnih mestih na celinskih površinskih vodah in na mestih na morju enkrat letno na 6 let. V primeru, da je (1) zadnja izmerjena vrednost višja od $OSK_{organizmi}$, (2) glede na predhodno analizo narašča in (3) za več kot 20 % presega geometrijsko povprečje zadnjih vsaj dveh do takrat izmerjenih vrednosti, se pogostost monitoringa spremeni. Od takrat dalje se snov v organizmih spremlja vsako leto. Analize se začne znova izvajati na 6 let takoj, ko eden od navedenih pogojev (1), (2), (3) ni izpolnjen.<br><br>Na operativnih merilnih mestih na celinskih površinskih vodah se odločitev za monitoring organizmov za dikofol sprejme od primera do primera glede na obstoječo problematiko. Monitoring organizmov se na teh mestih izvede enkrat letno na mestih, kjer so vrednosti OSK za celinske površinske vode presežene in kadar so hkrati v bližini evidentirane emisije dikofola. |

| | |
|---|---|
| **Zap. št.** | (35) |
| **Ime snovi** | Perfluorooktansulfonska kislina in njeni derivati (PFOS) |
| **CAS številka** | 1763-23-1 |
| **Fizikalno kemijske lastnosti** | Srednje topni v vodi, zelo slabo hlapni do srednje hlapni, zelo slabo hlapni iz vode, se slabo vežejo na sediment |
| **Usoda in obnašanje v okolju** | Hidrolitično in fotolitično stabilni, niso biorazgradljivi, se kopičijo v organizmih. |
| **Učinki na vodno okolje** | Akutno strupeni in kronično zelo strupeni za vodno okolje. |
| **Ocena kemijskega stanja na merilnih mestih** | Na celinskih površinskih vodah je bilo izvedenih 47 vzorčenj in laboratorijskih meritev. Na nobenem merilnem mestu v letih 2016, 2017 in 2018 vrednost $OSK_{organizmi}$ ni presežena, ocenjeno kemijsko stanje je za vse meritve dobro. Izjema je 1 meritev na merilnem mestu s šifro 3500, Sava, Prebačevo, za leto 2016, kjer je bila vrednost $OSK_{organizmi}$ presežena in je ocenjeno kemijsko stanje slabo. V organizmih morja je za PFOS zadnja leta za vse meritve ocenjeno kemijsko stanje dobro. |
| **Prisotno tveganje na merilnih mestih** | Ne[1] |

| | |
|---|---|
| **Predlog izvedbe monitoringa organizmov PFOS** | Iz ocene kemijskega stanja vidimo, da za PFOS na merilnih mestih v več kot 95 % ni prisotno tveganje za vodno okolje, presežena je ena vrednost, vse ostale so pod mejo določanja.<br><br>Iz fizikalno kemijskih lastnosti ter iz usode in obnašanja v okolju vidimo, da so mobilni v vodi in da se lahko preko vode in deloma preko atmosfere prenašajo na velike razdalje, so tudi obstojni in se kopičijo v organizmih.<br><br>Glede na navedeno predlagamo, da monitoring organizmov za PFOS izvedemo na nadzornih merilnih mestih na celinskih površinskih vodah in na mestih na morju enkrat letno na 6 let. V primeru, da je (1) zadnja izmerjena vrednost višja od $OSK_{organizmi}$, (2) glede na predhodno analizo narašča in (3) za več kot 20 % presega geometrijsko povprečje zadnjih vsaj dveh do takrat izmerjenih vrednosti, se pogostost monitoringa spremeni. Od takrat dalje se snov v organizmih spremlja vsako leto. Analize se začne znova izvajati na 6 let takoj, ko eden od navedenih pogojev (1), (2), (3) ni izpolnjen.<br><br>Na operativnih merilnih mestih na celinskih površinskih vodah se odločitev za monitoring organizmov za PFOS sprejme od primera do primera glede na obstoječo problematiko. Monitoring organizmov se na teh mestih izvede enkrat letno na mestih, kjer so vrednosti OSK za celinske površinske vode presežene in kadar so hkrati v bližini evidentirane emisije PFOS. |

[1] 46 od 47 meritev ne presega vrednosti $OSK_{organizmi}$ (97,9 %).

| | |
|---|---|
| **Zap. št.** | (37) |
| **Ime snovi** | Dioksin in dioksinom podobne spojine |
| **CAS številka** | Ni podatka |
| **Fizikalno kemijske lastnosti** | Zelo slabo topni, zelo hidrofobni, zelo slabo hlapni, srednje do zelo dobro hlapni iz vode, se slabo do zelo močno vežejo na sediment |
| **Usoda in obnašanje v okolju** | Hidrolitično stabilni, možna fotolitična razgradnja, slabo biorazgradljivi, se kopičijo v organizmih, se kopičijo v prehranjevalni verigi. |
| **Učinki na vodno okolje** | Akutno in kronično zelo strupeni za vodno okolje. |
| **Ocena kemijskega stanja na merilnih mestih** | Na celinskih površinskih vodah je bilo izvedenih 54 vzorčenj in laboratorijskih meritev. Na 47 merilnih mestih v letih 2012, 2013, 2014, 2015, 2016, 2017 in 2018, vrednost $OSK_{organizmi}$ ni presežena, ocenjeno kemijsko stanje je za vse te meritve dobro. Za naslednjih 7 meritev je vrednost $OSK_{organizmi}$ presežena: merilno mesto s šifro 3795, Sava, nad NEK Krško, za leto 2018; merilno mesto s šifro 4862, Kolpa, Radoviči (Metlika) za leto 2013; merilno mesto s šifro 4977, Lahinja; Geršiči za leto 2015; merilno mesto s šifro 499, Krupa, Klošter za leta 2013, 2015, 2016 in 2018. Za ta mesta je ocenjeno kemijsko stanje slabo. V organizmih morja je za dioksin zadnja leta za vse meritve ocenjeno kemijsko stanje dobro. |
| **Prisotno tveganje na merilnih mestih** | Ne[1] |

| | |
|---|---|
| **Predlog izvedbe monitoringa organizmov dioksina** | Iz ocene kemijskega stanja vidimo, da za dioksine na izbranih merilnih mestih v 87 % ni prisotno tveganje za vodno okolje. Izmerjene koncentracije z leti ne upadajo.<br><br>Iz fizikalno kemijskih lastnosti ter iz usode in obnašanja v okolju vidimo, da se lahko preko vezave na raztopljene organske snovi in preko atmosfere prenašajo na velike razdalje, so tudi obstojni in se kopičijo v organizmih.<br><br>Glede na navedeno predlagamo, da monitoring organizmov za dioksine izvedemo na nadzornih merilnih mestih na celinskih površinskih vodah in na mestih na morju enkrat letno na 6 let. V primeru, da je (1) zadnja izmerjena vrednost višja od $OSK_{organizmi}$, (2) glede na predhodno analizo narašča in (3) za več kot 20 % presega geometrijsko povprečje zadnjih vsaj dveh do takrat izmerjenih vrednosti, se pogostost monitoringa spremeni. Od takrat dalje se snov v organizmih spremlja vsako leto. Analize se začne znova izvajati na 6 let takoj, ko eden od navedenih pogojev (1), (2), (3) ni izpolnjen.<br><br>Na operativnih merilnih mestih na celinskih površinskih vodah se odločitev za monitoring organizmov za dioksin sprejme od primera do primera glede na obstoječo problematiko. Monitoring organizmov se na teh mestih izvede enkrat letno na mestih, kjer so vrednosti OSK za celinske površinske vode presežene in kadar so hkrati v bližini evidentirane emisije dioksina. |

[1] 47 od 54 meritev ne presega vrednosti $OSK_{organizmi}$ (87,0 %).

| | |
|---|---|
| **Zap. št.** | (43) |
| **Ime snovi** | Heksabromociklododekan (HBCDD) |
| **CAS številka** | 25637-99-4/ 3194-55-6/ 134237-50-6/ 134237-51-7/ 134237-52-8 |
| **Fizikalno kemijske lastnosti** | Slabo topen v vodi, zelo hidrofoben, zelo slabo hlapen, srednje hlapen iz vode, se veže na sediment. |
| **Usoda in obnašanje v okolju** | Hidrolitično stabilen, možna delna fotolitična razgradnja, slabo biorazgradljiv, se kopiči v organizmih, se kopiči v prehranjevalni verigi. |
| **Učinki na vodno okolje** | Akutno in kronično zelo strupen za vodno okolje. |
| **Ocena kemijskega stanja na merilnih mestih** | Na celinskih površinskih vodah je bilo izvedenih 42 vzorčenj in laboratorijskih meritev. Na nobenem merilnem mestu v letih 2016, 2017 in 2018 vrednost $OSK_{organizmi}$ ni presežena, ocenjeno kemijsko stanje je za vse meritve dobro. V organizmih morja je za HBCDD zadnja leta za vse meritve ocenjeno kemijsko stanje dobro. |
| **Prisotno tveganje na merilnih mestih** | Ne |

| | |
|---|---|
| **Predlog izvedbe monitoringa organizmov HBCDD** | Iz ocene kemijskega stanja vidimo, da za heksabromociklododekan (HBCDD) na merilnih mestih ni prisotno tveganje za vodno okolje in vse izmerjene koncentracije so pod mejo določanja.<br><br>Iz fizikalno kemijskih lastnosti ter iz usode in obnašanja v okolju vidimo, da se lahko preko vezave na raztopljene organske snovi in deloma preko atmosfere prenaša na velike razdalje, je tudi obstojen in se kopiči v organizmih.<br><br>Glede na navedeno predlagamo, da monitoring organizmov za HBCDD izvedemo na nadzornih merilnih mestih na celinskih površinskih vodah in na mestih na morju enkrat letno na 6 let. V primeru, da je (1) zadnja izmerjena vrednost višja od $OSK_{organizmi}$, (2) glede na predhodno analizo narašča in (3) za več kot 20 % presega geometrijsko povprečje zadnjih vsaj dveh do takrat izmerjenih vrednosti, se pogostost monitoringa spremeni. Od takrat dalje se snov v organizmih spremlja vsako leto. Analize se začne znova izvajati na 6 let takoj, ko eden od navedenih pogojev (1), (2), (3) ni izpolnjen.<br><br>Na operativnih merilnih mestih na celinskih površinskih vodah se odločitev za monitoring organizmov za HBCDD sprejme od primera do primera glede na obstoječo problematiko. Monitoring organizmov se na teh mestih izvede enkrat letno na mestih, kjer so vrednosti OSK za celinske površinske vode presežene in kadar so hkrati v bližini evidentirane emisije HBCDD. |

| | |
|---|---|
| **Zap. št.** | (44) |
| **Ime snovi** | Heptaklor in heptaklorepoksid |
| **CAS številka** | 76-44-8 / 1024-57-3 |
| **Fizikalno kemijske lastnosti** | Zelo slabo do slabo topna v vodi, zelo hidrofobna, slabo do srednje hlapna iz vode, se močno vežeta na sediment. |
| **Usoda in obnašanje v okolju** | Hidrolitično stabilen (heptaklor), poteka hidrolitična razgradnja (heptaklorepoksid), možna fotolitična razgradnja, slabo biorazgradljiva, se kopičita v organizmih, se kopičita v prehranjevalni verigi. |
| **Učinki na vodno okolje** | Akutno in kronično zelo strupena za vodno okolje. |
| **Ocena kemijskega stanja na merilnih mestih** | Na celinskih površinskih vodah je bilo izvedenih 36 vzorčenj in laboratorijskih meritev. Na nobenem merilnem mestu v letih 2015, 2016, 2017 in 2018 vrednost $OSK_{organizmi}$ ni presežena, parameter pa ni vključen v oceno kemijskega stanja, ker je meja določanja višja od $OSK_{organizmi}$ (glej poglavje 3, stran 21). V organizmih morja je za heptaklor in heptaklorepoksid zadnja leta za vse meritve ocenjeno kemijsko stanje dobro. |
| **Prisotno tveganje na merilnih mestih** | Ne |

| | |
|---|---|
| **Predlog izvedbe monitoringa organizmov heptaklora in heptaklorepoksida** | Na osnovi izmerjenih vrednosti ne moremo zaključiti o skladnosti izmerjenih vrednosti glede na $OSK_{organizmi,}$ ker za heptaklor in heptaklorepoksid ni na razpolago ustrezno občutljive analizne metode. Vse izmerjene koncentracije na vseh merilnih mestih so pod mejo določanja, ki znaša 2 μg/kg, medtem ko $OSK_{organizmi}$ znaša 0,0067 μg/kg.<br><br>Iz fizikalno kemijskih lastnosti ter iz usode in obnašanja v okolju vidimo, da se lahko preko vezave na raztopljene organske snovi in deloma preko atmosfere prenašata na velike razdalje, sta tudi obstojna in se kopičita v organizmih.<br><br>Glede na navedeno predlagamo, da monitoring organizmov za heptaklor in heptaklorepoksid izvedemo na nadzornih merilnih mestih na celinskih površinskih vodah in na mestih na morju enkrat letno na 6 let. V primeru, da je (1) zadnja izmerjena vrednost višja od $OSK_{organizmi}$, (2) glede na predhodno analizo narašča in (3) za več kot 20 % presega geometrijsko povprečje zadnjih vsaj dveh do takrat izmerjenih vrednosti, se pogostost monitoringa spremeni. Od takrat dalje se snov v organizmih spremlja vsako leto. Analize se začne znova izvajati na 6 let takoj, ko eden od navedenih pogojev (1), (2), (3) ni izpolnjen.<br><br>Na operativnih merilnih mestih na celinskih površinskih vodah se odločitev za monitoring organizmov za heptaklor in heptaklorepoksid sprejme od primera do primera glede na obstoječo problematiko. Monitoring organizmov se na teh mestih izvede enkrat letno na mestih, kjer so vrednosti OSK za celinske površinske vode presežene in kadar so hkrati v bližini evidentirane emisije heptaklora in heptaklorepoksida. |

# 5 Zaključek

V nalogi »Strokovne podlage za monitoring organizmov« smo izdelali strokovne podlage za časovno ustrezno izvedbo monitoringa stanja površinskih voda (rek, jezer in morja) na podlagi analiz organizmov, ob upoštevanju zahtev Direktive 2013/39/EU, ki predpisuje okoljske standarde kakovosti v organizmih za snovi, ki so navedene v preglednici 1.

Predstavili smo namen in cilj okoljskih standardov kakovosti za organizme in monitoring organizmov v okviru Vodne direktive. Podali smo pregled fizikalno kemijskih lastnosti ter podatke o usodi in obnašanju v okolju za snovi, za katere so določeni $OSK_{organizmi}$ za vodno okolje. Pripravili smo tudi pregled podatkov o učinkih obravnavanih snovi na vodno okolje in podatke o možnosti sekundarne zastrupitve. Ugotovili smo, da so vse snovi akutno in kronično zelo strupene za vodno okolje, heksaklorobutadien, živo srebro, dikofol in HBCDD pa se tudi kopičijo v prehranjevalni verigi, zato je cilj zaščite sekundarna zastrupitev. Večina obravnavanih snovi ima podobne lastnosti, vse so problematične za okolje, so obstojne, bioakumulativne in strupene za vodno okolje.

Po natančnem pregledu snovi smo nadalje predlagali pogostost monitoringa za ugotavljanje kemijskega stanja v organizmih. Ugotovili smo, da obstajajo utemeljeni razlogi za zmanjšanje pogostosti monitoringa in smo predlagali, da se monitoring izvaja enkrat letno na 6 let na nadzornih merilnih mestih na celinskih površinskih vodah in na mestih na morju za vse snovi, za katere so bili določeni $OSK_{organizmi}$ in so podani v preglednici 1 poročila. V primeru, da je (1) zadnja izmerjena vrednost višja od $OSK_{organizmi}$, (2) glede na predhodno analizo narašča in (3) za več kot 20% presega geometrijsko povprečje zadnjih vsaj dveh do takrat izmerjenih vrednosti, smo predlagali, da se pogostost monitoringa spremeni. Od takrat dalje se snov v organizmih spremlja vsako leto. Analize se začne znova izvajati na 6 let takoj, ko eden od navedenih pogojev (1), (2), (3) ni izpolnjen. Na operativnih merilnih mestih na celinskih površinskih vodah se odločitev za monitoring organizmov za snovi iz preglednice 1 sprejme od primera do primera glede na obstoječo problematiko. Monitoring organizmov se na teh mestih izvede enkrat letno na mestih, kjer so vrednosti OSK za celinske površinske vode presežene in kadar so hkrati v bližini evidentirane emisije merjene snovi. Natančnejši pregled podatkov za snovi in odločitev o izvajanju pogostosti monitoringa organizmov je podan v 4. poglavju poročila.

Z izvedbo naloge »Strokovne podlage za monitoring organizmov» smo zagotovili nadgradnjo na področju monitoringa organizmov. Strokovne podlage bodo omogočile uvedbo zahtev Direktive 2013/39/EU, ki se nanašajo na pogostost monitoringa kemijskega stanja celinskih voda in morja.

# 6 Viri


Pravne podlage

- Zakon o vodah RS (Uradni list RS, št. 67/02, 110/02-ZGO-1, 2/04-ZZdrl-A, 41/04-ZVO-1 in 57/08, 57/2012),
- Zakon o varstvu okolja (Uradni list RS, št. 39/06 – uradno prečiščeno besedilo, 49/06 – ZMetD, 66/06 – Odl. US, 33/07-ZPNačrt, 57/08-ZFO-1A in 70/08, 108/09, 48/2012, 57/2012, 97/2012),
- Direktiva 2000/60/ES Evropskega Parlamenta in Sveta z dne 23. oktobra 2000, ki določa okvir za delovanje Skupnosti na področju vodne politike (UL L št. 327 z dne 22. 12. 2000, str. 1) (v nadaljnjem besedilu: vodna direktiva),
- Direktiva 2008/105/ES Evropskega parlamenta in Sveta z dne 16. decembra 2008 o okoljskih standardih kakovosti na področju vodne politike, spremembi in poznejši razveljavitvi direktiv Sveta 82/176/EGS, 83/513/EGS, 84/156/EGS, 84/491/EGS, 86/280/EGS ter spremembi Direktive 2000/60/ES Evropskega parlamenta in Sveta,
- Direktiva 2013/39/EU o spremembi direktiv 2000/60/ES in 2008/105/ES v zvezi s prednostnimi snovmi na področju vodne politike
- Uredba o stanju površinskih voda (Uradni list RS, 14 /09, 98/10, 96/13),
- Pravilnik o monitoringu stanja površinskih voda (Uradni list RS, št. 10/09, 81/11).

Strokovne podlage

- Guidance Document No. 25 on Chemical Monitoring in Sediment and Biota under the Water Framework Directive,
- Guidance Document No. 32 on Biota Monitoring (the Implementation of EQSbiota) under the Water Framework Directive,
- Guidance Document No. 33 on Analytical Methods for Biota Monitoring under the Water Framework Directive,
- Technical Guidance for Environmental Quality Standards (Expert Group on Environmental Quality Standards),
- Metodologija AMPS (Analysis and Monitoring of Priority Substances),
- Buchmeier, G. (2013). Chemical monitoring in biota: the current practice, Norman, Expert Group Meeting, Brno,
- Kos Durjava, M. in Kolar, B. (2010). Strokovne podlage za vrednotenje parametrov kemijskega stanja površinskih voda ter posebnih onesnaževal. Zavod za zdravstveno varstvo Maribor,
- Kos Durjava, M., Arnuš, L., Baskar, M., Hajnžič, B., Podgornik, S., Pliberšek, K., Marčeta, B., Ramšak, L., Tavčar, T. in Jenič, A. (2016). Strokovne podlage za monitoring organizmov, Nacionalni laboratorij za zdravje, okolje in hrano, Maribor,
- Arle, J., Mohaupt, V. in Kirst, I. (2016). Monitoring of Surface Waters in Germany under the Water Framework Directive - A Review of Approaches, Methods and Results, 8, 217, Water,
- Fliedner, A, Lohmann, N., Rüdel, Teubner, D., Wellmitz, J. in Koschorreck, J. (2016). Current levels and trends of selected EU Water Framework Directive priority substances in freshwater fish from the German environmental specimen bank, 216, Environmental Pollution,
- Eljarrat, E. in Barceló, D. (2018). How do measured PBDE and HCBD levels in river fish compare to the European Environmental Quality Standards?, 160, Environmental Research.

# 7 Priloga

Priloga 1: Fizikalno-kemijske lastnosti, usoda in obnašanje v okolju in učinek na vodno okolje za snovi, za katere so določene $OSK_{organizmi}$

# PRILOGA 1

**Fizikalno-kemijske lastnosti, usoda in obnašanje v okolju in učinek na vodno okolje za snovi, za katere so določene $OSK_{organizmi}$**

(100 strani)

## (5) Bromirani difenil etri



# 5 ENVIRONMENTAL BEHAVIOUR

## 5.1 ENVIRONMENTAL DISTRIBUTION

Given that both c-pentaBDE and c-octaBDE are mixtures containing significant amounts of other brominated diphenyl ethers, notably tetra- and hexa- congeners for c-pentaBDE and hexa-, hepta- and nona- congeners for c-octaBDE, it was deemed of relevance to report hereunder physico-chemical parameters linked to environmental distribution for all the brominated diphenyl ethers above cited. In fact, these substances present physico-chemical similarities between each others that may allow a read-across of their ecotoxicological properties.

| **TetraBDE** | | **Master reference** |
|---|---|---|
| **Water solubility** ($mg.l^{-1}$) | 0.011 (*measured*)<br>$1.46\ 10^{-3}$ (*estimated-EPI*) | E.C., 2003 |
| **Volatilisation** | **TetraBDE is not likely to volatilize from water phase** | |
| **Vapour pressure** (Pa) | $2.5\ 10^{-4}$ – $3.3\ 10^{-4}$ (measured)<br>$3.2\ 10^{-5}$ (*estimated-EPI*) | E.C., 2003 |
| **Henry's Law constant** ($Pa.m^3.mol^{-1}$) | 0.86 (*estimated-EPI*)<br>10.6 (*estimated from vapour pressure and solubility*) | E.C., 2003 |
| **Adsorption** | **TetraBDE is very likely to adsorb on particulate matter.** | |
| **Organic carbon – water partition coefficient ($K_{OC}$)** | $K_{OC}$= 565 860 (*measured*)<br>$K_{OC}$= 71 560–122 900; 383 440 (*estimated from $K_{OW}$*) | E.C., 2003 |
| **Sediment – water partition coefficient ($K_{sed\text{-}water}$)** | 14 147 (*calculated from $K_{OC}$ = 565 860*) | E.C., 2011 |
| **Hydrophobicity** | **TetraBDE is a hydrophobic substance** | |
| **Octanol-water partition coefficient (Log Kow)** | 5.87 – 6.16 (*measured*)<br>6.77 (*estimated-EPI*) | E.C., 2003 |
| **Bioaccumulation – biomagnification** | cf. dedicated section 5.3 | |

| PentaBDE | | Master reference |
|---|---|---|
| **Water solubility** (mg.l$^{-1}$) | 13.3 $10^{-3}$ (commercial, *measured*)<br>2.4 $10^{-3}$ (*measured* for congener 2,2',4,4',5)<br>0.079 (*estimated-EPI*) | E.C., 2001 |
| **Volatilisation** | **PentaBDE is not likely to volatilize from water phase** | |
| **Vapour pressure** (Pa) | 4.69 $10^{-5}$ (commercial, *measured*)<br>2.9 $10^{-6}$ – 7.3 $10^{-5}$ (*measured*)<br>3.3 $10^{-6}$ (*estimated-EPI*) | E.C., 2001 |
| **Henry's Law constant** (Pa.m$^3$.mol$^{-1}$) | 0.36 (*measured*)<br>2 (commercial, *estimated from vapour pressure and solubility*)<br>0.78 – 522 (*estimated from vapour pressure and solubility*) | E.C., 2001 |
| **Adsorption** | **PentaBDE is very likely to adsorb on particulate matter.** | |
| **Organic carbon – water partition coefficient ($K_{OC}$)** | 983 340 (*measured*)<br>215 080 – 556 801; 2 $10^6$ (*estimated from $K_{OW}$*)<br>264 060 (commercial, *estimated from $K_{OW}$*) | E.C., 2001 |
| **Sediment – water partition coefficient ($K_{sed\text{-}water}$)** | 5 378 – 13 921 (*calculated from measured $K_{OC}$*) | E.C., 2011 |
| **Hydrophobicity** | **PentaBDE is a hydrophobic substance** | |
| **Octanol-water partition coefficient (Log Kow)** | 6.57 (commercial, *measured*)<br>6.46 – 6.97 (*measured*)<br>7.66 (*estimated-EPI*) | E.C., 2001 |
| **Bioaccumulation – biomagnification** | cf. dedicated section 5.3 | |

| HexaBDE | | | | Master reference |
|---|---|---|---|---|
| **Water solubility** (mg.l$^{-1}$) | 4.2 $10^{-6}$ (estimated-EPI) | | | E.C., 2003 |
| **Volatilisation** | **HexaBDE is not likely to volatilize from water phase** | | | |
| **Vapour pressure** (Pa) | 4.3 $10^{-6}$ – 9.5 $10^{-6}$ (measured)<br>3.8 $10^{-7}$ (estimated-EPI) | | | E.C., 2003 |
| **Henry's Law constant** (Pa.m$^3$.mol$^{-1}$) | 0.15 (*estimated-EPI*)<br>58.2; 659 – 1 456 (*estimated from vapour pressure and water solubility*) | | | E.C., 2003 |
| **Adsorption** | **HexaBDE is very likely to adsorb on particulate matter** | | | |
| **Organic carbon – water partition coefficient ($K_{OC}$)** | 1 250 000 (*measured*) | | | E.C., 2003 |
| | 453 520 – 3 270 000; 10 600 000 (*estimated from $K_{OW}$*) | | | |
| | | *measured* | *estimated* | Guan *et al.*, 2009 |
| | 2,2',4,4',5,5'-: | 1 740 000 | 49 000 000 | |
| | 2,2',4,4',5,6'-: | 2 690 000 | 40 700 000 | |
| **Sediment – water partition coefficient ($K_{sed\text{-}water}$)** | 31 251 (*calculated from measured $K_{OC}$*) | | | E.C., 2011 |
| **Hydrophobicity** | **HexaBDE is a hydrophobic substance** | | | |

| | | |
|---|---|---|
| **Octanol-water partition coefficient (Log Kow)** | 6.86 – 7.92 (*measured*)<br>8.55 (*estimated-EPI*) | E.C., 2003 |
| **Bioaccumulation – biomagnification** | cf. dedicated section 5.3 | |

| **HeptaBDE** | | **Master reference** |
|---|---|---|
| **Water solubility** (mg.l$^{-1}$) | 2.2 $10^{-7}$ (*estimated-EPI*) | E.C., 2003 |
| **Volatilisation** | **HeptaBDE is not likely to volatilize from water phase** | |
| **Vapour pressure** (Pa) | 4.4 $10^{-8}$ (estimated-EPI) | E.C., 2003 |
| **Henry's Law constant** (Pa.m$^3$.mol$^{-1}$) | 0.06 (*estimated-EPI*)<br>144 (*estimated from vapour pressure and solubility*) | E.C., 2003 |
| **Adsorption** | **HeptaBDE is very likely to adsorb on particulate matter** | |
| **Organic carbon – water partition coefficient ($K_{OC}$)** | 55 800 000 (*estimated from $K_{OW}$*) | E.C., 2003 |
| | *measured* *estimated*<br>2,2',3,4,4',5',6-: 1 480 000 115 000 000 | Guan *et al.*, 2009 |
| **Sediment – water partition coefficient ($K_{sed-water}$)** | 1 395 001 (*calculated from estimated $K_{OC}$*) | E.C., 2011 |
| **Hydrophobicity** | **HeptaBDE is a very hydrophobic substance** | |
| **Octanol-water partition coefficient (Log Kow)** | 9.44 (*estimated-EPI*) | E.C., 2003 |
| **Bioaccumulation – biomagnification** | cf. dedicated section 5.3 | |

| **OctaBDE** | | **Master reference** |
|---|---|---|
| **Water solubility** (mg.l$^{-1}$) | 5 $10^{-4}$ (commercial, *measured*)<br>1.1 $10^{-8}$ (*estimated-EPI*) | E.C., 2003 |
| **Volatilisation** | **OctaBDE is not likely to volatilize from water phase** | |
| **Vapour pressure** (Pa) | 6.59 $10^{-6}$ at 21°C (commercial, *measured*)<br>1.2 $10^{-7}$ – 2.3 $10^{-7}$ (measured)<br>4.9 $10^{-9}$ (*estimated-EPI*) | E.C., 2003 |
| **Henry's Law constant** (Pa.m$^3$.mol$^{-1}$) | 0.03 (*measured*)<br>7.9 $10^{-3}$ – 16 756 (*estimated from vapour pressure and solubility*)<br>10.6 (commercial, *estimated from vapour pressure and solubility*) | E.C., 2003 |
| **Adsorption** | **OctaBDE is very likely to adsorb on particulate matter.** | |
| **Organic carbon – water partition coefficient ($K_{OC}$)** | 1 363 040 (*extrapolated from measurements with other brominated diphenyl ethers*)<br>7.3 $10^{6}$ – 2.93 $10^{8}$ (*estimated from $K_{OW}$*)<br>156 640 (commercial, *estimated from $K_{OW}$*) | E.C., 2003 |
| **Sediment – water partition coefficient ($K_{sed-water}$)** | 34 077 (*calculated from extrapolated $K_{OC}$*) | E.C., 2011 |
| **Hydrophobicity** | **OctaBDE is a very hydrophobic substance** | |
| **Octanol-water partition coefficient (Log Kow)** | 6.29 (commercial, *measured*)<br>8.35 – 8.9 (*measured*)<br>10.33 (*estimated-EPI*) | E.C., 2003 |
| **Bioaccumulation – biomagnification** | cf. dedicated section 5.3 | |

| NonaBDE | | Master reference |
|---|---|---|
| **Water solubility** (mg.l$^{-1}$) | 5.6 $10^{-10}$ (*estimated-EPI*) | E.C., 2003 |
| **Volatilisation** | **NonaBDE is not likely to volatilize from water phase** | |
| **Vapour pressure** (Pa) | 5.4 $10^{-10}$ (estimated-EPI) | E.C., 2003 |
| **Henry's Law constant** (Pa.m$^3$.mol$^{-1}$) | 0.01 (*estimated-EPI*)<br>849 (*estimated from vapour pressure and solubility*) | E.C., 2003 |
| **Adsorption** | **NonaBDE is very likely to adsorb on particulate matter** | |
| **Organic carbon – water partition coefficient ($K_{OC}$)** | 1.54 $10^9$ (*estimated from $K_{OW}$*) | E.C., 2003 |
| **Sediment – water partition coefficient ($K_{sed\text{-}water}$)** | 38 500 001 (*calculated from estimated $K_{OC}$*) | E.C., 2011 |
| **Hydrophobicity** | **NonaBDE is a very hydrophobic substance** | |
| **Octanol-water partition coefficient (Log Kow)** | 11.22 (*estimated-EPI*) | E.C., 2003 |
| **Bioaccumulation – biomagnification** | cf. dedicated section 5.3 | |

## 5.2 ABIOTIC AND BIOTIC DEGRADATIONS

| | | Master reference |
|---|---|---|
| **Hydrolysis** | No information is currently available on the hydrolytic degradation of pentaBDE and octaBDE in aqueous solution. It is thought that these compounds will be hydrolytically stable under conditions found in the environment. | E.C., 2001<br>E.C., 2003 |
| **Photolysis** | From the available information it is clear that polybrominated diphenyl ethers have the potential to photodegrade in the environment. In water, and at environmentally relevant wavelengths, the most likely initial reaction products from these reactions are hydroxylated diphenyl ethers, which possibly then react further. The first step in the reaction is probably cleavage of a C-Br following the absorption of radiation, followed by reaction of the radical intermediate (radical cation intermediates species may be formed in water) with oxygen and/or water to give substituted (e.g. hydroxylated) products (Larson and Weber, 1994; Mill and Mabey, 1985). The formation of lower brominated diphenyl ethers during direct photolysis in the environment would require the presence of H-atom donors at concentrations sufficiently high to compete with other oxidants for the aromatic radical intermediate formed. It is not possible to say anything about the significance or rates of these reactions for polybrominated diphenyl ethers in the environment. | E.C., 2001<br>E.C., 2003 |
| | $DT_{50\ -\ pentaBDE\text{-}99}$ ≈12,6 d (estimated from Syracuse Research Corporation AOP estimation program). | E.C., 2001 |
| | In a mixture of methanol (80%) and water (20%) photolysis half-lives are:<br>$DT_{50\ -\ tetraBDE}$ = 12 – 16 d  $DT_{50\ -\ heptaBDE}$ = 1.2 d<br>$DT_{50\ -\ pentaBDE}$ = 2.4 d  $DT_{50\ -\ octaBDE\text{-}203}$ = 5h<br>$DT_{50\ -\ hexaBDE}$ = 1.2 d | Eriksson *et al.*, 2001a *quoted in* E.C., 2003 |
| | HexaBDE-153 is rapidly photohydrodebrominated in aquatic systems to some of the most prevalent penta- and tetra-BDE typically observed in environmental matrices | Rayne *et al.*, 2006 |
| **Biodegradation** | PentaBDE has been considered as Persistent in the framework of the POP Convention | E.C., 2001 |
| | PentaBDE is not readily biodegradable according to a standard OECD test | UNEP, 2006 |

| | | |
|---|---|---|
| | with aerobic activated sludge.<br>Biotic degradation of pentabromodiphenyl ether in sediment and water have not been reported in experimental studies but the half-lives for pentaBDE-99 and tetraBDE-47 have been estimated at 600 days (aerobic sediment) and 150 days (water) for both congeners. | |

In an experimental study, carps were fed with food spiked with individual BDE congeners for 62 days, and tissue and excreta were examined. Around 10% of pentaBDE-99 and 17% of heptaBDE-183 were reductively debrominated in the gut to lower brominated congeners, tetraBDE-47 and hexaBDE congeners, respectively, showing evidence of debromination into congener with one less bromine atom. Therefore, the authors showed that body burdens of BDE congeners in aquatic organisms may reflect direct uptake from exposure as well as debromination of more highly brominated congeners (Stapleton *et al.*, 2004).

In another study (Munschy *et al.*, 2011), accumulation and biotransformation of BDEs in fish (*Solea solea*) was observed. They showed that contamination efficiencies were related to their hydrophobicity potential and influenced biotransformation. Biotransformation was shown to be driven mostly by debromination process rather than biotransformation in hydroxylated metabolites.

Overall, several studies have been lead on diverse degradation processes which lead to debromination of BDE congeners. It is now considered that all highly brominated congener will end as low brominated congeners in environmental matrices (pers. comm., POP Review Committee, 2010).

## 5.3 BIOACCUMULATION AND BIOMAGNIFICATION POTENTIAL

| Congeners | BCF fish | Master reference |
|---|---|---|
| **tetraBDE** | 28 800 – 35 100 (*measured*)<br>19 480 – 37 090; 46 050 (*estimated from log $K_{OW}$*) | E.C., 2003 |
| **pentaBDE** | 44 550 (commercial, *estimated from log $K_{OW}$*)<br>1 440; 17 700 (*measured*)<br>34 141; 43 061 – 45 880 (*estimated from log $K_{OW}$*) | E.C., 2001 |
| **hexaBDE** | 5 640 (*measured*)<br>46 180 – 27 260; 12 200 (*estimated from log $K_{OW}$*) | E.C., 2003 |
| | up to 2 580 and 5 640 depending on the congener | CITI, 1982 *quoted in* UNEP, 2007 |
| **heptaBDE** | 2 100 (*estimated from log $K_{OW}$*) | E.C., 2003 |
| **octaBDE** | 39 980 (commercial, *estimated from log $K_{OW}$*)<br>6 670 – 16 390; 175 (*estimated from log $K_{OW}$*) | E.C., 2003 |
| | Experimental results indicate that octaBDE does not bioconcentrate. A single study on a mixed commercial octabromodiphenyl ether product indicated essentially no bioaccumulation in carp (Cyprinus carpio) (CBC, 1982 cited in E.C., 2003). Assuming that the actual concentration of octabromodiphenyl ether in the water was around 0.5 µg/l, BCFs would be of the order of <10-36 l/kg.<br>Bioconcentration is however considered relevant for hexaBDE, which is included in the commercial octaBDE product (see BCF values for hexaBDE congeners in the corresponding table above. | E.C., 2003 |
| **nonaBDE** | 7 (*estimated from log $K_{OW}$*) | E.C., 2003 |

| Congeners | BAF | Master reference |
|---|---|---|
| **triBDE** | Freshwater food web (South-China reservoir surrounded by several e-waste recycling workshops) including invertebrates (1 snail and 1 prawn species), fish (3 carp species) and snakes (2 species):<br>BDE-28: $BAF_{snail}$ = 794 | Wu *et al.*, 2008 |

| | | |
|---|---|---|
| | Lake trouts from Lake Michigan[7]<br>BDE-47: $BAF_{trout}$ = 19.9 $10^6$ | Streets *et al.*, 2006 |
| **tetraBDE** | No available information | |
| **pentaBDE** | Lake trouts from Lake Michigan[7]<br>BDE-99: $BAF_{trout}$ = 5 $10^6$<br>BDE-100: $BAF_{trout}$ = 31.6 $10^6$ | Streets *et al.*, 2006 |
| **hexaBDE** | See details above for TriBDE-28. BDE-154: $BAF_{snail}$ = 199 526 | Wu *et al.*, 2008 |

[7] In their study, Streets et al. (2006) report very high values of BAF compared to the other study reported above (Wu *et al.*, 2008). This may be partly explained by the large differences in exposure scenarios. In fact, water concentrations reported in Streets et al. (2006) are ca. 1 000 times lower compared to water concentrations reported by Wu et al. (2008) or 3 times lower to Law et al. (2006), while concentrations in lake trout in Lake Michigan (Streets *et al.*, 2006) are higher compared to data fish concentrations from Lake Geneva (Cheaib *et al.*, 2009, cf. section 6.2). Furthermore, Lake trout has very high lipid content (approx. 15%) and is a high trophic level species which could also partly explain the high values of BAF.

| Congeners | Biomagnification parameters | Master reference |
|---|---|---|
| **TMF values** | | |
| **triBDE** | Marine food web including invertebrates (5 species), fish (9 species) and seabirds (2 species):<br>BDE-28: TMF = 1.47 (invertebrates and fish)<br>BDE-28: TMF = 3.2 (seabirds) | Zhang *et al.*, 2010 |
| | Freshwater food web (reservoir surrounded by several e-waste recycling workshops) including invertebrates (1 snail and 1 prawn species), fish (3 carp species) and snakes (2 species):<br>BDE-28: TMF = 1.64 | Wu *et al.*, 2009 |
| **tetraBDE** | BDE-47: TMF = 1.6 (significantly ≠ from 1)<br>BDE-49: TMF = 1.2<br>BDE-66: TMF = 0.44 (significantly ≠ from 1) | Kelly *et al.*, 2008 |
| | Marine food web including invertebrates (5 species), fish (9 species) and seabirds (2 species):<br>BDE-47: TMF = 3.91 (invertebrates and fish)<br>BDE-47: TMF = 19.54 (seabirds) | Zhang *et al.*, 2010 |
| | Freshwater food web (reservoir surrounded by several e-waste recycling workshops) including invertebrates (1 snail and 1 prawn species), fish (3 carp species) and snakes (2 species):<br>BDE-47: TMF = 2.28 | Wu *et al.*, 2009 |
| | Freshwater food web including phytoplankton, zooplankton, mussels and fish (6 species):<br>BDE-47: TMF = 1.5 | Law *et al.*, 2006 |
| **pentaBDE** | Trophic magnification factors not significantly different from 1 in an Arctic marine food web<br>BDE-99: TMF = 0.76<br>BDE-100: TMF = 0.96 | Kelly *et al.*, 2008 |
| | Marine food web including invertebrates (5 species), fish (9 species) and seabirds (2 species):<br>BDE-99: TMF = 3.21 (invertebrates and fish)<br>BDE-99: TMF = 84.72 (seabirds)<br>BDE-100: TMF = 3.71 (invertebrates and fish)<br>BDE-100: TMF = 51.76 (seabirds) | Zhang *et al.*, 2010 |
| | Freshwater food web (reservoir surrounded by several e-waste recycling workshops) including invertebrates (1 snail and 1 prawn species), fish (3 carp species) and snakes (2 species):<br>BDE-99: TMF = 0.53<br>BDE-100: TMF = 2.64 | Wu *et al.*, 2009 |
| | Freshwater food web including phytoplankton, zooplankton, mussels and fish (6 species):<br>BDE-99: TMF = 0.7<br>BDE-100: TMF = 1.6 | Law *et al.*, 2006 |
| **hexaBDE** | Trophic magnification factors not significantly different from 1 in an Arctic marine food web<br>BDE-153: TMF = 0.59<br>BDE-154: TMF = 0.46 | Kelly *et al.*, 2008 |
| | Marine food web including invertebrates (5 species), fish (9 species) and seabirds (2 species):<br>BDE-153: TMF = 1.36 (invertebrates and fish)<br>BDE-153: TMF = 97.05 (seabirds)<br>BDE-154: TMF = 2.77 (invertebrates and fish)<br>BDE-154: TMF = 23.77 (seabirds) | Zhang *et al.*, 2010 |
| | Freshwater food web (reservoir surrounded by several e-waste recycling workshops) including invertebrates (1 snail and 1 prawn species), fish (3 carp species) and snakes (2 species): | Wu *et al.*, 2009 |

| Congeners | Biomagnification parameters | Master reference |
|---|---|---|
| | **TMF values** | |
| | BDE-153: TMF = 0.81<br>BDE-154: TMF = 2.25 | |
| **heptaBDE** | Marine food web including invertebrates (5 species), fish (9 species) and seabirds (2 species):<br>BDE-183: TMF = 0.53 (invertebrates and fish)<br>BDE-183: TMF = 13.68 (seabirds) | Zhang *et al.*, 2010 |
| | Freshwater food web (reservoir surrounded by several e-waste recycling workshops) including invertebrates (1 snail and 1 prawn species), fish (3 carp species) and snakes (2 species):<br>BDE-183: TMF = 0.81 | Wu *et al.*, 2009 |
| **octaBDE** | No data available | |
| **nonaBDE** | No data available | |
| **SumBDEs** | Marine food web including invertebrates (5 species), fish (9 species) and seabirds (2 species):<br>SumBDEs: TMF = 2.37 (invertebrates and fish)<br>SumBDEs: TMF = 29.17 (seabirds) | Zhang *et al.*, 2010 |
| | Freshwater food web (reservoir surrounded by several e-waste recycling workshops) including invertebrates (1 snail and 1 prawn species), fish (3 carp species) and snakes (2 species):<br>SumBDEs: TMF = 1.86 | Wu *et al.*, 2009 |

| Congeners | Biomagnification parameters (continued) | Master reference |
|---|---|---|
| | **Single BMF1 values** | |
| **tetraBDE**<br>**BDE-47** | $BMF_{zoopk-fish}$ = 1.48 (liver) ; 2.25 (muscle)<br>$BMF_{fish.pred-fish.prey}$ = 1.12 – 1.59 (livre) ; 1.07 – 1.17 (muscle) | Kuo *et al.*, 2010 |
| | Range (geometric mean):<br>$BMF_{zoopk-zoopk}$ = 10.9 (4.1 - 29.1)<br>$BMF_{zoopk-fish}$ = 2.6 (0.4 - 10.1) | Sørmo *et al.*, 2006 |
| **pentaBDE** | $BAF_{fish}$ = 16 – 20 (Bioaccumulation factors, defined as concentration in fish / concentration in food) | Holm *et al.*, 1993 as cited *in* E.C., 2001 |
| | BDE-99: $BMF_{zoopk-fish}$ = 0.4 (liver) ; 0.73 (muscle)<br>BDE-99: $BMF_{fish-fish}$ = 0.88 – 0.89 (liver) ; 0.49 – 0.61 (muscle)<br>BDE-100: $BMF_{zoopk-fish}$ = 1.45 (liver) ; 1.52 (muscle)<br>BDE-100: $BMF_{fish-fish}$ = 1.14 – 1.41 (liver) ; 1.09 – 1.18 (muscle) | Kuo *et al.*, 2010 |
| | Range (geometric mean):<br>BDE-99: $BMF_{zoopk-zoopk}$ = 5.6 (0.65 - 47.6)<br>BDE-99: $BMF_{zoopk-fish}$ = 0.9 (0.04 - 3.4)<br>BDE-100: $BMF_{zoopk-fish}$ =0.6 (0.2 ; 1.6) | Sørmo *et al.*, 2006 |
| **hexaBDE** | Biomagnification factors estimated for two hexaBDE isomers for several food chains examples, using the North Sea data:<br>$BMF_{fish-invertebrate}$ = ~0.6 – 0.7 | de Boer *et al.*, 2001 as cited *in* E.C., 2003 |
| **heptaBDE** | No data available | |
| **octaBDE** | No data available | |
| **nonaBDE** | No data available | |

| Congeners | Biomagnification parameters (continued) | Master reference |
|---|---|---|
| | **Single BMF2 values** | |
| **tetraBDE** | $BMF_{polar\ bear\ -\ ringed\ seal}$ : geometric mean of 5 locations (range)<br>BDE-47: 3.5 (1.8 – 7.4) | Muir *et al.*, 2006 |
| | $BMF_{harbor\ seal\ -\ fishes}$ : range (geometric mean of 7 marine fish species)<br>BDE-47: 38.1 (21.4 – 109)<br>BDE-49: 0.4 (0.12 – 1.03)<br>BDE-66: 0.1 (0.04 – 0.83)<br>BDE-75: 0.3 (0.05 – 0.63) | Shaw *et al.*, 2009 |
| | BDE-47: $BMF_{mammal\ -\ fish}$ 56<br>BDE-47: $BMF_{mammal\ -\ mammal}$ 0,5 | Sørmo *et al.*, 2006 |
| | Mean +/- s.d.:<br>BDE-47: $BMF_{harbor\ seal\ -\ fish}$ = 8.4 +/- 5.7 (juveniles) ; 4.6 +-/ 2.4 (adults)<br>BDE-47: $BMF_{harbor\ porpoise\ -\ fish}$ = 18 +/- 21(juveniles) ; 15 +/- 10 (adults) | Weijs *et al.*, 2009 |
| **pentaBDE** | Geometric mean of 5 locations (range)<br>BDE-99: $BMF_{polar\ bear\ -\ ringed\ seal}$ = 4.5 (1 – 11)<br>BDE-100: $BMF_{polar\ bear\ -\ ringed\ seal}$ = 3.1 (0.6 – 8.8) | Muir *et al.*, 2006 |
| | Range (geometric mean of 7 marine fish species)<br>BDE-99: $BMF_{harbor\ seal\ -\ fishes}$ = 37.6 (17.9 – 213)<br>BDE-100: $BMF_{harbor\ seal\ -\ fishes}$ = 10.3 (6.9 – 29.8) | Shaw *et al.*, 2009 |
| | BDE-99: $BMF_{ringed\ seal\ -\ fish}$ = 13.7<br>BDE-99: $BMF_{polar\ bear\ -\ ringed\ seal}$ = 0.3<br><br>BDE-100: $BMF_{ringed\ seal\ -\ fish}$ = 26.1<br>BDE-100: $BMF_{polar\ bear\ -\ ringed\ seal}$ = 0.3 | Sørmo *et al.*, 2006 |
| | Mean +/- s.d.:<br>BDE-99: $BMF_{harbor\ seal\ -\ fish}$ = 5.9 +/- 6.1 (juveniles) ; 2.9 +/- 1.2 (adults)<br>BDE-99: $BMF_{harbor\ porpoise\ -\ fish}$ = 19 +/- 24 (juveniles) ; 33 +/- 23 (adults)<br><br>BDE-100: $BMF_{harbor\ seal\ -\ fish}$ = 1.7 +/-1.1 (juveniles) ; 1.3 +/- 0.7 (adults)<br>BDE-100: $BMF_{harbor\ porpoise\ -\ fish}$ = 13 +/- 15 (juveniles) ; 15 +/- 9.7 (adults) | Weijs *et al.*, 2009 |
| **hexaBDE** | Biomagnification factors estimated for two hexaBDE isomers for several food chains examples, using the North Sea data:<br>$BMF_{porpoise\ -\ fish}$ = 40 – 70<br>$BMF_{seal\ -\ fish}$ = 5 – 10 | de Boer *et al.*, 2001 as cited *in* E.C., 2003 |
| | $BMF_{polar\ bear\ -\ ringed\ seal}$ : geometric mean of 4 locations (range)<br>BDE-153: BMF= 49.6 (8.8 – 130)<br>BDE-154: BMF= 1.0 (0.2 – 2.9) | Muir *et al.*, 2006 |
| | $BMF_{harbor\ seal\ -\ fishes}$ : range (geometric mean of 7 marine fish species)<br>BDE-153: 367.7 (148 – 700)<br>BDE-154: 26.4 (11.3 – 447)<br>BDE-155: 64.0 (12.4 – 236) | Shaw *et al.*, 2009 |
| | BDE-153: $BMF_{polar\ bear\ -\ ringed\ seal}$ = 7.5<br><br>BDE-154: $BMF_{ringed\ seal\ -\ fish}$ = 7.9<br>BDE-154: $BMF_{polar\ bear\ -\ ringed\ seal}$ = 0.32 | Sørmo *et al.*, 2006 |
| | Mean +/- s.d.:<br>BDE-99: $BMF_{harbor\ seal\ -\ fish}$ = 15 +/- 13 (juveniles) ; 15 +/- 7.8 (adults)<br>BDE-99: $BMF_{harbor\ porpoise\ -\ fish}$ = 17 +/- 21 (juveniles) ; 77 +/- 53 (adults)<br><br>BDE-100: $BMF_{harbor\ seal\ -\ fish}$ = 2.2 +/-1.5 (juveniles) ; 4.8 +/- 3.6 (adults)<br>BDE-100: $BMF_{harbor\ porpoise\ -\ fish}$ = 16 +/- 17 (juveniles) ; 50 +/- 32 (adults) | Weijs *et al.*, 2009 |
| **heptaBDE** | No data available | |
| **octaBDE** | No data available | |
| **nonaBDE** | No data available | |

| | | |
|---|---|---|
| **SumBDEs** | BMF value derived from Osprey egg based on measurements in egg, several fish species and their relative contribution in Osprey diet: $BMF_{fish-birds\ eggs}$ = 25.1 | Chen *et al.*, 2010 |
| | $BMF_{harbor\ seal-fishes}$ = 17.1 – 76.5 | Shaw *et al.*, 2009 |

Overall, measured BCF values for BDE congeners range from very low values for highly brominated congeners (<5) to very high values for lower brominated congeners (up to 35 100 (measured value) for tetraBDE). Considering the fact that any highly brominated BDE congeners ends as debrominated via diverse degradation processes, the highest measured **BCF of 35 100** for tetraBDE congeners **should be retained**. This choice is consistent with the application of the worst case.

Looking at the values reported here above, the single BMF1 values are in a range below 10 for all BDE congeners. However, looking more closely at these values, it appears that maximal BMF1 values (5.6 and 10.9) are encountered only for a specific trophic interval, i.e. from zooplankton to zooplankton. The third maximal value is reported by Sormo et al. (2006) 2.6 for BMF1 from zooplankton to fish.

Thus, a value of 5 for BMF1 could be proposed, that covers almost all trophic chains among the ones reported in TMF studies, except the ones including top predators, e.g. seabirds. In line with the TGD-EQS, the food chain is defined with its trophic levels as water –BCF→ aquatic organisms –BMF1→ fish → fish-eating predator for freshwater ecosystems. It seems therefore that a **BMF1 value of 5** would be appropriate to cover biomagnification from lower trophic levels to fish species. Such a value is still a worst case, considering the high BAF values reported by Streets and his collaborators (2006) as well as the wide range of BMF values in general.

For marine ecosystems, however, another trophic level may be introduced: water –BCF→ aquatic organisms –BMF1→ fish –BMF2→ fish-eating predator → top predator. As regards BMF2, the values reported above are rather low for tetraBDE congeners other than BDE-47, but some very high values are reported for tetraBDE-47 as well as some values for pentaBDE, the highest values being reported for hexaBDE congeners. Indeed, values as high as 700 are reported by Shaw et al. (2009) for hexaBDE-153. However, on the overall, it is more frequent to encounter values between 10 and 70.TMF studies show a high degree of biomagnification for top predators, e.g. seabirds. The data reported by Kelly et al., 2008 however indicate a low degree or absence of biomagnification of PBDEs in a marine Arctic food web. The authors explain that the field observations suggest PBDEs exhibit a relatively rapid rate of depuration though biotransformation in Arctic marine organisms, which is consistent with laboratory studies in fish and rats.

Considering the high variability of the data reported and additional evidence that BDEs can be eliminated by top predators, a **BMF2 value of 20** is proposed as reasonable worst case.

# 7 EFFECTS AND QUALITY STANDARDS

The data reported in this section hereafter correspond to the most relevant effect data extracted from pentaBDE and octaBDE EU-RAR (E.C., 2001; E.C., 2003).

## 7.1 ACUTE AND CHRONIC AQUATIC ECOTOXICITY

The data considered as valid for effects assessment purpose in the RAR were not further assessed. Concentrations are all expressed as in commercial products when commercial products were tested.

Since EU-RARs were published in 2001, 2002 and 2003, other studies were available on exposure of aquatic organisms to PBDE congeners and/or commercial products. Some are reported in the table hereunder and were assessed for their reliability, but there are numerous articles (e.g. Crump *et al.*, 2008; Muirhead *et al.*, 2005; Raldúa *et al.*, 2008; Timme-Laragy *et al.*, 2006) which report endpoints that are not usually accepted as effects assessment endpoints (developmental and behavioural effects, genotoxic effects, dietary exposure instead of direct exposure). Other studies have not been validated because not deemed reliable enough for effects assessment purpose (e.g. Breitholtz and Wollenberger, 2003; Key *et al.*, 2008). Only studies which could be attributed a Klimisch code (Klimisch *et al.*, 1997) 1 or 2 were reported in the tables.

### 7.1.1 Organisms living in the water column

| ACUTE EFFECTS | | | Reliability | Master reference |
|---|---|---|---|---|
| **Algae & aquatic plants ($mg.l^{-1}$)** | **Freshwater** | No information available | | |
| | | *Selenastrum capricornutum* / 96h<br>Compound tested: c-pentaBDE<br>24h-$EC_{10}$ = 2.7 $10^{-3}$ – 3.1 $10^{-3}$<br>48h and 96h : no effects observed | Evaluated in EU-RAR (E.C., 2001) | Palmer *et al.*, 1997c |
| | **Marine** | *Skeletonema costatum* / 72h / growth rate<br>Compound tested: TetraBDE (BDE-47)<br>48h-$EC_{50}$= 0.07<br>48h-NOEC= 6.6 $10^{-3}$ | 2 | Källqvist *et al.*, 2006 |
| **Invertebrates ($mg.l^{-1}$)** | **Freshwater** | No information available | | |
| | | ***Daphnia magna* / 48 h**<br>Compound tested: c-pentaBDE<br>**$EC_{50\ -\ mortality,\ immo}$ = 0.014 (mm)**<br>$NOEC_{mortality,\ immo}$ = 4.9 $10^{-3}$ (mm) | Evaluated in EU-RAR (E.C., 2001) | Palmer *et al.*, 1997a |
| | | *Daphnia magna* / 21d<br>Compound tested: c-pentaBDE<br>96h-$EC_{50immo}$ =0.017 (mm)<br>7-21d-$EC_{50immo}$ = 0.014 (mm) | | Drottar and Krueger, 1998 |
| | **Marine** | No information available | | |
| | **Sediment** | No information available | | |
| **Fish ($mg.l^{-1}$)** | **Freshwater** | *Oryzias latipes* / 48h<br>Compound tested: c-pentaBDE, c-octaBDE and c-decaBDE<br>48h-$LC_{50}$ > 500 for the three compounds | Evaluated in EU-RARs (E.C., 2001; E.C., 2002; E.C., 2003) | CITI, 1982 |
| | | *Oncorhynchus mykiss* / 96h<br>Compound tested: c-pentaBDE<br>96h-$LC_{50}$ and NOEC > 0.021 | Evaluated in EU-RAR (E.C., 2001) | Palmer *et al.*, 1997b |
| | **Marine** | No information available | | |
| | **Sediment** | No information available | | |

mm : mean measured concentrations

***Notes regarding some of the acute tests reported in the table above:***

*Selenastrum capricornutum* / 96h / c-pentaBDE (Palmer *et al.*, 1997c as cited in E.C., 2001)

The effects observed after 24h of exposure had disappeared by 48 hours exposure. The results of this study, and significance of the effects seen, are difficult to interpret, as it appears that the test substance was removed from solution (by adsorption onto the algal cells) during the experiment, but it may indicate that the commercial pentaBDE has the potential to cause effects on algae at similar concentrations as seen in long-term studies with *Daphnia magna*.

*Skeletonema costatum* / 96h / tetraBDE (Källqvist *et al.*, 2006)

Because of the high specific growth rate (2.35/d) in the control, the exponential phase was not maintained for 72 h in the control and at the two lowest concentrations of BDE 47, and analysis of the data therefore was based on growth rates measured during the first 48 h. Although lead over a 72h-exposure duration, this study can not be used to provide chronic data as such.

*Daphnia magna* / 48 h / c-pentaBDE (Palmer *et al.*, 1997a as cited in E.C., 2001)

It was stated in the test report that the effects seen could have been due to physical impairment (undissolved test substance adsorbed onto the daphnids and adversely affecting respiration, swimming, etc.) rather than a direct toxic effect.

*Oryzias latipes* (CITI, 1982 and Palmer *et al.*, 1997b as cited in E.C., 2001)

No effects were observed up to the highest concentration tested, which were far above the water solubility of the compound tested.

| CHRONIC EFFECTS | | | Valid according to | Master reference |
|---|---|---|---|---|
| **Algae & aquatic plants ($mg.l^{-1}$)** | **Freshwater** | *Selenastrum capricornutum* / 96h<br>Compound tested: c-pentaBDE<br>24h-$EC_{10}$ = 2.7 $10^{-3}$ – 3.1 $10^{-3}$<br>48h and 96h : no effects observed | Evaluated in EU-RAR (E.C., 2001) | Palmer *et al.*, 1997c |
| | **Marine** | No information available | | |
| **Invertebrates ($mg.l^{-1}$)** | **Freshwater** | *Daphnia magna* / 21d<br>Compound tested: c-pentaBDE<br>21d-$NOEC_{growth}$ = 5.3 $10^{-3}$ (mm) | Evaluated in EU-RAR (E.C., 2001) | Drottar and Krueger, 1998 |
| | | *Daphnia magna* / 21d<br>Compound tested: c-octaBDE<br>$NOEC_{survival, repro, growth}$ > 0.002 (n)<br>$NOEC_{survival, repro, growth}$ > 1.7 $10^{-3}$ (m) | Evaluated in EU-RAR (E.C., 2003) | Graves *et al.*, 1997 |
| | | *Daphnia magna* / 21d / reproduction<br>Compound tested: TetraBDE (BDE-47)<br>NOEC= 0.014 | 2 | Källqvist *et al.*, 2006 |
| | **Marine** | No information available | | |
| **Fish ($mg.l^{-1}$)** | **Freshwater** | *Oncorhynchus mykiss* / ELS / 87 days<br>Compound tested: c-pentaBDE<br>60d post-hatch-$NOEC_{growth}$ = 8.9 $10^{-3}$ (mm) | Evaluated in EU-RAR (E.C., 2001) | Wildlife, 2000d |
| | **Marine** | ***Psetta maxima* / ELS (part)**<br>- 2d exposure of embryos<br>$NOEC_{tetraBDE-47}$= 2.03 $10^{-3}$<br>$NOEC_{pentaBDE-99}$= 3.22 $10^{-3}$<br>- **4d exposure of larvae**<br>**$NOEC_{tetraBDE-47}$= 4.9 $10^{-4}$**<br>$NOEC_{pentaBDE-99}$= 1.61 $10^{-3}$ | 2 | Mhadhbi *et al.*, 2010 |
| | **Sediment** | No information available | | |
| **Other taxonomic groups** | | No information available | | |

om: organic matter content; oc: organic carbon content; n: nominal concentrations; mm: mean measured concentrations

***Notes regarding some of the chronic tests reported in the table above:***

*Selenastrum capricornutum* / 96h / c-pentaBDE (Palmer *et al.*, 1997c as cited in E.C., 2001)

See acute toxicity section.

*Daphnia magna* / 21d / c-octaBDE (Graves *et al.*, 1997 as cited in E.C., 2003)

Since octaBDE is a mixture of congeners between hexa- to nonaBDE, some consideration has to be given as to whether the lower brominated components, particularly the hexaBDE, could be more toxic than indicated by the results of the test. In the test, stock solutions of the test substance were prepared by dissolving in dimethylformamide, with one stock solution being prepared for each concentration tested. These stock solutions were then injected into the diluter mixing chambers to give the desired test concentrations, with the solvent concentration being 0.07 ml/l in all cases. This method ensures that the composition of the substance in solution is as close as possible to that in the commercial preparation, providing all the test substance enters into solution. Since the hexaBDE component is likely to be the most soluble of all the components in the commercial octaBDE, it is very likely that this component was present in true solution and so the concentration of this component can be estimated from the nominal concentration using the known composition of the commercial substance tested (e.g. 5.5% hexaBDE). Thus the NOEC of >2 µg/l for the commercial compound is equivalent to a NOEC of >0.11 µg/l for the hexaBDE component.

In section 5.1, the water solubility of the hexaBDE component is estimated/extrapolated to be around 47 µg/l. Thus it is theoretically possible for the hexaBDE isomers to be present in solution at concentrations higher than those used in this experiment. As part of the 21-day reproduction test carried out for the commercial octaBDE, a range finding 9-day Daphnia immobilisation test was carried out using higher nominal concentrations (0.0081, 0.027, 0.09, 0.3 and 1 mg/l) of the commercial octaBDE. Details of the test system used are not reported. Deaths occurred in seven out of the ten exposed Daphnia at the 1 mg/l nominal concentration after two to three days but no other mortalities were noted. The numbers of neonates produced were reported as 32 in the control, 21 in the solvent control, 0 at 0.0081 mg/l, 19 at 0.027 mg/l, 27 at 0.09 mg/l 0 at 0.3 mg/l and 0 at 1.0 mg/l. The significance of these results is unknown. The test concentrations used in this range finding test exceed the water solubility of the substance by a considerable amount and thus the mortality seen at 1 mg/l could have been due to a physical effect caused by undissolved test substance. However, it is possible that the effects seen were related to the dissolved chemical. Since the nominal concentration tested was well in excess of the water solubility of the commercial mixture, then each component of the mixture could be present in solution at concentrations close to their individual solubilities. If this is assumed then the effects seen could be due to the most water soluble component of the commercial mixture at a concentration of around 4.7 µg/l. The results of this analysis should be treated with caution due to the assumptions made, and the fact that the experiment was a range finding, rather than definitive, test.

*Daphnia magna* / 21d / tetraBDE (Källqvist *et al.*, 2006)

The distribution of the individual data shows a larger variation at 14 mg.l-1 than in the control. Three animals at this exposure level had a higher number of offspring than the average for the control animals, whereas the remaining seven animals showed lower reproductive output than the control mean. Although the high variation in reproduction at 14 $mg.l^{-1}$ may, in itself, be an effect of exposure to BDE 47, further studies to reveal the toxicological relevance were not undertaken.

*Psetta maxima* / ELS / tetraBDE and pentaBDE (Mhadhbi *et al.*, 2010)

Missing information on material and methods, notably on water quality parameters such as dissolved oxygen and pH.

### $QS_{water, eco}$ derivation

*Chemicals considered:* The ecotoxicological data retrieved on aquatic organisms address ecotoxicity of the commercial mixture c-pentaBDE as well as c-octaBDE as well as some data on individual tetra- and penta-congeners, BDE 47 and BDE 99, respectively. The best satisfactory approaches would be either:

- to derive congener-specific QS values which would allow EQS compliance with concentrations of these congeners in the media, or
- to identify the most toxic congener and use it as a reference in a toxic equivalence approach for the determination of an overall EQS.

Most of the tests were conducted on commercial mixture and it is not possible to derive congener-specific QS values based on the commercial product ecotoxicological data because even if the content of the different congeners in each commercial product is well-known, the contribution of these congeners to the overall toxicity is not well-attested.

There are not enough reliable congener-specific ecotoxicological data available to allow the derivation of congener-specific QS values or identify the most toxic congener. Moreover, there were not enough congener-specific data to range the BDE congeners as a function of their toxicity. It is rather well-known that according to their physico-chemical properties, the more brominated the less soluble and the less bioaccumulative (for higher bromination levels) the congeners are, but it is not possible to presume on their direct toxicity properties based on this information.

*Based on the information available, and considering the relationships between BDE congeners (i.e., possibilities for higher brominated compounds to degrade in lower brominated compounds) it is proposed to use all the data from the cited commercial products and their main components. The dataset contain data for algae, invertebrates and fish for acute and chronic exposures, and QS values will be derived based on the worst case basis, i.e. derived from the lowest acute and chronic ecotoxicological data.*

*Freshwater versus marine waters data:* The Guidance Document on EQS derivation (E.C., 2011) states that "*in principle, ecotoxicity data for freshwater and saltwater organisms should be pooled for organic compounds, if certain criteria are met*" and that "*the presumption that for organic compounds saltwater and freshwater data may be pooled must be tested, except where a lack of data makes a statistical analysis unworkable*."

This is the case for polybrominated diphenyl ethers. In fact, there are too few marine data (solely one acute data on marine algae and one marine data on marine flatfish) to perform a "*meaningful statistical comparison*" and no further indications of "*a difference in sensitivity between freshwater vs saltwater organisms*". Therefore, in this case, the data sets may be combined for QS derivation according to the Guidance Document on EQS derivation (E.C., 2011).

*QS derivation:*

As explained above, the acute and chronic dataset can be considered as complete (data available for algae, invertebrates and fish) and the lowest available data are used to derive QS useful for the sum of BDEs, thus to be compared to the sum of the available BDEs monitored in the media.

The lowest available data are found for exposure of *Daphnia magna* for acute exposures, with a 48h-$EC_{50}$ of 14 $\mu g.l^{-1}$ and for turbot *Psetta maxima* embryos exposed 4d, with a NOEC of 0.49 tetraBDE $\mu g.l^{-1}$.

These toxicity data are equal or below water solubility of the different BDE component tested, i.e. 13 $\mu g.l^{-1}$ for c-pentaBDE and 11 $\mu g.l^{-1}$ for tetraBDE. QS can therefore be derived on the basis of the lowest available ecotoxicological data.

Algae, crustaceans and fish being represented for both acute and chronic dataset, standard assessment factors of 100 and 1000 can be applied to the lowest data to derive $MAC_{freshwater, eco}$ and $MAC_{marine\ water, eco}$, respectively. Standard assessment factors of 10 and 100 are applied to the lowest data to derive $AA\text{-}QS_{freshwater, eco}$ and $AA\text{-}QS_{marine\ water, eco}$, respectively.

| **Tentative $QS_{water}$**<br>**Assessment factor method** | **Relevant study for derivation of QS** | **AF** | **Tentative QS** |
|---|---|---|---|
| $MAC_{freshwater, eco}$ | *Daphnia magna* / 48 h | 100 | 0.14 |
| $MAC_{marine\ water, eco}$ | $EC_{50\ -\ mortality,\ immo}$= 0.014 $mg_{c\text{-}pentaBDE}.l^{-1}$ | 1000 | 0.014 |
| $AA\text{-}QS_{freshwater, eco}$ | *Psetta maxima* / 4d exposure of larvae | 10 | 0.049 |
| $AA\text{-}QS_{marine\ water, eco}$ | NOEC= 4.9 $10^{-4}$ $mg_{tetraBDE}.l^{-1}$ | 100 | 0.0049 |

### 7.1.2 Sediment-dwelling organisms

| **SEDIMENT – CHRONIC EFFECTS** | | **Valid according to** | **Master reference** |
|---|---|---|---|
| **Sediment dwelling invertebrates ($mg.kg^{-1}_{dw}$)** | Spiked sediment test / 28d<br>Compound tested: c-pentaBDE<br>*Hyalella azteca*<br><2% om-28d-$NOEC_{survival,\ growth}$ = 6.3 (n)<br>*Chironomus riparius*<br><2% om-28d-$NOEC_{survival,\ growth}$ = 16 (m) | Evaluated in EU-RAR (E.C., 2001) | Wildlife, 2000a<br>Wildlife, 2000b |

| | | | |
|---|---|---|---|
| | ***Lumbriculus variegatus***<br>**<2% om-28d-NOEC$_{survival, repro, growth}$ > 3.1 (n)** | | Wildlife, 2000c |
| | *Lumbriculus variegatus* / 28d / Spiked sed<br>Compound tested: c-octaBDE<br>• c-octaBDE:<br>2.4% oc-NOEC$_{survival, repro, growth}$ >1 340 (mm)<br>5.9% oc-NOEC$_{survival, repro, growth}$ >1 272 (mm) | Evaluated in EU-RARs (E.C., 2003) | Krueger *et al.*, 2001a; Krueger *et al.*, 2001b |

Commercial pentaBDE exposure 28d spiked sediment tests

According to the Guidance Document on EQS derivation (E.C., 2011), for sediment organisms, the NOEc should be normalised to the standard organic matter or organic carbon content of sediment. The actual organic carbon contents of the sediments used in the tests are unknown and organic matter content are reported as <2% in each test. Since organic matter contents are usually very approximately two times higher than the organic carbon contents, this would imply that the organic carbon contents of the sediments used were very low at <1%. Assuming this value, the NOEC values of 6.3, 16 and 3.1 mg.kg$^{-1}_{dw}$, are equivalent to lowest NOEc of 30.5, 48 and 15.5 mg.kg$^{-1}_{dw}$.

*Lumbriculus variegatus* / 28d (Krueger *et al.*, 2001a; Krueger *et al.*, 2001b as cited in E.C., 2003)

The amount of hexaBDE component present in the commercial octaBDE tested was not given. If it is assumed that the test substance contained 5.5% hexaDE (typical of current products) then the estimated NOECs for the hexaBDE component alone based on these results would be ≥74 mg/kg dry weight for the 2.4% organic carbon content sediment and ≥70 mg/kg dry weight for the 5.9% organic carbon content sediment.

### QS$_{sediment}$ derivation

A QS$_{sediment}$ can be estimated from the use of sediment-dwelling organisms toxicity data by applying an assessment factor of 10 to the lowest NOEC from the 5%oc long-term studies of 15.5 mg.kg$^{-1}_{dw}$.

The TGD-EQS recommends favouring the use of chronic tests carried out on benthic organisms when available for the derivation of QS$_{sediment}$. Only results obtained with commercial mixtures c-penta-BDE and c-octa-BDE are available for benthic organisms, and they may be considered as acceptable since PBDEs occurs in mixture in the environment.

For pelagic species however, the QS is based on a result obtained with tetra-BDE which lead to the lowest NOEC. For comparison purpose then, QS$_{sediment}$ is then also calculated using the equilibrium partitioning method from the test conducted on *Psetta maxima* with tetra-BDE. The comparison shows that the experimental result is comprised within the range of calculated values using the equilibrium partitioning method, although the large range of Koc available for PBDE must be emphasised.

Whatever the compound used for the derivation of QS$_{sediment}$, and the method applied, the results are higher than the overall EQS driven by the human health protection.

In line with the EQS-TGD, the lowest endpoint from experimental data on benthic organisms is preferred.

| **Tentative QS$_{water}$**<br>**Assessment factor method** | **Relevant study for derivation of QS** | **AF** | **Tentative QS** |
|---|---|---|---|
| AA-QS$_{freshwater, sed.}$ | *Lumbriculus variegatus* / 28d / 5% oc<br>NOEC > 15.5 mg.kg$^{-1}_{dw}$<br>NOEC > 5.96 mg.kg$^{-1}_{ww}$ | 10 | 596 µg.kg$^{-1}_{ww}$<br>1 550 µg.kg$^{-1}_{dw}$<br>corresponding[2] to<br>2.1 10$^{-5}$ – 0.433 µg.l$^{-1}$ |
| | *Psetta maxima* / 4d exposure of larvae<br>NOEC= 4.9 10$^{-4}$ mg$_{tetraBDE}$.l$^{-1}$ | EqP<br>Additional AF of 10[1] | 0.049 µg.l$^{-1}$<br>corresponding[2] to<br>6.7 – 1.4.10$^{5}$ µg.kg$^{-1}_{ww}$<br>17.5 – 3.7.10$^{5}$ µg.kg$^{-1}_{dw}$ |

| | | | |
|---|---|---|---|
| $AA\text{-}QS_{marine\ water,\ sed.}$ | *Lumbriculus variegatus* / 28d / 5% oc<br>NOEC > 15.5 $mg.kg^{-1}_{dw}$<br>NOEC > 5.96 $mg.kg^{-1}_{ww}$ | 50 | 119 $\mu g.kg^{-1}_{ww}$<br>310 $\mu g.kg^{-1}_{dw}$<br>corresponding[2] to<br>$4.1\ 10^{-6} – 8.6.10^{-2}\ \mu g.l^{-1}$ |
| | *Psetta maxima* / 4d exposure of larvae<br>NOEC= $4.9\ 10^{-4}\ mg_{tetraBDE}.l^{-1}$ | EqP<br>Additional AF of 10[1] | $0.0049\ \mu g.l^{-1}$<br>corresponding[2] to<br>$0.7 – 1.4.10^{4}\ \mu g.kg^{-1}_{ww}$<br>$1.75 – 3.7.10^{4}\ \mu g.kg^{-1}_{dw}$ |

[1] an additional assessment factor of 10 is being applied given the high $K_{ow}$ values of BDE congeners and commercial products (log $K_{ow}$ > 5) to take into account the possible ingestion of sediment.

[2] corresponding values in water using conversion via Equilibrium Partitioning (EqP) method with $K_{OC\text{-}BDE\ congeners}$= 71 560 – $1.5\ 10^{9}\ l.kg^{-1}$.

## 7.2 SECONDARY POISONING

*According to the Guidance Document on EQS derivation (E.C., 2011), c-pentaBDE and c-octaBDE as well as all their main components (tetra- to nona-congeners) trigger the bioaccumulation criteria given the high values of log $K_{ow}$ (above 5), the high values of BCF (mostly above 1 000) and that the toxicity data reported for oral toxicity of mammals which demonstrate a somewhat high toxicity (NOEC as low as 0.4 mg.kg$^{-1}$ $_{feed\ ww}$, see below).*

*Oral exposure is expected to be the most relevant exposure pathway for BDEs. Biota-sediment accumulation factors for hexaBDE and heptaBDE on two freshwater fish species were reported between 1 and 3 and it was concluded that 100% of the exposure was associated to food or food plus sediment (van Beusekom et al., 2006).*

As for direct toxicity (see section 7.1), the interpretation of the toxicity data for BDE compounds is not straight forward as data are not available for all congeners separately and as the relative toxicity of these congeners is not elucidated.

The available physico-chemical properties and BCF values (see section 5.1) indicate that tetraBDE as well as pentaBDE and hexaBDE congeners have a much higher bioconcentration potential than the other components of pentaBDE and octaBDE commercial products (heptaBDE, octaBDE and nonaBDE congeners) and so are likely to have a higher potential to cause adverse effects on organisms in the environment. Wherever possible, the effects of the tetraBDE, pentaBDE and hexaBDE components are considered in interpreting the toxicity data for deriving secondary poisoning linked QS.

The data considered as valid for effects assessment purpose in the RAR were not further assessed.

Since EU-RARs were published in 2001, 2002 and 2003, other studies were available on dietary exposure of birds and mammals to PBDE congeners and/or commercial products. Some are reported in the table hereunder and were assessed for their reliability, but there are numerous articles which report endpoints that are not usually accepted as effects assessment endpoints such as developmental and behavioural effects and/or single dose dietary exposure (Viberg *et al.*, 2003a; Kuriyama *et al.*, 2005; Viberg *et al.*, 2006), exposure through egg cell (McKernan *et al.*, 2009).

In an *in vitro* study (Frouin *et al.*, 2010), it was shown that immune system of marine mammals was affected when harbour seal cells were exposed to 5.8 mg BDE-47.l$^{-1}$, 6.8 mg BDE-99.l$^{-1}$ and 7.7 mg BDE-153.l$^{-1}$, respectively. However, these data are not dietary exposure data and therefore not usable for calculating $QS_{biota,\ sec.pois.}$ value.

| **Secondary poisoning of top predators** | | **Master reference** |
|---|---|---|
| **Mammalian oral toxicity** | Rats / Oral / 30 d / effects on liver / exposure to c-pentaBDE<br>NOAEL = 0.45 mg.kg$^{-1}$.d$^{-1}$ | E.C., 2001 |
| | CD-1 Swiss mice / oral administration (by trained self-administration from a modified syringe once a day or via gavage to dams) of 0.6, 6, 18 or 30 mg BDE-99.kg$^{-1}$ $_{bw}$ from GD6 to PND21<br>Effects: hyperactivity and alterations in anxiety-like behavior<br>LOAEL = 0.6 mg.kg$^{-1}$ $_{bw}$.d$^{-1}$<br>NOAEL= 0.2 mg.kg$^{-1}$ $_{bw}$.d$^{-1}$ ($CF_{LOAEL->NOAEL}$=3)<br>**NOEC= 4 mg.kg$^{-1}$ $_{food}$ ($CF_{NOAEL->NOEC}$=20)** | Branchi *et al.*, 2002<br>Branchi *et al.*, 2005 |

| | | |
|---|---|---|
| | Male mice / oral administration of one single dose of 0.8 and 12 mg BDE-99.kg$^{-1}_{bw}$<br>Effects: neurotoxicity<br>LOAEL = 0.8 mg.kg$^{-1}_{bw}$.d$^{-1}$ | Eriksson *et al.*, 2001b |
| | Sprague-Dawley rats / administration by gavage to a dose of 2 mg.kg$^{-1}_{bw}$.d$^{-1}$ from GD6 to PND21<br>Effects: poor short-term memory when tested in the Morris water maze at PND34-36, and lower antioxidant enzyme activity in the brain at PND37 | Cheng *et al.*, 2009 |
| | Wistar rats / administration by gavage of a single dose of 0.06 and 0.3 mg pentaBDE-99 (98% purity).kg$^{-1}_{bw}$ / rats dosed at GD 6<br>Effects : reduced sperm production in male offspring at adulthood (age: 150 d) and effects on motor activity<br>As the exposure was a single exposure of the dams, the offspring were exposed *in utero* but also post-natally through lactation. Therefore, it was not possible to calculate the actual internal dose that the offsprings were exposed to in this study. It is however likely that the body burden in the offspring during the period studied would be lower but not far lower than the body burden of the dams. LOAEL= 0.06 mg.kg$^{-1}_{bw}$.d$^{-1}$ | Kuriyama *et al.*, 2005 |
| | Rat / Oral / 13 weeks / Increased liver weight<br>Dietary exposure to c-octaBDE<br>LOAEL= 7.2 mg.kg$^{-1}_{bw}$.d$^{-1}$<br>NOAEL= 2.4 mg.kg$^{-1}_{bw}$.d$^{-1}$ (CF$_{LOAEL->NOAEL}$=3)<br>NOEC= 48 mg.kg$^{-1}_{biota\ ww}$ (CF$_{NOAEL->NOEC}$=20) | Great Lakes Chemical Corporation, 1977<br>as cited *in* E.C., 2003 |
| | **Rabbit / Oral /exposure days 7-19 of gestation / foetotoxicity**<br>Dietary exposure to c-octaBDE<br>NOAEL= 2 mg.kg$^{-1}_{bw}$.d$^{-1}$<br>**NOEC= 66.6 mg.kg$^{-1}_{biota\ ww}$** (CF$_{NOAEL->NOEC}$ =33.3) | Breslin *et al.*, 1989 as cited *in* E.C., 2003 |
| **Avian oral toxicity** | Negative correlation between concentration ΣpolyBDE in egg and average productivity for *Falco peregrinus*.<br>Congeners 2,2',4,4',5,5'-HexaBDE ; 2,2',4,4',5,6'-HexaBDE and 2,2',3,4,4',5',6-HeptaBDE constituting approx 50% of total PBDE. | Johansson *et al.*, 2009 |
| | *Falco sparverius* / oral / 71d year$^{-1}$ / Increased time to egg laying, decreased thickness and mass of eggshell, decreased hatching and reproductive success.<br>Dietary exposure to c-pentaBDE (0.3 and 1.6 mg.kg$^{-1}$.d$^{-1}$)<br>Resulting concentrations in eggs: ca. 290 and 1 100 mg.kg$^{-1}_{ww}$.<br>Time to egg laying, thickness and mass of eggshell significantly associated with concentrations of 2,2',4,4',5,5'-HexaBDE (73 mg.kg$^{-1}_{ww}$, mean) and 2,2',4,4',5,6'-HexaBDE (48 mg.kg$^{-1}_{ww}$, mean) in eggs. | Fernie *et al.*, 2009 |

As for aquatic ecotoxicity, results are available mainly for the commercial mixtures of c-pentaBDE and c-octaBDE. The information on individual congener is insufficient to determine the contribution of each compound to the overall toxicity of the mixtures.

The lowest LOAEL= 0.06 mg.kg$^{-1}_{bw}$.d$^{-1}$ is from the study from Kuriyama *et al.*, 2005 where pentaBDE-99 (98% purity) was administered to rats. According to the Joint FAO/WHO expert committee on food additives (JECFA, 2006b; JECFA, 2006a), some "dioxin-like" effects found with BDE compounds are supposed to be mainly due to minor "dioxin-like", non-BDE contaminants (i.e. impurities of the commercial mixtures). Moreover, Bakker and its collaborators (Bakker et al., 2008) state that "*PBDE impaired postnatal*

*spermatogenesis resulting from prenatal exposure has been reported as the most sensitive toxic effect of PBDE toxicity with a LOAEL in rats of 60 µg.kg$^{-1}_{bw}$ (Kuriyama et al., 2005). However, for the same effect a NOAEL of 12.5 ng.kg$^{-1}_{bw}$ was reported for 2,3,7,8-TCDD (Ohsako et al., 2001). Thus, a BDE 99 solution of more than 99.99% purity is needed to exclude 2,3,7,8-TCDD as cause for the observed toxicity. This is significantly higher than the reported 98% purity of the solution actually used (Kuriyama et al., 2005). As none of the BDE solutions used in toxicity studies fulfills the mentioned purity criterion, the outcome of these studies is ambiguous".*

In summary, there is thus an obvious kinetic similarity between BDEs and dioxins whereas the mechanistic similarities are much weaker. Therefore, the use of the lowest Ah-receptor-dependent endpoints (such as reduced sperm production in male offspring at adulthood by Kuriyama et al.) may not be relevant until this ambiguity has been solved. Studies with purified BDE material has however confirmed that effects on liver, thyroid and developmental and neurotoxic effects can also be attributed to BDEs.

The next lowest NOEC= 0.4 mg.kg$^{-1}_{food}$ is derived from a test in which pregnant rats administered a single dosage of c-pentaBDE exhibited reduced sperm production in male offspring at adulthood.

Given the data set available and the above considerations, it is proposed to use the studies of Branchi et al. (2002, 2005) for the determination of the $QS_{biota, sec. pois}$.

Overall, BCF values for BDE congeners range from very low values for highly brominated congeners to very high values for lower brominated congeners. Considering the fact that any highly brominated BDE congeners ends as debrominated via diverse degradation processes, the highest measured BCF of 35 100 for tetraBDE congeners should be retained. This choice is consistent with the application of the worst case (see section 5.1).

Moreover, values chosen to be applied as BMF1 and BMF2 values are 5 and 20, respectively (see section 5.1).

Therefore, for the derivation of BDEs $QS_{biota\ secpois}$, the following bioaccumulation and biomagnification values are used: BCF=35 100, $BMF_1$ = 5 and $BMF_2$ = 20.

| Tentative $QS_{biota\ sec.\ pois.}$ | Relevant study for derivation of QS | Assessment factor | Tentative QS |
|---|---|---|---|
| **Biota** | NOEC= 4 mg.kg$^{-1}_{food}$ | 90 [1] | 44.4 µg.kg$^{-1}_{biota\ ww}$ corresponding to 2.5 $10^{-4}$ µg.l$^{-1}$ (freshwater) 1.3 $10^{-5}$ µg.l$^{-1}$ (marine waters) |

[1] An assessment factor of 90 is deemed appropriate to take account of extrapolation of QS from NOEC given that the corresponding study consists in exposure of sensible life stages during gestational and post natal periods.

*Given the above considerations on bioaccumulation and biomagnification issues (see section 5.3 and above in section 7.2), the fact that these properties depend on the congener considered, and given that biota repartition depends largely on geographical parameters, the recommendation of a given biota to monitor is more particularly tricky. However, it is well acknowledged that most BDEs covered in the present fact sheet do bioconcentrate (e.g. tetraBDE, pentaBDE and hexaBDEs) and that some BDEs do biomagnify along the trophic food chain. Therefore, fish should be recommended as the trophic level to monitor when considering BDE congeners (ideally it would even be recommendation of a carnivorous fish).*

## (15) Fluoranten



# 5 ENVIRONMENTAL BEHAVIOUR

## 5.1 ENVIRONMENTAL DISTRIBUTION

| | | Master reference |
|---|---|---|
| Water solubility (mg.l$^{-1}$) | 0.2 | Mackay *et al.*, 1992 *in* E.C., 2008a |
| Volatilisation | **Fluoranthene is not likely to volatilise from surface water.** | |
| Vapour pressure (Pa) | 1.2 $10^{-3}$ at 25°C | Mackay *et al.*, 1992 *in* E.C., 2008a |
| Henry's Law constant (Pa.m$^3$.mol$^{-1}$) | 1.1 at 25°C | Mackay *et al.*, 1992 *in* E.C., 2008a |
| Adsorption | **The value 97 724 is used for derivation of QS** | |
| Organic carbon – water partition coefficient ($K_{OC}$) | log $K_{OC}$ = 4.99 (*calculated from* $K_{OW}$)<br>$K_{OC}$ = 97 724 | Karickhoff *et al.*, 1979 |
| Sediment – water partition coefficient ($K_{sed\text{-}water}$) | 2 444 (*calculated from* $K_{OC}$) | E.C., 2011 |
| Bioaccumulation | **The BCF value of 4 800 is used for derivation of QSbiota secpois. and BMF1 = BMF2 = 1 given the absence of biomagnification (Bleeker, 2009).** | |
| Octanol-water partition coefficient (Log Kow) | 5.2 | Mackay *et al.*, 1992 *in* E.C., 2008a |
| BCF | 1 179 (*calculated from exp.* $K_{OW}$) | US-EPA, 2008 |
| | Geometric means per taxa based on data reported in the BCF dedicated table hereafter:<br>- BCF polychaetes = 720<br>- BCF molluscs = 3 932<br>- BCF crustaceans ≅ 4 800<br>- BCF insects = 1 496<br>- BCF fish = 2 439<br>- BCF amphibians = 1 007<br>BCF is set to the highest geometric mean, that is to say 4 000.<br>Moreover, these data demonstrate an absence of biomagnification given that higher trophic levels (fish and amphibians) present lower BCF values than lower trophic levels such as molluscs. Therefore, trophic dilution seems more likely than biomagnification and BMF values should be set to 1 by default. | Bleeker, 2009 |
| BSAF fish | 2 – 6 (*Ictalurus nebulosus*) | van der Oost *et al.*, |

| | | |
|---|---|---|
| | 0.0005–0.001 (*Fundulus heteroclitus*)<br>0.00016 (*Salvelinus namaycush*) | 1994<br>*in* E.C., 2008a |

**Table summarising BCF values for fluoranthene in several aquatic species (Bleeker, 2009)**

| Taxa | Species | Test system (a) | Chem. Analysis (b) | BCF ($l.kg^{-1}$) | Type (c) | Reliability (d) | Reference |
|---|---|---|---|---|---|---|---|
| **Pisces** | *Pimephales promelas* | FT | HPLC | 2439 | Equi. | 2 | Carlson *et al.*, 1979 |
| **Mollusca** | *Mya arenaria* | FT | HPLC | 4120 | Kin. | 1 | McLeese and Burridge, 1987 |
| | *Mytilus edulis* | FT | HPLC | 5920 | Kin. | 1 | McLeese and Burridge, 1987 |
| | *Perna viridis* | SR | GC | 12250[1] | Equi. | 2 | Richardson *et al.*, 2005 |
| | *Utterbackia imbecillis* (glochidia) | FT | HPLC | 1735, 1813 | Equi | 2 | Weinstein, 2001 |
| **Crustacea** | *Crangon septemspinosa* | FT | HPLC | 180 | Kin. | 1 | McLeese and Burridge, 1987 |
| | *Daphnia magna* | SR | HPLC | 1742 | Equi. | 2 | Newsted and Giesy, 1987 |
| | *Diporeia* spp. | SR | 14C | 15136 – 58884[2] | Kin. | 2 | Schuler *et al.*, 2004 |
| | *Hyalella azteca* | SR | 14C | 1202 – 5370[4] | Kin. | 2 | Schuler *et al.*, 2004 |
| **Insecta** | *Chironomus tentans* (3rd instar larvae) | SR | 14C | 891 – 2512[4] | Kin. | 2 | Schuler *et al.*, 2004 |
| **Polychaeta** | *Nereis virens* | FT | HPLC | 720 | Kin. | 1 | McLeese and Burridge, 1987 |
| **Amphibia** | *Rana pipiens* | FT | HPLC | 611 – 1659[4] | Equi. | 1 | Monson *et al.*, 1999 |

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

[1] In this study BCF values are based on lipid weight, values given in this table are normalized to 5% lipid content.

[2] Values represent (a range of) BCF values from (a range of) different exposure concentrations.

## 5.2 ABIOTIC AND BIOTIC DEGRADATIONS

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

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

# 7 EFFECTS AND QUALITY STANDARDS

Final CTPht EU-RAR (E.C., 2008a) states that "PAHs can be toxic via different mode of actions, such as non-polar narcosis and phototoxicity. The last is caused by the ability of PAHs to absorb ultraviolet A (UVA) radiation (320–400 nm), ultraviolet B (UVB) radiation (290–320 nm), and in some instances, visible light (400–700 nm). This toxicity may occur through two mechanisms: photosensitization, and photomodification. Photosensitization generally leads to the production of singlet oxygen, a reactive oxygen species that is highly damaging to biological material. Photomodification of PAHs, usually via oxidation, results in the formation of new compounds and can occur under environmentally relevant levels of actinic radiation (Lampi et al., 2005). The photo[induced]toxic effects can be observed after a short period of exposure, which explains why for PAHs like anthracene, fluoranthene and pyrene, where photo[induced]toxicity is most evident, the acute toxicity values are even lower than the chronic toxicity values. there is a growing body of evidence which suggests that photo[induced]toxic PAHs may be degrading aquatic habitats, particularly those in highly contaminated areas with shallow or clear water (Weinstein and Oris, 1999). For example, the photoinduced chronic effects of anthracene have been reported at those UV intensities occurring at depths of 10 to 12 m in Lake Michigan (Holst and Giesy, 1989). In addition to direct uptake of PAHs from the water column, another potential route of exposure for aquatic organisms is their accumulation from sediments (see e.g. Clemens *et al.*, 1994; Kukkonen and Landrum, 1994), followed by subsequent solar ultraviolet radiation exposures closer to the surface. Other authors (Ankley et al., 2004) also concluded in their peer review that PAHs are present at concentrations in aquatic systems such that animals can achieve tissue concentrations sufficient to cause photoactivated toxicity. Although UV penetration can vary dramatically among PAH-contaminated sites, in their view it is likely that at least some portion of the aquatic community will be exposed to UV radiation at levels sufficient to initiate photoactivated toxicity. They do recognize that at present time, the ability to conduct PAH photoactivated risk assessment of acceptable uncertainty is limited by comprehensive information on species exposure to PAH and UV radiation during all life stages. PAH exposure and uptake, as well as UV exposure, are likely to vary considerably among species and life stages as they migrate into and out of contaminated locations and areas of high and low UV penetration. For all but sessile species, these patterns of movements are the greatest determinant of the risk for photoactivated toxicity."

Despite these uncertainties, it is thought that the photo[induced]toxic effects cannot be ignored in the effects assessment and EQS derivation processes. Therefore these effects are also considered and it should be noted that the UV exposure levels of the selected studies did not exceed the UV levels under natural sun light conditions.

## 7.1 ACUTE AND CHRONIC AQUATIC ECOTOXICITY

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

Many ecotoxicity data are available to assess fluoranthene effects. Almost all data were reported in the tables below but preference was given to L(E)Cx > EC10 > NOEC for acute data as well as to NOEC > EC10 > L(E)Cx for chronic data. In the same vein, preference was always given to sublethal effects compared to mortality whenever both endpoints were available. When EC10 and NOEC were available but EC10 was lower, the EC10 value was preferred to the NOEC value.

Fluoranthene being very phototoxic, information on the absence/presence of light as well as the type was reported in the tables as much as possible.

Whenever it was possible, for each species, endpoints are reported for tests for which results were based on measured concentrations (reported as (m) in the tables hereunder) rather than nominal concentrations (reported as (n) in the tables hereunder). Also, when available, information is given on the type of exposure, i.e.: static (s), static closed (sc), renewal (r), renewal closed (rc), continuous flow (cf), or intermittent flow system (if).

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

| | Available ecotoxicological information for organisms living in water column | |
|---|---|---|
| | **Fresh water species** | **Marine species** |
| **Acute** | 9 taxonomic groups<br>- algae, crustaceans, and fish<br>- macrophytes, coelenterates, annelids, molluscs, insects and amphibians | 5 taxonomic groups<br>- crustaceans and fish<br>- annelids, molluscs and echinoderms |
| **Chronic** | 6 taxonomic groups<br>- algae, crustaceans, and fish<br>- macrophytes, insects and amphibians | 4 taxonomic groups<br>- crustaceans,<br>- ascidiaceans, molluscs and echinoderms |

The Technical Guidance Document on EQS derivation (E.C., 2011) states that "*in principle, ecotoxicity data for freshwater and saltwater organisms should be pooled for organic compounds, if certain criteria are met*" and that "*the presumption that for organic compounds saltwater and freshwater data may be pooled must be tested, except where a lack of data makes a statistical analysis unworkable*."

For fluoranthene in fact, there are enough data to perform a "*meaningful statistical comparison*" and the statistical analysis made showed no further indications of "*a difference in sensitivity between freshwater vs saltwater organisms*" (Verbruggen, in prep.). Moreover, the mode of action (cf. reference to narcosis above) is an additional piece of information allowing no differentiation between the two media.

Therefore, in this case, the data sets may be combined for QS derivation according to the Technical Guidance Document on EQS derivation (E.C., 2011).

Fluoranthene appears to be extremely phototoxic when some organisms are exposed in combination with ultraviolet radiation, such as sunlight. The lowest chronic NOECs or EC10 are in between 1.0 and 8.6 µg.l$^{-1}$. The acute L(E)$C_{50}$ values for fluoranthene with exposure under laboratory lighting are comparable to or even lower than the chronic NOEC values, like the outlier $LC_{50}$ of 0.1 µg.l$^{-1}$ reported for the marine fish *Pleuronectes americanus* (Spehar et al., 1999). The 96h-$LC_{50}$ for the freshwater oligochaete *Lumbriculus variegatus* and *Hydra americana* were 1.2 µg.l$^{-1}$ and 2.2 µg.l$^{-1}$, respectively, with ultraviolet light at 359-587 µW/cm² UV-A and 63-80 µW/cm² UV-B and a photoperiod of 12:12 h light:dark. The 48h-$LC_{50}$ for *Daphnia magna* was 1.6 µg.l$^{-1}$, with ultraviolet light at 783- 850 µW/cm² UV-A and 104 µW/cm² UV-B and a photoperiod of 12:12 h light:dark (Spehar et al., 1999).
Based on the dataset available and the recommendation of the Technical Guidance Document on EQS derivation (E.C., 2011), assessment factors of 10 and 100 should be used to derive $QS_{freshwater}$ and the $QS_{marine\ water}$, respectively. It should be noted that the additional marine assessment factor (AF) 10 is applicable for both the MAC-$QS_{water}$ and the AA-$QS_{water}$ values. In fact, this AF addresses the higher uncertainty in derivation of marine QS compared to freshwater QS because of the higher biodiversity of marine ecosystems and the fact that marine ecosystems include specific taxonomic groups not represented in the dataset (e.g. echinoderms).

| **Tentative $QS_{water}$ Assessment factor method** | **Relevant study for derivation of QS** | **AF** | **Tentative QS** |
|---|---|---|---|
| **$MAC_{freshwater, eco}$** | *Pleuronectus americanus* / 96h | 10 | 0.01 µg.l$^{-1}$ |
| **$MAC_{marine\ water, eco}$** | $LC_{50\ -\ UV\ light}$ = 1 10$^{-4}$ mg.l$^{-1}$ | 100 | 0.001 µg.l$^{-1}$ |
| **AA-$QS_{freshwater, eco}$** | *Hyalella azteca* / 10d | 10 | 0.1 µg.l$^{-1}$ |
| **AA-$QS_{marine\ water, eco}$** | $LC_{10\ -\ mortality\ -\ UV\ light}$ = 0.001 mg.l$^{-1}$<br>*Mulinea lateralis* / 48h / embryo-larval<br>$EC_{50\ -development\ -\ UV\ light}$ = 1.1 10$^{-3}$ mg.l$^{-1}$ | 100 | 0.01 µg.l$^{-1}$ |

These $MAC_{water,\ eco}$ and AA-$QS_{water,\ eco}$ assessments are not satisfactory as the MAC values are lower than the chronic AA-QS by a factor of 10 for both freshwater and marine species.

| | | | | |
|---|---|---|---|---|
| | | *Schizopera knabeni*<br>6h-$EC_{10\ -\ grazing\ rate}$ = 189 (m)<br>27h-$EC_{10\ -\ grazing\ rate}$= 9 (m) | | Lotufo, 1997<br>Lotufo, 1998 |

| | Available ecotoxicological information for sediment-dwelling organisms | |
|---|---|---|
| | **Benthic fresh water species** | **Benthic marine species** |
| **Acute** | 2 invertebrates taxonomic groups<br>- crustaceans<br>- insects | 4 invertebrates taxonomic groups<br>- annelids<br>- molluscs<br>- crustaceans<br>- echinoderms |
| **Chronic** | 3 invertebrates taxonomic groups<br>- annelids<br>- crustaceans<br>- insects | 1 invertebrates taxonomic groups<br>- crustaceans |

The Technical Guidance Document on EQS derivation (E.C., 2011) states that "*in principle, ecotoxicity data for freshwater and saltwater organisms should be pooled for organic compounds, if certain criteria are met*" and that "*the presumption that for organic compounds saltwater and freshwater data may be pooled must be tested, except where a lack of data makes a statistical analysis unworkable.*"

For fluoranthene in fact, there are enough data to perform a "*meaningful statistical comparison*" and the statistical analysis made showed "*the tested marine species are equally sensitive as freshwater species*" (Verbruggen, in prep.). Moreover, the mode of action (cf. reference to narcosis above) is an additional information allowing no to differentiate between the two media.

Therefore, in this case, the freshwater and marine data sets may be combined for QS derivation according to the Technical Guidance Document on EQS derivation (E.C., 2011).

The lowest effect concentration for fluoranthene in sediment is found for mortality and growth of *Chironomus riparius* (Verrhiest *et al.*, 2001) but the available value is a LOEC and results for the same species vary widely (see NOEC of 166 $mg.kg^{-1}_{dw}$ from Stewart and Thompson, 1995). The lowest relevant value is therefore chosen as the 14d-$EC_{10}$ for reproduction of the marine crustacean *Schizopera knabeni* (Lotufo, 1997). This value of 41 $mg.kg^{-1}_{dw}$ corresponds to organic carbon content of 10% and should be normalised to 5% organic carbon as recommended by the Technical Guidance Document on EQS derivation (E.C., 2011), becoming a value of ca. 20 $mg.kg^{-1}_{dw}$. For this species a more sensitive endpoint (grazing after one day exposure) was also found but this did not apparently affect reproduction in longer exposure duration of 14 d. Therefore, reproduction is chosen as the most sensitive and environmentally relevant parameter for derivation of $AA\text{-}QS_{water,\ sed}$.

Because freshwater data are available for annelids, crustaceans, and insects, an assessment factor of 10 can be applied to this value for derivation of $AA\text{-}QS_{freshwater,\ sed}$.

The marine studies with benthic annelids, crustaceans and echinoderms appear chronic rather than acute; exposure duration being 10 or 14 days. The AF of 10 covers all observed effects, i.e. resulting in an $AA\text{-}QS_{marine\ water,\ sed}$ of 2 $mg.kg^{-1}_{dw}$. With 8 species with a reliable NOEC or $EC_{10}$ of which 4 are marine crustacean species, and additional information in the form of (sub)chronic $E(L)C_{50}$s for marine species from additional taxonomic groups, an AF of 10 is deemed sufficiently conservative. This is confirmed by the water data for which there are many marine data available, but they do not show an increased sensitivity compared to freshwater species.

Against this argument, the point could be made that the acute $LC_{50}$ of 18 $mg.kg^{-1}_{dw}$ for the mollusc *Mercenaria mercenaria* is at the low end of the range of data in the chronic dataset (lowest value of 9 $mg.kg^{-1}_{dw}$ among NOECs or $LC_{10}$ values), suggesting that the chronic dataset may not cover the most sensitive species. However, there are evidences from other PAHs (e.g. fluoranthene and naphthalene), that molluscs do not apparently show an increased sensitivity compared to other taxa.

Therefore, an assessment factor of 10 is applied to the lowest value of 20 $mg.kg^{-1}_{dw}$ for derivation of AA-$QS_{marine\ water,\ sed}$.

If the equilibrium partitioning method were applied to AA-$QS_{water,\ eco}$, then corresponding values in sediments would be more stringent, i.e. 103.8 $\mu g.kg^{-1}_{dw}$. However, given the rather substantial sediment dataset, it does not seem relevant to apply this estimation method to derive the AA-$QS_{water,\ sed}$ values.

| **Tentative $QS_{water}$**<br>**Assessment factor method** | **Relevant study for derivation of QS** | **AF** | **Tentative QS** |
|---|---|---|---|
| **AA-$QS_{freshwater,\ sed}$** | *Schizopera knabeni* / 14d / normalised 5% organic carbon<br>$EC_{10\ -\ reproduction}$ = 20 $mg.kg^{-1}_{dw}$ | 10 | 2 000 $\mu g.kg^{-1}_{dw}$<br>corresponding to 4.09 $\mu g.l^{-1}$<br>*via* the EqP method |
| **AA-$QS_{marine\ water,\ sed}$** | | 10 | 2 000 $\mu g.kg^{-1}_{dw}$<br>corresponding to 4.09 $\mu g.l^{-1}$<br>*via* the EqP method |

## 7.2 SECONDARY POISONING

*Based on the Technical Guidance Document on EQS derivation (E.C., 2011), this substance does trigger the bioaccumulation criteria given the high values of log KOW (5.2) and the high value of BCF (7 692).*

Data on the PAH toxicity to birds are scarce (Albers and Laoughlin, 2003; Patton and Dieter, 1980) and Final CTPHT EU-RAR (E.C., 2008a) states that "*from these data it is not possible to derive a NOAEL for birds for either of the PAHs*".

The toxicity dataset for mammals is also rather limited, almost all of the long term studies being designed to assess carcinogenic potency of PAH (i.e. "*not considered appropriate for secondary poisoning assessment*"). A $QS_{biota\ secpois}$ is however tentatively derived hereunder.

| **Secondary poisoning of top predators** | | **Master reference** |
|---|---|---|
| **Mammalian oral toxicity** | Mice / Gavage / 90d / Nephropathy, increased liver weight, hematological alterations and clinical effects<br>NOAEL = 125 $mg.kg^{-1}_{bw}.d^{-1}$<br>NOEC = 1037 $mg.kg^{-1}_{food}$ | US-EPA, 1988<br>as cited *in*<br>US-EPA, 1990 |
| **Avian oral toxicity** | No information available | |

| **Tentative $QS_{biota\ secpois}$** | **Relevant data for derivation of QS** | **AF** | **Tentative $QS_{biota,\ sec\ pois}$** |
|---|---|---|---|
| **Biota** | NOEC = 1037 $mg.kg^{-1}_{food}$ | 90 | 11 522 $\mu g.kg^{-1}_{biota\ ww}$<br>corresponding to<br>2.4 $\mu g.l^{-1}$ (freshwater)<br>2.4 $\mu g.l^{-1}$ (saltwater) |

## 7.3 HUMAN HEALTH

*Based on the Technical Guidance Document on EQS derivation (E.C., 2011), this substance does trigger the bioaccumulation criteria given the high values of log KOW (5.2) and the high value of BCF (7 692). Hence, protection of human health from consumption of fishery products is relevant.*

| **Human health via consumption of fishery products** | | **Master reference** |
|---|---|---|
| **Mammalian oral toxicity** | Mice / Gavage / 90d<br>NOAEL = 125 $mg.kg^{-1}_{bw}.d^{-1}$ | US-EPA, 1988<br>as cited *in*<br>US-EPA, 1990 |
| **CMR** | Not classified as carcinogenic, mutagenic or reprotoxic | E.C., 2008b |
| | Test on benzo[a]pyrene<br>Rat / Gavage / 2years / Hepatic and rumen cancer<br>Virtually Safe Dose = 5 $10^{-6}$ mg B[a]P.$kg^{-1}_{bw}.d^{-1}$ | Kroese *et al.*, 2001 |
| | Fluoranthene is a suspected carcinogen and the potency of fluoranthene relative to the potency of benzo[a]pyrene is 0.01. | Kalberlah *et al.*, 1995 as cited *in* IPCS, 1998<br>Baars *et al.*, 2001 |
| | Fluoranthene is a suspected carcinogen and the potency | Nisbet and Lagoy, |

| | | |
|---|---|---|
| | of fluoranthene relative to the potency of benzo[a]pyrene is 0.001. | 1992<br>Doornaert and Pichard, 2003 |

According to the weight of evidence and a read-across approach on PAH compounds, Baars *et al.*, 2001 and Doornaert and Pichard, 2003 concluded that fluoranthene is a suspected carcinogen and that a non-threshold approach is warranted for risk estimation. The two institutes used a carcinogenic potency approach to estimate the potency of PAHs relative to the potency of benzo[a]pyrene, defined as 1. Baars *et al.*, 2001 and Doornaert and Pichard, 2003 used the same original toxicological value of 0.2 $mg.kg^{-1}.d^{-1}$, based on tumor development in a variety of organs and tissues observed in a chronic oral (gavage) rat study (Kroese *et al.*, 2001) to calculate a virtually safe dose (VSD). Baars *et al.*, 2001adopted a relative potency value for fluoranthene of 0.01 (Kalberlah *et al.*, 1995 as cited *in* IPCS, 1998) while Doornaert and Pichard, 2003 considered a relative potency value for fluoranthene of 0.001 (Nisbet and Lagoy, 1992). Therefore, the virtually safe doses estimated for fluoranthene are 5 $10^{-4}$ $mg.kg^{-1}.d^{-1}$ and 5 $10^{-3}$ $mg.kg^{-1}.d^{-1}$ for Baars *et al.*, 2001 and Doornaert and Pichard, 2003, respectively. These values represent the oral exposure that is associated with a $10^{-6}$ excess lifetime cancer risk and are reported in the table hereunder for the derivation of $QS_{biota\ hh}$.

| Tentative $QS_{biota\ hh}$ | Relevant data for derivation of QS | AF | Threshold Level ($mg.kg^{-1}_{bw}.d^{-1}$) | Tentative $QS_{biota,\ hh}$ |
|---|---|---|---|---|
| **Human health** | NOAEL = 125 $mg.kg^{-1}_{bw}.d^{-1}$ | 3000 | US-EPA RfD = 4.167 $10^{-2}$ (1) | 2536 $\mu g.kg^{-1}_{biota\ ww}$ corresponding to 0.528 $\mu g.l^{-1}$ (fresh and marine waters) |
| | Cf. above paragraph | | Doornaert and Pichard, 2003 VSD = 5 $10^{-3}$ | 304 $\mu g.kg^{-1}_{biota\ ww}$ corresponding to 0.063 $\mu g.l^{-1}$ (fresh and marine waters) |
| | | | Baars *et al.*, 2001 VSD = 5 $10^{-4}$ | 30 $\mu g.kg^{-1}_{biota\ ww}$ corresponding to 6.3 $10^{-3}$ $\mu g.l^{-1}$ (fresh and marine waters) |

(1) Value endorsed by US-EPA, 1990

Although fluoranthene is not classified as carcinogenic by E.C. (E.C., 2008b), for purpose of effects assessment, a conservative choice is made that is to use the value derived by Baars *et al.*, 2001 to assess protection of human health from consumption of fishery products.

| **Human health via consumption of drinking water** | | **Master reference** |
|---|---|---|
| **Existing drinking water standard(s)** | No existing regulatory standard | Directive 98/83/EC |
| **Drinking water standard (*calculated*)** | 1.8 $\mu g.l^{-1}$ (based on the above cited threshold level of 5 $10^{-4}$ $mg.kg^{-1}_{bw}.d^{-1}$) | E.C., 2011 |

## (16) Heksaklorobenzen

### 4 Physical and chemical properties

| Property | Value | Reference |
|---|---|---|
| Molecular weight | 284.8 | [7] |
| Vapour pressure | 0.0023 Pa at 25°C<br>1.1 – 1.45 mPa (20 °C)<br>2.5 mPa (25 °C) | [7]<br>[5]<br>[5] |
| Henry's law constant | 131 Pa/mol per $m^3$ | [7] |
| Solubility in water | 5 µg/l at 25°C<br>5 – 6 µg/L (20 – 25°C) | [7]<br>[5] |

### 5 Environmental fate and partitioning

| Property | Value | Ref. | Comments |
|---|---|---|---|
| Hydrolysis<br>Photolysis | | | |
| Biodegradation | | | |
| Partition coefficients | | | |
| log Kow | 5.5 (5-6.92)<br>5.31<br>5.73<br>3.93 – 6.53 | [7]<br>[6]<br>[1]<br>[5] | |
| Koc | 36,308 (3,000-180,000)<br>log Koc 5.11<br>10,800 – 1,200,000 | [7]<br>[6]<br>[5] | <br><br>Sediment |
| Bioaccumulation | | | |
| BCF: | | | |
| Fish | 18,000 (maximum 22,000) | [1] | Geometric mean of whole body BCF of freshwater and marine fish |
| Fish | 8,000 – 230,000 | [5] | "average" BCF ≈50,000 |
| Fish | 2,040 – 45,000 | [7] | (2,040) proposed for risk assessment |
| Fish | 38,795 | [15] | 90-percentile of 22 individual $BCF_{fish}$ |
| Fish | 78,700 | [15] | 90-percentile of BCFof cyprinid fish |
| Bivalves | 7,000<br>4,000 – 10,000 | [1]<br>[5] | Calculated BCF |
| BAF fish (field): | ≈42,000 | | See annex 1 |

## 6 Effect data (aquatic environment)

Table 6.1: Overview on toxicity data of most sensitive species from different sources (master reference).

| Species | Taxonomic Group | Duration | Effect | Endpoint | Value µg/l | Master reference | Reference in master reference | Comments on data reliability in master reference # |
|---|---|---|---|---|---|---|---|---|
| **Freshwater** | | | | | | | | |
| *Daphnia magna* | Crustacea | 21 d | Reproduction | NOEC | 0.13 | [5] | Scheubel 1984 | Test result is valid – quality checked by the German Federal Environmental Agency * |
| *Gammarus lacustris* | Crustacea | 28 d | Survival | NOEC | 1.8 | [7], [5] | Nebeker *et al.*, 1989 | [7]: RI 2 |
| *Micropterus salmoides* | Pisces | 28 d | | EC0 | 2 | [5] | Laseter et al. 1976 | |
| *Gammarus lacustris* | Crustacea | 28 d | Mortality | LC0 | 2.5 | [5] | Alberti 1983 | |
| *Oncorhynchus mykiss* | Pisces | 90 d | Growth, survival | NOEC | 3.7 | [7] | US EPA (1987)<br>Spehar (2000) | RI 2; NOEC = maximum concn. Tested. |
| *Pimephales promelas* | Pisces | 28 d | Survival | NOEC | ≥ 3.8 | [5] | Nebeker et al. 1989 | |
| *Lumbriculus variegatus* | Annelida | 49 d | Survival, growth, asexual reproduction | NOEC | 4.7 | [7] | Nebeker *et al.*, 1989 | RI 2; Worms held in quartz sand |
| *Pimephales promelas* | Pisces | 32 d | Hatch, survival, growth | NOEC | 4.8 | [7] | Carlson and Kosian, 1987; Ahmad *et al.*, 1984 | RI 1; NOEC = maximum concn. Tested |
| *Daphnia magna* | Crustacea | 7 d | Mortality | NOEC | 5 | [7] | Nebeker *et al.*, 1989 | RI 2 |
| *Selenastrum capricornutum* | Algae | 96 h | Growth | NOEC | 14 | [5] | Calamari et al. 1983 | |
| *Daphnia magna* | Crustacea | 21 d | Reproduction | NOEC | 17 | [7] | Caspers *et al.*, 1993 | RI 1 |
| *Selenastrum capricornutum* | Algae | 3 h | Photosynthesis | NOEC | 18 | [7] | Calamari *et al.*, 1983 | RI 2 |
| | | | | | | | | |
| *Daphnia magna* | Crustacea | 48 h | Mortality | LC50 | 4.73 | [5] | Abernethy et al. 1986 | |
| *Daphnia magna* | Crustacea | 48 h | Immobility | LC50 | >5 | [7] | Nebeker *et al.*, 1989 | RI 1; Solubility limit. Also no mortality after 7 days. |
| *Tanytarsus dissimilis* | Insecta | 48 h | Mortality | LC50 | >5.8 | [7] | Call *et al.*, 1983 | RI 1 |
| *Leuciscus idus* | Pisces | 48 h | Mortality | LC50 | 7 | [7] | Knie *et al.*, 1983 | RI 3 |
| *Daphnia magna* | Crustacea | 24 h | Immobility | EC50 | 7.5 | [6] | Umweltbundesamt (1976), cité dans Rhin-Meuse (1991) | |
| *Scenedesmus abundans* | Algae | 96 h | Growth | EC50 | 10 | [5] | Geyer et al. 1985 | |
| *Procambarus clarki* | Crustacea | 96 h | Mortality | LC50 | >27 | [7] | Laska *et al.*, 1978 | RI 1; 10d LC50 also >0.027 mg/l. No significant mortality at 0.027 mg/l. |
| *Brachydanio rerio* | Pisces | 48 h | Mortality | LC50 | >30 | [7] | Calamari *et al.*, 1983 | RI 1No mortality |
| *Selenastrum capricornutum* | Algae | 96 h | Growth | EC50 | <30 | [6], [5] | Calamari *et al* (1983 | |

## (16) Hexachlorobenzene

| Species | Taxonomic Group | Duration | Effect | Endpoint | Value µg/l | Master reference | Reference in master reference | Comments on data reliability in master reference # |
|---|---|---|---|---|---|---|---|---|
| *Selenastrum capricornutum* | Algae | 96 h | Growth | EC50 | >30 | [7] | Calamari *et al.*, 1983 | RI 1; 12% inhibition at this concn. |
| *Selenastrum capricornutum* | Algae | 3 h | Photosynthesis | EC50 | 30 | [7] | Calamari *et al.*, 1983 | RI 2; . Approx. value based on 2 concentrations. |
| *Lepomis macrochirus* | Pisces | 96 h | Mortality | LC50 | >78 | [7] | Call *et al.*, 1983 | RI 1; No mortality |
| *Oncorhynchus mykiss* | Pisces | 96 h | Mortality | LC50 | >81 | [7] | Call *et al.*, 1983; Ahmad *et al.*, 1984 | RI 1; No mortality or other symptoms |
| *Bufo bufo japonicus* | Amphibia | 24 h | Mortality | LC50 | 4200 | [5] | Niimi et al. 1980 | |
| *Saltwater* | | | | | | | | |
| *Thalassiosira pseudonana and Dunaliella tertiolecta (mixed)* | Algae | 72 h | Growth, cell size | NOEC | >100 | [7] | Biggs *et al.*, 1979 | RI 3 ; Maximum concn. tested. |
| *Artemia salina* | Crustacea | 24 h | Mortality | LC50 | 4.73 | [5] | Abernethy et al. 1986 | |
| *Crangon septemspinosa* | Crustacea | 96 h | Mortality | LC50 | >7.2 | [7] | McLeese and Metcalfe., 1980 | RI 1 ; No mortalities. Renewal after 48h. |
| *Lagodon rhomboides* | Pisces | 96 h | Mortality | LC50 | >8.4 | [7] | Parrish *et al.*, 1975 | RI 1; No mortalities |
| *Cyprinodon variegatus* | Pisces | 96 h | Mortality | LC50 | 13 | [5] | Mayer 1987 | |
| *Cyprinodon variegates* | Pisces | 96 h | Mortality | LC50 | >13.3 | [7] | Parrish *et al.*, 1975 | RI 1; No mortalities |
| *Palaemonetes pugio* | Crustacea | 96 h | Mortality | LC50 | >17 | [7] | Parrish *et al.*, 1975 | RI 1 |
| *Penaeus duorarum* | Crustacea | 96 h | Mortality | LC50 | >25 | [7] | Parrish *et al.*, 1975 | RI 1 ; 33% mortality at this concn. |
| *Lagodon rhomboides* | Pisces | 96 h | Mortality | LC50 | 100 | [5] | Mayer 1987 | |
| *Solea solea* | Pisces | 96 h | Mortality | LC50 | 142 | [5] | Furay et al. 1995 | |
| *Platichthys flesus* | Pisces | 96 h | Mortality | LC50 | 199 | [5] | Furay et al. 1995 | |
| *Ophryotrocha diadema* | Annelida | 48 h | Mortality | LC50 | >10000 | [7] | Parker, 1984 | RI 3; Greatly above solubility. |
| *Crassostrea virginia* | Mollusca | 48 h | Embryo larval development | EC50 | >1000 | [7] | US EPA, 1987 | RI 3; Embryo-larval development |
| *Crassostrea virginia* | Mollusca | 48 h | Morphology | EC50 | 1000 | [5] | Zaroogian 1981 | |

# RI = reliability index (by Euro Chlor, based on IUCLID system): 1 (valid without restriction); 2 ( valid with restrictions, to be considered with care); 3 (invalid); 4 (not assignable)

* The test was conducted according to EU test guideline 79/831 Rev 1. A clear dose-response relationship was observed. Test concentrations were: control, 0.13, 0.25, 0.5, 1.0 and 1.67 µg/l. The respective numbers of offspring produced per adult animal were: 62, 57, 45, 30, 24, 15. Controls met the quality criteria set in the guideline [10]. The report can be borrowed from the Library of the Federal Environmental Agency.

Table 6.2: Toxicity Data of HCB in Sediment Dwelling Organisms

| Species | Treatment | Validity # | Reference in [7] |
|---|---|---|---|
| *Crangon septemspinosa* | No evidence of mortality in *Crangon septemspinosa* treated for 96 hours at a concentration of 2.1 mg/kg (normalized to 2% OC). | 2 | McLeese & Metcalfe, (1980) |
| *Chironomus tentans* | No significant mortality or reduction in growth following a 14-day exposure to sediments spiked at a measured concentration of 84 mg/kg (2% OC). | 1 | Barber *et al* (1997) |
| *Hyella azteca* | No significant mortality or reduction in growth following a 14-day exposure to sediments spiked at a measured concentration of 84 mg/kg (2% OC). | 1 | Barber *et al* (1997) |
| *Leptocheirus plumulosus* | No significant mortality or reduction in growth following a 10-day exposure to sediments spiked at a concentration of 120 mg/kg (2% OC). | 1 | Fuchsman *et al* (1998) |
| *Hyella azteca* | No significant mortality or reduction in growth following a 10-day exposure to sediments spiked at a concentration of 120 mg/kg (2% OC) in freshwater and at a salinity of 10‰ . | 1 | Fuchsman *et al* (1998) |
| *Chironomus tentans)* | No significant mortality or reduction in growth following a 10-day exposure to sediments spiked at a concentration of 120 mg/kg (2% OC). | 1 | Fuchsman *et al* (1998) |

# Reliability index (by Euro Chlor, based on IUCLID system): 1 (valid without restriction); 2 ( valid with restrictions, to be considered with care); 3 (invalid); 4 (not assignable)

Table 6.3: Mammal and bird oral toxicity data relevant for the assessment of non compartment specific effects relevant for the food chain (secondary poisoning)

| Species | | Duration | Effect | NOEC mg/kg food | Reference in [8] |
|---|---|---|---|---|---|
| *Mustela vision* | Mink | 1 generation | Mortality, reproduction | 0.5 | RIVM Rep. No. 679101012 |
| *Mustela putorius* | European ferret | 1 generation | Mortality, reproduction | 0.5 | |
| *Coturnix c. japonica* | Quail | 90 d | Reproduction | 5 | |
| *Rattus norvegicus* | Rat | 2 and 4 generations | Reproduction | 18 | |
| *Canis domesticus* | Dog | 1 y | Mortality, Growth | 52 | |
| *Felix domesticus* | Cat | 1 generation | Reproduction | 88 | |

Table 6.4: Summary on Endocrine Disrupting (ED) potential of Hexachlorobenzene

| | |
|---|---|
| Hexachlorobenzene is a substance with evidence of ED or evidence of potential ED, already regulated or being addressed under existing legislation | [2] |
| No hints on endocrine disrupting properties of the substance have been found in the information provided by Member States or NGOs | |

## (17) Heksaklorobutadien

### 4 Physical and chemical properties

| Property | Value: | Ref. |
|---|---|---|
| Molecular weight | 260.8 (g/mol) | [1] |
| Vapour pressure | 20 Pa at 20°C<br>36 Pa (20 °C) | [1]<br>[5] |
| Henry's law constant | 1630 Pa.m$^3$/mol at 25°C | [1] |
| Solubility in water | 3.2 mg/l at 20°C<br>4 mg/L (20 °C)<br>3 mg/L<br>2 mg/L<br>3.23 (25 °C) | [1]<br>[5]<br>[5]<br>[5]<br>[5] |

### 5 Environmental fate and partitioning

| Property | Value: | Ref: | Comments: |
|---|---|---|---|
| Hydrolysis | not relevant under enviromental conditions | [5] | |
| Biodegradation | half life in natural water 4-52 weeks | [1] | |
| Partition coefficients | | | |
| log Kow | 4.78 to 4.9<br>4.9 | [1], [5]<br>[6] | |
| Koc | log Koc 3.95-4.05<br>log Koc 4.51<br>1260000 l/kg (sediment)<br>25100 L/kg (sediment)<br>2400 L/kg (soil, calculated) | [1]<br>[6]<br>[5]<br>[5]<br>[5] | |
| Bioconcentration | | | |
| BCF fish: | | | |
| *Salmo gairdneri* | 5800 - 17000 | [1] | 17,000 used for risk assessment in [1] |
| *Poecilia latipinna* & *Micropterus salmonides* | although variable normally below 50 | [1] | |
| *Pleuronectes patessa* & *Limanda limanda* | 500 – 700 (flesh)<br>7000 – 10000 (liver) | [1] | |
| *Oncorhynchus mykiss* | 2000 - 19000 | [5] | |
| *Micropterus salmonides* | 1.4 – 112.9 | [5] | |
| *Poecilia latipinna* | 1.7 – 196 | [5] | |
| *Cynoscion nebulosis* | 264 | [5] | |
| *Micropogonias undulatus* | 696 | [5] | |
| *Ictalurus furcatus* | 1171 | [5] | |
| BCF bivalves: | | | |
| *Mytilus edulis* | 900 – 2000 | [5] | |
| BCF oligochaete worms: | 29000 (based on dry wt) | [1] | |

| Property | Value: | Ref: | Comments: |
|---|---|---|---|
| Biomagnification: | [1]: 2 publications: fish were fed with food contaminated with HCBD. In one study no clear evidence on bioconcentration but results variable and inconclusive. In other study no evidence of bioaccumulation was seen.<br><br>[1]: A number of authors have examined data to determine if HCBD might biomagnify through the food chain. For example Goldbach *et al.* (1976) examined levels of HCBD in fish of prey and found that concentrations in fish such as pike and perch were in fact lower than in the prey fish. No correlation between age and HCBD residues was found. Based on these findings the authors concluded there is no significant biomagnification to higher trophic levels. This conclusion is supported by Pearson and McConnell (1975) who concluded that there was little evidence for biomagnification of HCBD up the food chain. Similarly Laseter *et al.* (1976) concluded that HCBD was not concentrated to a great extent and accumulated irregularly.<br><br>[1]: Studies in mammalian species have shown that when rats received oral doses of HCBD as part of a mixture of seven different chlorinated hydrocarbons, there was no evidence of accumulation in the selected organs examined (Jacobs *et al.*, 1974). No other data have been found concerning the accumulation of HCBD in mammalian tissues. | | |

## 6 Effect data (aquatic environment)

Table 6.1: Overview on toxicity data of most sensitive species from different sources (master reference).

| Species | Taxonomic Group | Duration | Effect | Endpoint | Value µg/l | Master reference | Reference in master reference | Comments on data reliability in master reference [#] |
|---|---|---|---|---|---|---|---|---|
| **Freshwater** | | | | | | | | |
| *Brachydanio rerio* | Pisces | 14 d | feeding behaviour and position | NOEC | 5 | [5], [1] | Röderer 1990 | The study was evaluated by DE-EPA and is considered valid [1]: RI 4 |
| *Carassius auratus* | Pisces | 67 d | growth | NOEC | 9.6 | [1] | Leeuwangh et al. (1975) | RI 2; |
| *Pimephales promelas* | Pisces | 32 d | larval survival | NOEC<br>LOEC | 6.5<br>13 | [1], [5] | Benoit et al. 1982), Walbridge et al. (1983) | [1]: RI 1 |
| *Daphnia magna* | Crustacea | 21 d | reproduction | NOEC<br>LOEC<br>EC10<br>EC50 | 4.4<br>9.1<br>14<br>30 | [10] | | RI 1 |
| *Haematococcus pluralis* | Algae | 4 h | growth | EC10 | >2000 | [1] | Knie et al. (1983) | RI 3 |
| *Scenedesmus quadricauda* | Algae | 8 d | growth | toxicity threshold (NOEC) | >25000 | [1], [5] | Bringmann & Kuehn (1977) | [1]: RI 3 |
| *Scenedesmus subspicatus* | Algae | 7 d | growth | EC3 | >25000 | [5] | Niemitz et al. 1979 | |
| | | | | | | | | |
| *Carassius auratus* | Pisces | 96 h | mortality | LC50 | 90 | [1] | Leeuwangh et al. (1975), EPA (1980) | RI 2 |
| *Oncorhynchus mykiss* | Pisces | 96 h | mortality | LC50 | 320 | [1] | Call et al. (1983), EPA (1980) | RI 2; also 192h LC50 of 0.121 mg/l |
| *Oncorhynchus mykiss* | Pisces | 192 h (8d) | mortality | LC50 | 121 | [6] | Call et al (1983) | |
| *Pimephales promelas* | Pisces | 96 h | larval survival and weight | LC50 | 90 | [1], [5] | Geiger et al. (1985) | [1]: RI 1 |
| *Asellus aquaticus* | Crustacea | 96 h | mortality | LC50 | 130 | [1], [6], [5] | Leeuwangh et al. (1975) | [1]: RI 2 |
| *Daphnia magna* | Crustacea | 24 h | mortality | LC50 | 500 | [1], [7] | Knie et al. 1983 | [1]: RI 3 |
| *Lymnaea stagnalis* | Mollusca | 96 h | mortality | LC50 | 210 | [1], [5] | Leeuwangh et al. (1975) | [1]: RI 2 |

[#] RI = reliability index (by Euro Chlor, based on IUCLID system): 1 (valid without restriction); 2 ( valid with restrictions, to be considered with care); 3 (invalid); 4 (not assignable)

Table 6.1: (continued) Overview on toxicity data of most sensitive species from different sources (master reference).

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| **Saltwater** | | | | | | | | |
| *Eliminius modestus (nauplii)* | Crustacea | 48 h | mortality | LC50 | 870 | [1] | Pearson & McConnell (1975) | RI 2 |
| *Mysidopsis bahia* | Crustacea | 96 h | mortality | LC50 | 59 | [5], [1] | EPA 1980 | [1]: RI 4 |
| *Cyprinodon variegatus* | Pisces | 96 h | mortality | LC50 | 3600 | [1] | Dow Chemical Company (1978) | RI 2; Limited method information |
| *Limanda limanda* | Pisces | 96 h | mortality | LC50 | 450 | [1] | Pearson & McConnell (1975) | RI 1; Method designed for compounds with high volatility |
| *Crassostrea gigas* | Mollusca | 48 h | larval development | EC50<br>EC10<br>NOEC | ≥ 21<br>≥ 21<br>≥ 21 | [10] | | RI 1 |
| *Psammechinus miliaris* | Echinoder-mata | 48 h | larval development | EC50<br>EC10<br>NOEC | ≥ 21<br>≥ 21<br>≥ 21 | [10] | | RI 1 |

[#] RI = reliability index (by Euro Chlor, based on IUCLID system): 1 (valid without restriction); 2 ( valid with restrictions, to be considered with care); 3 (invalid); 4 (not assignable)

Table 6.2: Mammal and bird oral toxicity data relevant for the assessment of non compartment specific effects relevant for the food chain (secondary poisoning) [1]

| Species | Type of study | NOAEL | Reference in [1] |
|---|---|---|---|
| Rat, Mouse | chronic toxicity | 0.2 mg/kg bw/d | WHO-IPCS 1994 |
| Rat | reproductive toxicity | 20 mg/kg bw/d | WHO-IPCS 1994 |
| Japanese Quail | sub-chronic toxicity | 3 mg/kg bw/d | |

**Summary on endocrine disrupting potential**

Hexachlorobutadiene is not mentioned in [2]. No hints on endocrine disrupting properties of the substance have been found in the information provided to the consultant by Member States or other experts.

## (21) Živo srebro in njegove spojine

### 4 Physical and chemical properties

| Property | Value | Ref. | Comments |
|---|---|---|---|
| Mol. Weight: | | | |
| Water Solubility | 20-30 ng/l | [10] | elemental Hg |
| Vapour Pressure: | 0.25 Pa (25 °C) | [10] | elemental Hg |

### 5 Environmental fate and partitioning

| Property | Value: | Ref: | Comments: |
|---|---|---|---|
| Partition coefficients | | | |
| Kp | $1.46*10^6$ | [6] | |
| Kd | 316,000 $m^3/m^3$ | [10] | Used in the risk assessment by [10] |
| $Kp_{water-SPM}$ | 100,000 l/kg (mean value) | [7] | |
| | 124000 - 164000 L/kg (suspended pariculate matter)<br>57000 L/kg<br>250000 - 330000 L/kg<br>5000 – 900000 L/kg | [5] | Figures from different reports cited in [5] |
| Bioaccumulation | | | |
| BCF fish: | | | |
| Trout | 5 ($HgCl_2$, 50 µg/L, 4 d, 5°C) | [5] | |
| *Oncorhynchus mykiss* | 1800 ($HgCl_2$, freshw., whole body, 60 d)<br>85700 ($HgCH_3Cl$, freshw., whole body, 75 d) | [5] | |
| *Pimephales promelas* | 4994 ($HgCl_2$, freshw., whole body, 287 d)<br>44130 – 81670 ($HgCH_3Cl$, whole body, 336 d) | [5] | |
| *Salvelinus fontinalis* | 11000 – 33000 ($HgCH_3Cl$, muscle, 273 d) | [5] | |
| Riverine fish | 1000 – 15000 (freshwater, muscle, natl. environment)<br>2000 – 10000 (freshwater, muscle, natl. environment) | [5] | |
| Fish | 3030 (OSPAR 1996, geometric mean for inorganic mercury)<br>3640 (OSPAR 1996) ; 8140 (Slooff et al. 1996) – geometric means for methyl mercury | [10] | |
| BCF molluscs: | | | |
| | 24- 2500 (calculated from mean Hg conc. in marine molluscs and mean conc. of dissolved Hg in North Sea estuaria) | [10] | |
| | 3500 (mean BCF for organic Hg in molluscs) | [10] | |
| *Mytilus edulis* | 190 –5300 (BCF range of inorganic Hg; Slooff et al. 1995) | [10] | |
| | 1750 (geometric mean, OSPAR 1996) | [10] | |
| Biomagnification: | | | |
| | Mercury can lead to biomagnification with an increase in concentration in subsequent trophic levels. Mercury, and methylmercury in particular, can also be accumulated to a large extent from food which leads to higher mercury levels under field conditions than expected on the basis of the theoretical BCF-values. This should be taken into account for higher trophic levels (secondary poisoning). | [10] | |
| BAF fish (field measurements) | 21700 (Sloof et al. 1995)<br>1600 000 – 6800000 (US-EPA 1997<br>120000 – 27000000 (US-EPA 2001);<br>200000 – 78000000 (France 2004) | [14]<br>[15]<br>[16]<br>[17] | geometric means for methyl mercury, |

## 6 Effect data (aquatic environment)

Table 6.1: Overview on toxicity data of most sensitive species from different sources (master reference). Values are related to inorganic Hg, bold records indicate those data used for the SSD (see 8.1)

| Species | Taxonomic Group | Duration | Effect | Endpoint | Value µg Hg/l | Master reference | Reference in master reference | Comments on data reliability in master reference * |
|---|---|---|---|---|---|---|---|---|
| ***Freshwater, (sub)chronic*** | | | | | | | | |
| ***Scenedesmus acuminatus*** | **Algae** | **72 h** | **Growth** | **EC10** | **0.2** | **[5]** | **Kusel-Fetzmann 1989** | |
| ***Salvelinus fontinalis*** | **Pisces** | **730 d** | | **NOEC** | **0.29** | **[5]** | **Mance 1987** | |
| ***Pimephales promelas*** | **Pisces** | **30-60 d** | **Growth** | **NOEC** | **0.3** | **[8]** | **RIVM Rep. 601501001, 601014008** | **geometric mean (n=4)** |
| *Pimephales promelas* | Pisces | 41 w | Growth and reproduction | NOEC | 0.5 | [10] | Snarski & Olson, 1982 | RI: 2 |
| *Pimephales promelas* | Pisces | 60 d | Growth | NOEC<br>LOEC | 1<br>2 | [6] | Snarski et Olson (1982) | |
| *Pimephales promelas* | Pisces | 32 d | Growth and mortality | NOEC | 0.63 | [10] | Spehar & Fiandt, 1986 | RI: 1 |
| ***Hyalella azteca*** | **Crustacea** | **6-10 w** | **Reproduction** | **NOEC<br>LOEC** | **0.62<br>2.42** | **[10]** | **Borgmann et al., 1993** | **RI: 2** |
| ***Daphnia magna*** | **Crustacea** | **21 d** | **Reproduction** | **NOEC** | **0.7** | **[8]** | **RIVM Rep. 601501001, 601014008** | **geometric mean (n=3)** |
| *Daphnia magna* | Crustacea | 21 d | Reproduction | NOEC<br>LOEC | 0.72<br>1.28 | [6] | Biesinger et al (1982) | |
| *Daphnia magna* | Crustacea | 21 d | Mortality, growth | NOEC<br>LOEC | 2.2<br>7.0 | [10] | Enserink et al., 1991 | RI: 2 |
| ***Brachydanio rerio*** | **Pisces** | **14 d** | **Mortality** | **NOEC** | **1** | **[8]** | **RIVM Rep. 601501001, 601014008** | |
| ***Scenedesmus capricornutum*** | **Algae** | **72 h** | **Growth** | **EC10** | **1** | **[5]** | **Kusel-Fetzmann 1989** | |
| *Scenedesmus capricornutum* | Algae | 10 d | Growth | NOEC | 9 | [8] | RIVM Rep. 601501001, 601014008 | |
| ***Microcystis aeruginosa*** | **Cyanobacteria** | **8 d** | **Growth** | **NOEC** | **2.5** | **[8]** | **RIVM Rep. 601501001, 601014008** | |
| ***Chilomonas paramecium*** | **Protozoa** | **48 h** | **Growth** | **NOEC** | **8** | **[8]** | **RIVM Rep. 601501001, 601014008** | |
| ***Ceriodaphnia dubia*** | **Crustacea** | **7 d** | **Reproduction and mortality** | **NOEC** | **8.5** | **[10]** | **Spehar & Fiandt, 1986** | **RI: 1, also used in** RIVM Rep. 601501001, 601014008 |
| ***Enthosiphon sulcatum*** | **Protozoa** | **72 h** | **Growth** | **NOEC** | **9** | **[8]** | **RIVM Rep. 601501001, 601014008** | |
| *Daphnia similis* | Crustacea | 28 d | Mortality | NOEC | 10 | [8] | RIVM Rep. 601501001, 601014008 | |
| ***Cyclops sp.*** | **Crustacea** | **14 d** | **Reproduction** | **NOEC** | **18** | **[8]** | **RIVM Rep. 601501001, 601014008** | |
| *Scenedesmus acutus* | Algae | 10 d | Growth | NOEC | 20 | [8] | RIVM Rep. 601501001, 601014008 | |
| ***Chara vulgaris*** | **Macroalgae** | **14 d** | **Growth** | **NOEC** | **20** | **[10]** | **Heumann, 1987** | **RI: 1, also used in** RIVM Rep. 601501001, 601014008 |

Substance Data Sheet
Final Version of 15.01. 2005

**(21) Mercury and its Compounds**

| Species | Taxonomic Group | Duration | Effect | Endpoint | Value µg Hg/l | Master reference | Reference in master reference | Comments on data reliability in master reference * |
|---|---|---|---|---|---|---|---|---|
| *Scenedesmus quadricauda* | Algae | 8 d | Growth | NOEC | 35 | [8] | RIVM Rep. 601501001, 601014008 | |
| ***Viviparus bengalensis*** | **Mollusca** | **7 d** | **Mortality** | **NOEC** | **45** | **[8]** | **RIVM Rep. 601501001, 601014008** | geometric mean (n=6) |
| *Selenastrum capricornutum* | Algae | 96 h | Growth | NOEC | 80 | [6] | Sloof et al (1983) | |
| *Chlorella vulgaris* | Algae | 33 d | Growth | NOEC | 100 | [8] | RIVM Rep. 601501001, 601014008 | |
| **Freshwater, acute** | | | | | | | | |
| *Carassius auratus* | Pisces | 8 d | Mortality | LC50 | 0.7 | [5] | Westerman 1984 | |
| *Gastrophryne carolinensis* | Amphibia | 7 d | Mortality | LC50 | 1 | [5] | Birge et al. 1979 | |
| *Crangonyx pseudogracilis* | Crustacea | 96 h | Mortality | LC50 | 1 | [10] | Martin & Holdich, 1986 | RI: 2 |
| *Daphnia magna* | Crustacea | 48 h | Mortality | LC50 | 3 | [6] | Canton et Adema (1978) | |
| *Daphnia pulex* | Crustacea | 48 h | Immobilisation | EC50 | 3.8 | [10] | Elnabarawy & Welter, 1986 | RI: 2 |
| *Chrysophrys major* | Pisces | 96 h | Mortality | LC50 | 4 | [5] | Lan et al. 1991 | |
| *Daphnia magna* | Crustacea | 48 h | Immobilisation | EC50 | 5.2 | [10] | Khangarot & Ray, 1987b | RI: 2 |
| *Selenastrum capricornutum* | Algae | 96 h | Growth | EC50 | 9 | [5], [10] | Chen et al, 1997 | RI: 2 |
| *Chironomus sp* | Insecta | 96 h | Mortality | LC50 | 20 | [5] | Rehwoldt et al. 1973 | |
| *Poecilia reticulata* | Pisces | 96 h | Mortaliy | LC50 | 26 | [10] | Khangarot & Ray, 1987b | RI: 2 |
| *Chironomus tentans* | Insecta | 48 h | Intoxication | EC50 | 29 | [5]; [10] | Khangarot et al. 1989 | RI: 1 |
| *Bufo melanostictus* | Amphibia | 4 d | Mortality | LC50 | 43.6 | [5] | Khangarot et al. 1987 | |
| *Rana hexadactyla (tadpoles)* | Amphibia | 96 h | Mortality | LC50 | 51 | [10] | Khangarot et al., 1985 | RI: 1 |
| *Tubifex tubifex* | Annelida | 96 h | Intoxication | EC50 | 51 | [5] | Khangarot 1991 | |
| *Pimephales promelas* | Pisces | 7 d | Growth | LC50 | 74 | [6] | Snarski et Olson (1982) | |
| *Pimephales promelas* | Pisces | 4 d<br>7 d | Mortality | LC50<br>LC50 | 168<br>74 | [10] | Snarski & Olson, 1982 | RI: 1 |
| *Viviparus bengalensis* | Mollusca | 7 d | Mortality | LC50 | 80 | [10] | Muley & Mane, 1988 | RI: 1 |
| *Thymallus arcticus (alevins)* | Pisces | 96 h | Mortality | LC50 | 124 | [10] | Buhl & Hamilton, 1991 | RI: 2 |
| *Cyprinus carpio (juvenile)* | Pisces | 96 h | Mortality | LC50 | 160 | [10] | Alam & Maughan, 1992 | RI: 2 |
| *Oncorhynchus mykiss* | Pisces | 96 h | Mortality | LC50 | 193 | [10] | Buhl & Hamilton, 1991 | RI: 2 |
| *Caenorhabditis elegans* | Nematoda | 96 h | Mortality | LC50 | 440 | [10] | Williams & Dusenberry, 1990 | RI: 2 |
| **Saltwater, (sub)chronic** | | | | | | | | |
| ***Clavopsella michaeli*** | **Coelenterata** | **8 d** | **Reproduction** | **NOEC** | **0.1** | **[8]** | **RIVM Rep. 601501001, 601014008** | |
| ***Crepidula fornicata*** | **Mollusca** | **112 d** | **Reproduction** | **NOEC**<br>LOEC | **0.25**<br>0.42 | **[10]** | **Thain, 1984** | **RI: 1, also used in** RIVM Rep. 601501001, 601014008 |
| ***Mysidopsis bahia*** | **Crustacea** | **44 d** | **Reproduction and mortality, life cycle** | **NOEC**<br>LOEC | **0.8**<br>1.6 | **[10]** | **Gentile et al., 1982** | **RI: 1, also used in** RIVM Rep. 601501001, 601014008 |

## (21) Mercury and its Compounds

| Species | Taxonomic Group | Duration | Effect | Endpoint | Value µg Hg/l | Master reference | Reference in master reference | Comments on data reliability in master reference * |
|---|---|---|---|---|---|---|---|---|
| ***Streptotheca tamesis*** | **Algae** | **10 d** | **Growth** | **NOEC** | **0.9** | **[8]** | **RIVM Rep. 601501001, 601014008** | |
| *Synechococcus bacillaris* | Algae | 10 d | Growth | NOEC | 0.9 | [8] | RIVM Rep. 601501001, 601014008 | |
| ***Fucus serratus*** | **Macroalgae** | **10 d** | **Growth** | **NOEC** | **0.9** | **[10]** | **Strömgren, 1980** | **RI: 2** |
| ***Crassostrea virginica*** | **Mollusca** | **42 – 48 h** | **Hatching** | **NOEC** | **1** | **[8]** | **RIVM Rep. 601501001, 601014008** | |
| ***Laminaria saccharina*** | **Macroalgae** | **14 d** | **Development of zoospores** | **NOEC**<br>LOEC | **1**<br>5 | **[10]** | **Thompson & Burrows, 1984** | **RI: 2** |
| ***Skeletonema costatum*** | **Algae** | **6 d** | **Growth** | **NOEC** | **1** | **[10]** | **Rice et al, 1973** | **RI: 2** |
| *Skeletonema costatum* | Algae | 10 d | Growth | NOEC | 9 | [8] | RIVM Rep. 601501001, 601014008 | |
| ***Cristigera sp.*** | **Protozoa** | **4-9 h** | **Reproduction** | **NOEC** | **2.5** | **[8]** | **RIVM Rep. 601501001, 601014008** | |
| ***Mercenaria mercenaria*** | **Mollusca** | **8-10 d** | **Reproduction** | **NOEC** | **4** | **[8]** | **RIVM Rep. 601501001, 601014008** | |
| ***Callinectes sapidus*** | **Crustacea** | **10 – 35 d** | **Mortality** | **NOEC** | **4.9** | **[10]** | **McKenney & Costlow, 1982** | **RI: 1, also used in** RIVM Rep. 601501001, 601014008 |
| *Palvetia canaculata* | Algae | 10 d | Growth | NOEC | 5 | [8] | RIVM Rep. 601501001, 601014008 | |
| ***Clupea harengus membras*** | **Pisces** | **250 – 300 h** | **ELS, hatching of larve, mortality** | **NOEC** | **5** | **[9]** | **Ojaveer et al. 1980** | |
| ***Penaeus indicus*** | **Crustacea** | **28 d** | **Growth** | **NOEC** | **6** | **[8]** | **RIVM Rep. 601501001, 601014008** | |
| *Fucus spiralis* | Macroalgae | 10 d | Growth | NOEC | 9 | [10] | Strömgren, 1980 | RI: 2 |
| ***Ctenodrilus serratus*** | **Annelida** | **21-31 d** | **Reproduction** | **NOEC** | **10** | **[8]** | **RIVM Rep. 601501001, 601014008** | **geometric mean (n=2)** |
| ***Fundulus heteroclitus*** | **Pisces** | **32 d** | **Hatching** | **NOEC** | **10** | **[8], [10]** | RIVM Rep. 601501001, 601014008 | **RI: 1** |
| ***Ophryotrocha diadema*** | **Annelida** | **28 d** | **Reproduction** | **NOEC** | **71** | **[8]** | **RIVM Rep. 601501001, 601014008** | **geometric mean (n=2)** |
| **Saltwater, acute** | | | | | | | | |
| *Mytilus galloprovincialis* | Mollusca | 48 h | Development | EC50 | 3.5 | [5] | Pavicic et al. 1994 | |
| *Mya arenaria* | Mollusca | 7d | Mortality | LC50 | 4 | [5] | Eisler et al. 1977 | |
| *Crassostrea gigas* | Mollusca | 48 h | Development | EC50 | 4.2 | [5] | Glickstein 1978 | |
| *Crassostrea virginica* | Mollusca | 96 h | Embryos | LC50 | 5.6 | [10] | Calabrese et al., 1973 | RI: 1 |
| *Mytilus edulis* | Mollusca | 48 h | Embryos, abnormal transformation | EC50 | 5.8 | [10] | Martin et al., 1981 | RI: 1 |
| *Ditylum brightwelli* | Algae | 120 h | Growth | EC50 | 10 | [10] | Canterford & Canterford, 1980 | RI: 2 |
| *Acartia tonsa* | Crustacea | 7 d | Mortality | LC50 | 10 | [10] | Sosnowski & Gentile, 1978 | RI:2 |
| *Capitella capitata* | Annelida | 96 h | Trochophore larvae | LC50 | 14 | [10] | Reish & Carr, 1978 | RI: 2 |
| *Neanthes arenaceodentata* | Annelida | 96 h | Mortality | LC50 | 20 | [10] | Reish & Carr, 1978 | RI: 2 |
| *Penaeus merguiensis (juvenile)* | Crustacea | 96 h | Mortality | LC50 | 30 - 290 | [10] | Denton & Burdon-Jones, 1982 | RI: 1 |

| Species | Taxonomic Group | Duration | Effect | Endpoint | Value µg Hg/l | Master reference | Reference in master reference | Comments on data reliability in master reference * |
|---|---|---|---|---|---|---|---|---|
| *Fundulus heteroclitus (embyros)* | Pisces | 96 h | Mortality | LC50 | 67 | [10] | Sharp & Neff, 1980 | RI: 1 |
| *Artemia franciscana* | Crustacea | 3 d | Hatching, emergence | NOEC | 2 | [8] | RIVM Rep. 601501001, 601014008 | |
| *Ilyanassa obsoleta* | Mollusca | 2.5 h | Development | NOEC | 2 | [8] | RIVM Rep. 601501001, 601014008 | |

# RI = reliability index (by Euro Chlor, based on IUCLID system): 1 (valid without restriction); 2 ( valid with restrictions, to be considered with care); 3 (invalid); 4 (not assignable)

Table 6.2: Mammal and bird oral toxicity data for inorganic mercury

| Species | | Duration | Effect | NOEC mg/kg food | Reference: |
|---|---|---|---|---|---|
| *Coturnix c. japonica* | Japanese quail | 365 d | egg-fertility | 4 | [8]: RIVM Rep. No. R679101012 |
| *Gallus domesticus* | Chicken | 21 d | egg-hatching | 10 | [8]: RIVM Rep. No. R679101012 |
| *Mus musculus* | Mouse | 560 d | body weight | 20 | [8]: RIVM Rep. No. R679101012 |

Table 6.3: Mammal and bird oral toxicity data for methylmercury according to RIVM report 601501009 [14]

| Species | | Duration | Effect | NOEC food [mg/kg] | Reference |
|---|---|---|---|---|---|
| **Mammals** | | | | | |
| *Mamaca spec.* | rhesus monkey | 365 d | growth | 0.22 | Kawaskaki et al. 1986 |
| *Rattus norwegicus* | Norwegian rat | 3 gen | reproduction | 0.43 | Verschuren et al. 1976 |
| *Mustela vison* | American mink | 60 d | mortality | 0.5 | Wren 1987 |
| *Mustela vison* | American mink | 93 d | mortality | 1.2 | Wobeser et al. 1976 |
| *Mustela vison* | American mink | 100 d | mortality | 2.5 | Jenelöv et al. 1976 |
| *Mus musculus* | domestic mouse | 60 d | growth | 2.25 | Berthoud et al. 1976 |
| **Birds** | | | | | |
| *Anas platyrhynchos* | mallard duck | 3 gen | egg production | 0.25 | Heinz 1979 |
| *Phasianus colchicus* | ring necked pheasant | 20 d | mortality | 0.36 | Gardiner 1972 |
| *Gallus domesticus* | chicken | 20 d | mortality | 0.36 | Gardiner 1972 |
| *Gallus domesticus* | chicken | 20 d | mortality | 0.86 | Fimreite 1970 |
| *Coturnix c. japonica* | Japanese quail | 63 d | mortality | 1.7 | Hill & Soares 1984 |
| *Poephila guttata* | zebra finch | 67 d | mortality | 2.7 | Scheuhamer 1988 |
| *Buteo jamaicensis* | red-tailed hawk | 84 d | mortality, growth | 2.8 | Fimreite & Karstad 1971 |
| *Colinus virginianus* | bobwhite quail | 54 d | mortality | 4.3 | Spann et al. 1986 |

## 6.1 Summary on endocrine disrupting potential

Mercury is not mentioned in the Community Strategy for Endocrine Disruptors [2]. No hints on possible effects of Hg and its compounds on the endocrine system have been found in the information provided to the consultant by Member States and NGOs.

**(28) Benzo(a)piren**

# 5 ENVIRONMENTAL BEHAVIOUR

## 5.1 ENVIRONMENTAL DISTRIBUTION

| **Benzo[a]pyrene** | | **Master reference** |
|---|---|---|
| **Water solubility** (mg.l$^{-1}$) | 1.54 $10^{-3}$ | Mackay *et al.*, 1992 *in* E.C., 2008a |
| **Volatilisation** | Benzo[a]pyrene is not likely to volatilise from surface water. | |
| **Vapour pressure** (Pa) | 7.3 $10^{-7}$ at 25°C | Mackay *et al.*, 1992 *in* E.C., 2008a |
| **Henry's Law constant** (Pa.m$^3$.mol$^{-1}$) | 0.034 at 20°C | Mackay *et al.*, 1992 *in* E.C., 2008a |
| **Adsorption** | **The value of 831 764 is used for derivation of QS** | |
| **Organic carbon – water partition coefficient ($K_{OC}$)** | log $K_{OC}$ = 5.92 (*calculated from* $K_{OW}$)<br>$K_{OC}$ = 831 764 | Karickhoff *et al.*, 1979 |
| **Sediment – water partition coefficient($K_{sed\text{-}water}$)** | 20 795 (*calculated from* $K_{OC}$) | E.C., 2011 |
| **Bioaccumulation** | **BCF, $BMF_1$ and $BMF_2$ values recommended for back calculation of $QS_{biota}$ values to water reported in the dedicated following section 0.** | |
| **Octanol-water partition coefficient (Log Kow)** | 6.11 (*estimated*) | Mackay et al., 1992 *in* E.C., 2008a |
| | 6.13 (*experimental*) | US-EPA, 2008 |

## 5.2 ABIOTIC AND BIOTIC DEGRADATIONS

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

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

## 5.3 BIOACCUMULATION AND BIOMAGNIFICATION POTENTIAL

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

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

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

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

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

# 7 EFFECTS AND QUALITY STANDARDS

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

that the UV exposure levels of the selected studies did not exceed the UV levels under natural sun light conditions.

## 7.1 ACUTE AND CHRONIC AQUATIC ECOTOXICITY

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

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

Averaged measured concentrations are tagged as (mm).

### 7.1.1 Benzo[a]pyrene

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

[(1)] exposure in the dark

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

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

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

[1] 6000-8000 lux on the level of the solutions

[2] 16:8 h photoperiod.

[3] 16:8 h photoperiod, yellow light

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

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

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

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

## 7.2 SECONDARY POISONING

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

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

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

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

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

| | |
|---|---|
| **Avian oral toxicity** | No available information |

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

**(34) Dikofol**

# 5 ENVIRONMENTAL BEHAVIOUR

## 5.1 ENVIRONMENTAL DISTRIBUTION

| | | Master reference |
|---|---|---|
| **Water solubility** ($mg.l^{-1}$) | 0.8 | DEFRA, 1996 |
| **Volatilisation** | **According to Henry constant, Dicofol is not likely to volatilize.** | |
| **Vapour pressure** (Pa) | $5.3\ 10^{-5}$ at 25°C | DEFRA, 1996 |
| **Henry's Law constant** ($Pa.m^3.mol^{-1}$) | 0.015 | US-EPA, 1998 |
| **Adsorption** | **The $K_{OC}$ range 5 000 – 21 096 is used for derivation of quality standards.** | |
| **Organic carbon – water partition coefficient ($K_{OC}$)** | $K_{OC}$ – p,p'-dicofol = 5 000 – 6 983 (mean=5 080)<br>$K_{OC}$ – o,p'-dicofol = 13 949 – 21 096 (mean=16 995) | Daly, 1987<br>Cook, 2003 |
| **Sediment – water partition coefficient($K_{susp-water}$)** | p,p'-dicofol = 127.8<br>o,p'-dicofol = 425.7 | *Calculated from $K_{oc}$* |
| **Bioaccumulation** | **Dicofol is likely to highly bioaccumulate. Biota Quality Standards are back calculated into water by using the following values: BCF=25 000; $BMF_1$=1 and $BMF_2$=42 (see below).** | |
| **Octanol-water partition coefficient (Log Kow)** | $K_{OW}$ – p,p'-dicofol = 4.08<br>$K_{OW}$ – o,p'-dicofol = 4.32 | E.C., 2008a |



| | | |
|---|---|---|
| **BCF (measured)** | *Pimephales promelas* – 28d = 8 050 – 13 500 | Rasenberg, 2003, as cited *in* OSPAR, 2004 |
| | *Lepomis macrochirus* – 28d – (p, p'-dicofol)<br>$BCF_{end\ of\ exposure}$= 10 000<br>$BCF_{steady\text{-}state}$= 25 000 (extrapolated) | Tillman, 1986 as cited *in* E.C., 2008a |
| **Biomagnification potential** | In a study lead by Kelly *et al.*, 2007b for which supporting material is available (Kelly *et al.*, 2007a) dicofol biomagnification was studied among other organic chemicals. Experimental trophic magnification factors could not be calculated but BMF values for dicofol were calculated from the physicochemical properties (log Kow and log Koa). Resulting model calculated values are a $BMF_1$ <1 and a $BMF_2$ value of 42 which are deemed sufficiently reliable for the purpose of EQS derivation.<br>It is noted that the modeled BMF1 of 1 may be low given to the high aquatic BCF. BMF2 can however be considered as a worst case because potential metabolism has not been taken into account. | Kelly *et al.*, 2007b<br>Kelly *et al.*, 2007a |

## 5.2 ABIOTIC AND BIOTIC DEGRADATIONS

| | | Master reference |
|---|---|---|
| **Hydrolysis** | Dicofol is stable under acidic conditions. Dicofol hydrolysis is very rapid within neutral and alcaline conditions. One transformation product is dichlorobenzophenone. | US-EPA, 1998 |
| **Photolysis** | At neutral pH, samples without a photosensitiser:<br>$DT_{50\ -\ exposed}$ = 15d for o,p'-dicofol ; 93d for p,p'-dicofol<br>$DT_{50\ -\ dark}$ = 149 for o,p'-dicofol ; 32 for p,p'-dicofol<br>(Study considered as supplementary, some of the recoveries are out of range) | Carpenter, 1988a; Carpenter, 1988b |
| **Biodegradation** | Dicofol biodegrades slowly in aerobic conditions in water/sediment systems. There is no information on mineralisation process or degradation products.<br>$DT_{50\ (water/sediment)}$ = 70-84 d | OSPAR, 2004 |

# 7 EFFECTS AND QUALITY STANDARDS

## 7.1 ACUTE AND CHRONIC AQUATIC ECOTOXICITY

Whenever it was possible, information on media renewal and analytical measurement of concentrations were reported. In the tables hereunder, static or flow-through systems are reported as (s) and (ft), respectively, while endpoints based on measured or nominal concentrations are reported as (m) and (n), respectively. ELS stands for "Early Life Stage" toxicity test and FLC for "Full Life Cycle" toxicity test.

| **ACUTE EFFECTS** | | | **Klimisch codes** | **Master reference** |
|---|---|---|---|---|
| **Algae & aquatic plants ($mg.l^{-1}$)** | **Freshwater** | *Scenedesmus subspicatus* / 96h<br>$EC_{50}$ = 0.073 | 4 [1] | RCC, 1983 |
| | **Marine** | No data available | | |
| **Invertebrates ($mg.l^{-1}$)** | **Freshwater** | *Daphnia magna* / 48h<br>$EC_{50}$ = 0.14 | 4 | US-EPA, 1998 |
| | **Marine** | *Crassostrea virginica* / 96h<br>$EC_{50}$ = 0.0151 | 4<br>Core [2] | Office of Pesticide Programs, 2000 |
| | **Sediment** | No data available | | |
| **Fish ($mg.l^{-1}$)** | **Freshwater** | *Oncorhyncus mykiss* / 96h<br>$LC_{50}$ = 0.11 (m, ft) | 2 | Bowman and Ritchie, 1990<br>as cited *in* E.C., 2006 |
| | | *Pimephales promelas* / 96h<br>$LC_{50}$ = 0.183 (m, s) | 2 | Ritchie *et al.*, 1992<br>as cited *in* E.C., 2006 |
| | | *Oncorhyncus clarki* / 96h<br>$EC_{50}$ = 0.012 | 4 | OSPAR, 2004 |
| | | *Oncorhyncus clarki* / 96h<br>$EC_{50}$ = 0.053 | 4 | Mayer and Ellersieck, 1986 |
| | **Marine** | No data available | | |
| | **Sediment** | No data available | | |
| **Other taxonomic groups** | | No data available | | |

*[1] It was not possible to check the exact validity of the test but this study is not determinant for derivation of the quality standard since Dicofol action mode is not meant to affect plants and algae.*

*[2] The three study categories used by the US-EPA to classify studies are core, supplemental, and invalid. Classification as "core data" means that all essential information was reported and the study was performed according to recommended EPA or ASTM methodology. For more details, please see http://www.ipmcenters.org/Ecotox/DatabaseGuidance.pdf.*

| CHRONIC EFFECTS | | | Validity | Master reference |
|---|---|---|---|---|
| Algae & aquatic plants ($mg.l^{-1}$) | Freshwater | No data available | | |
| | Marine | No data available | | |
| Invertebrates ($mg.l^{-1}$) | Freshwater | | | |
| | Marine | No data available | | |
| | Sediment | No data available | | |
| Fish ($mg.l^{-1}$) | Freshwater | *Oncorhyncus mykiss* / juvenile / 21d<br>NOEC = 0.0032 (m, ft) | 2 | Ritchie *et al.*, 1992 as cited *in* E.C., 2006 |
| | | *Oncorhyncus mykiss* / ELS / 99d<br>NOEC = 0.0091 (m, ft) | 2 | Rhodes *et al.*, 1994 as cited *in* E.C., 2006 |
| | | *Pimephales promelas* / FLC / 290d<br>NOEC = 0.00452 (m, ft) | 2 | Ritchie *et al.*, 1992 as cited *in* E.C., 2006 |
| | | *Oncorhynchus mykiss* / ?<br>NOEC = 0.001 | 4 | McAllister, 1991 |
| | | *Oncorhynchus mykiss* / 45d<br>NOEC = 0.00395 | 4<br>Core (2) | Office of Pesticide Programs, 2000 |
| | Marine | No data available | | |
| | Sediment | No data available | | |
| Other taxonomic groups | | No data available | | |

Acute and chronic ecotoxicological data could be retrieved from various sources but only data on fish could be validated. In the non-public DAR elaborated in the context of Directive 91/414/EEC there are some more invertebrates' ecotoxicological data but tests were deemed not acceptable by the assessors because of the absence of analytical measurement (acute test) or because of a too poor correlation between nominal and measured concentrations which made the approximation of effects concentrations "*too far from real*" (NOEC= 0.125 $mg.l^{-1}$). US-EPA Aquire database reports a number of other studies on invertebrates, the validity of which could not be thoroughly checked, but some NOEC values are as low as 10 $\mu g.l^{-1}$ for *Daphnia magna*. This is still higher than the lowest validated NOEC for fish and these values all together are about 4 orders of magnitude higher than the proposed $QS_{biota,\ sec.pois.}$ when back calculated in water. Therefore, it was considered acceptable not to derive a $QS_{water,\ eco}$ because pelagic organisms are deemed protected by $QS_{biota,\ sec.pois.}$.

| Tentative $QS_{water}$ | Relevant study for derivation of QS | Assessment factor | Tentative QS |
|---|---|---|---|
| $MAC_{freshwater,\ eco}$ | Data available could not be validated | - | - |
| $MAC_{marine\ water,\ eco}$ | | - | - |
| $AA\text{-}QS_{freshwater,\ eco}$ | | - | - |
| $AA\text{-}QS_{marine\ water,\ eco}$ | | - | - |
| $AA\text{-}QS_{freshwater,\ sed.}$ | - | - | - |
| $AA\text{-}QS_{marine\ water,\ sed.}$ | - | - | - |

$AA\text{-}QS_{water,\ eco}$ and $MAC\text{-}QS_{water,\ eco}$ could not be derived with a sufficient degree of confidence as they would be based on tests which could not be validated (Klimisch code 3 or 4).

## 7.2 SECONDARY POISONING

| Secondary poisoning of top predators | | Master reference |
|---|---|---|
| **Mammalian oral toxicity** | Rat / Oral / 90d / Effects on liver, thyroid, and stomach.<br>NOAEL = 0.07 $mg.kg^{-1}_{bw}.d^{-1}$<br>NOEC = 1 $mg.kg^{-1}_{feed\ ww}$ (Conversion Factor (CF) study specific) | US-EPA, 1998; WHO, 1992; WHO, 2007 |
| | Rat / Oral / 2y / Effects on liver and adrenal cortical cells.<br>NOAEL = 0.22 $mg.kg^{-1}_{bw}.d^{-1}$<br>NOEC = 5 $mg.kg^{-1}_{feed\ ww}$ (CF study specific) | US-EPA, 1998; WHO, 1992; WHO, 2007 |
| | Dog / Oral / 1 y / Hormonal effects (Cortisol)<br>*According to US-EPA*<br>NOAEL = 0.12 $mg.kg^{-1}_{bw}.d^{-1}$<br>NOEC = 5 $mg.kg^{-1}_{feed\ ww}$ (CF study specific)<br>*According. to WHO*<br>NOAEL = 0.82 $mg.kg^{-1}_{bw}.d^{-1}$<br>NOEC = 30 $mg.kg^{-1}_{feed\ ww}$ (CF study specific) | US-EPA, 1998<br>WHO, 1992 |
| **Avian oral toxicity** | *Falco sparverius* / Reproduction<br>NOAEL = 0.125 $mg.kg^{-1}_{bw}.d^{-1}$<br>NOEC = 1 $mg.kg^{-1}_{feed\ ww}$ (CF = 8) | Office of Pesticide Programs, 2000 |
| | *Anas platyrhynchos* / 1 generation / Reproduction<br>NOAEL = 0.26 $mg.kg^{-1}_{bw}.d^{-1}$<br>NOEC = 2.5 $mg.kg^{-1}_{feed\ ww}$ (CF study specific) | Beavers *et al.*, 1992<br>as cited *in* E.C., 2006 |

US-EPA report a NOAEL (0.12 $mg.kg^{-1}_{bw}.d^{-1}$) from a one year study on beagle dogs whereas WHO selected a different NOAEL (0.82 $mg.kg^{-1}_{bw}.d^{-1}$) from the same study (WHO, 1992). In the Assessment Report drafted for the purpose of Directive 91/414/EC, the rapporteur selected the same NOAEL of 0.82 $mg.kg^{-1}_{bw}.d^{-1}$ as WHO, but discarded the study since the results were only partially available (E.C., 2006). It is to be noted that the first assessment made by the US-EPA (US-EPA, 1998) was based on this one-year dog study whereas the 2006 revision used a new dermal study.

The most relevant studies on rats are reported above, with a NOAEC of 1 ppm obtained from the 90-days studies and 5 ppm from a 2 years study.

The chosen value for $QS_{biota,\ sec.\ pois}$ is the reproduction study on the American kestrel (reduced shell thickness). This study is preferred to the 90 days study on rat corresponding to the same 1 ppm NOEC (effects on liver, thyroid and stomach) which when repeated did not reproduced this thyroid effect in a second 13-week study using dietary concentrations of 0, 50, 200, 1000 or 3000 mg/kg.

Dicofol is considered as suspected endocrine disrupter for wildlife (see Section 2). Thus an additional factor of 5 could be applied to the assessment factor expected for protection of top predators from secondary poisoning. However, given that the toxicological data used should be sufficiently protective to cover effects on thyroid, it is deemed acceptable not to use this additional assessment factor. The BCF value used for back calculation of $QS_{biota,\ sec.\ pois}$ in water is 25 000, which is extrapolated for steady state from laboratory study on *Lepomis macrochirus* exposed to p,p'-isomer (cf. section 5.1). The BMF values used also for this calculation are $BMF_1$=1 and $BMF_2$=42 (see section 5.1).

| Tentative $QS_{biota}$ | Relevant study for derivation of QS | Assessment factor | Tentative QS |
|---|---|---|---|
| **Biota** | *Falco sparverius* / Reproduction<br>NOEC = 1 $mg.kg^{-1}_{feed\ ww}$ | 30[1] | 33.33 $\mu g.kg^{-1}_{biota\ ww}$<br>corresponding to<br>1.33 $10^{-3}$ $\mu g.l^{-1}$ (freshwater)<br>3.17 $10^{-5}$ $\mu g.l^{-1}$ (marine waters) |

[1] *Default value of 30 for birds according to the Technical Guidance on EQS derivation (E.C., 2011).*

## 7.3 HUMAN HEALTH

| Human health via consumption of fishery products | | Master reference |
|---|---|---|
| **Mammalian oral toxicity** | Rat / Oral / 90d / Effects on liver, thyroid, and stomach.<br>NOAEL = 0.07 $mg.kg^{-1}_{bw}.d^{-1}$ | US-EPA, 1998; WHO, 1992; WHO, 2007;E.C., 2006 |
| | Rat / Oral / 2y / Effects on liver and adrenal cortical cells.<br>NOAEL = 0.22 $mg.kg^{-1}_{bw}.d^{-1}$ | US-EPA, 1998; WHO, 1992; WHO, 2007<br>E.C., 2006 |
| | Dog / Oral / 1 y / Hormonal effects (Cortisol)<br>*According to US-EPA*<br>NOAEL = 0.12 $mg.kg^{-1}_{bw}.d^{-1}$<br>*According. to WHO*<br>NOAEL = 0.82 $mg.kg^{-1}_{bw}.d^{-1}$ | US-EPA, 1998<br>WHO, 2007<br>E.C., 2006 |
| **CMR** | Not classified for any carcinogenic, mutagenic or reprotoxic effects according to Regulation 1272/2008/EC | E.C., 2008b |

The chosen value for $QS_{biota\ hh}$ is the NOAEL from the two year study on rat, which covers diverse systemic effects on a long period including effects on liver and adrenal cortical cells. This data was retained by WHO for defining an acceptable daily intake (WHO, 1992), as well as the Draft Assessment Report prepared for the purpose of Directive 91/414/EC (E.C., 2006). Both WHO, 1992 and E.C., 2006 proposed the application of an assessment factor of 100.

The values used for back calculation of $QS_{biota,\ hh}$ in water are: BCF=25 000, $BMF_1$=1 and $BMF_2$=42 (see section 5.1).

| Tentative $QS_{biota,\ hh}$ | Relevant study for derivation of $QS_{biota,\ hh}$ | AF | Threshold level | Tentative $QS_{biota,\ hh}$ |
|---|---|---|---|---|
| **Human health** | 0.22 $mg.kg^{-1}_{bw}.d^{-1}$ | 100 | 0.002 $mg.kg^{-1}_{bw}.d^{-1}$ | 134 $\mu g.kg^{-1}_{biota\ ww}$<br>corresponding to<br>5.36 $10^{-3}$ $\mu g.l^{-1}$ (freshwater)<br>1.28 $10^{-4}$ $\mu g.l^{-1}$ (marine waters) |

| Human health via consumption of drinking water | | Master reference |
|---|---|---|
| **Existing drinking water standard(s)** | 0.1 $\mu g.l^{-1}$ (preferred regulatory standard) | Directive 98/83/EC |
| **Drinking water standard(s) (*calculated*)** | | |

The existing regulatory standards (Directive 98/83/EC) are less stringent than the proposed $QS_{water}$. Therefore, a quality standard for drinking water abstraction is not needed.

**(35) Perfluorooktansulfonska kislina in njeni derivati (PFOS)**

# 5 ENVIRONMENTAL BEHAVIOUR

## 5.1 ENVIRONMENTAL DISTRIBUTION

| | | Master reference |
|---|---|---|
| **Water solubility** ($mg.l^{-1}$) | 519mg/l at 20°C<br>570mg/l in pure water<br>370mg/l in fresh water<br>12.4mg/l at 22-23°C in natural seawater | Environment Agency, 2004<br>RIVM 2010 |
| **Volatilisation** | Volatilisation from water surfaces is negligible | Environment Agency, 2008 |
| **Vapour pressure** (Pa) | $3.31x10^{-4}$ Pa (measured for the potassium salt) (may be associated uncertainties with this result as suggestion that this result may be due to volatile impurities in the substance)<br>$1.9x10^{-9}$ Pa (calculated for the potassium salt)<br>$3.1x10^{-11}$ Pa (calculated for the diethanolamine salt)<br>0.85 Pa (calculated for the acid) | Environment Agency, 2004 |
| **Henry's Law constant** ($Pa.m^3.mol^{-1}$) | $3.19x10^{-4}$ Pa | Environment Agency,2004 |
| **Adsorption** | | |
| **Organic carbon – water partition coefficient ($K_{OC}$)** | $K_{OC}$ = 66 (However study considered to be of low reliability).<br>Kd in sediment 7.42 | Environment Agency,2008 |
| **Sediment – water partition coefficient($K_{sed-water}$)** | 5.16 (potassium salt) | Environment Agency, 2004 |
| **Bioaccumulation** | | |
| **Octanol-water partition coefficient (Log Kow)** | A reliable measured value is not available. The reliability of Kow prediction tools for PFOS is not | Environment Agency, 2004 |

| | | |
|---|---|---|
| | known. | |
| BCF (measured) | 2796<br>(This value was chosen as the BCF for fish in the voluntary risk assessment) | Environment Agency, 2004<br>3M, 2003 in RIVM 2010 |

## 5.2 ABIOTIC AND BIOTIC DEGRADATIONS

| | | Master reference |
|---|---|---|
| **Hydrolysis** | No hydrolysis (Estimated half life of >41years at 25°C) | Environment Agency, 2004 |
| **Photolysis** | No evidence of photolysis (estimated half life of >3.7years) | Environment Agency, 2004 |
| **Biodegradation** | None of the available studies showed biodegradation of PFOS in the aquatic environment under either aerobic or anaerobic conditions | Environment Agency,2004 |

# 7 EFFECTS AND QUALITY STANDARDS

The available data on the toxicity of PFOS to aquatic life has been collated and reviewed by an number of organisations, including OECD (2002), RIVM (2010) and Environment Canada (2006). Some of the key acute and chronic toxicity studies for PFOS are outlined in the tables below.

## 7.1 ACUTE AND CHRONIC AQUATIC ECOTOXICITY

| ACUTE EFFECTS | | | Master reference |
|---|---|---|---|
| Algae & aquatic plants ($mg.l^{-1}$) | Freshwater | *Selenastrum capricornutum* /96 h<br>$EC_{50}$ : 71mg/l and 126mg/l | Environment Agency,2004 |
| | | Selenastrum capricornutum/96h<br>$EC_{50}$: 48.2mg/l * | Environment Agency,2008 |
| | | Pseudokirchneriella subcapitata / 72 h $EC_{50}$: 120 mg/l | OECD, 2002 in RIVM 2010 |
| | | *Navicula pelliculosa* / 96 h<br>$EC_{50}$: 283 mg/l | OECD, 2002 in RIVM 2010 |
| | | *Chlorella vulgaris*/96h<br>$EC_{50}$: 81.6 mg/l | Environment Agency,2004<br>Boudreau et al, 2003 in RIVM 2010 |
| | | *Anabaena flos-aquae* / 96h<br>$EC_{50}$: 176 mg/l | Environment Agency,2004<br>OECD, 2002 in RIVM 2010 |
| | | *Lemna gibba* / 7d $EC_{50}$: 31.1mg/l | Environment Agency,2004<br>Boudreau et al, 2003 in RIVM 2010 |
| | Marine | *Skeletonema costatum*/96 h<br>$EC_{50}$ : >3.2mg/l | Environment Agency,2004 |
| Invertebrates ($mg.l^{-1}$) | Freshwater | *Daphnia magna* / 48 h<br>$EC_{50}$ : 27 mg/l | Environment Agency,2004 |
| | | *Daphnia magna* / 48 h<br>$EC_{50}$: 4 mg/l ** | Environment Agency,2008 |
| | | *Daphnia magna* / 48 h<br>$EC_{50}$: 48 mg/l (geometric mean of 6 values) | OECD, 2002, Boudreau et al, 2003, Ji et al 2008, and Li, 2009 in RIVM 2010 |
| | | *Daphnia pulicaria* / 48 h<br>$EC_{50}$: 124 mg/l | Boudreau et al, 2003 in RIVM 2010 |
| | | *Moina macrocopa / 48* h<br>$EC_{50}$: 18 mg/l | Ji et al, 2008 in RIVM, 2010 |
| | | *Neocaridina denticulate* / 96 h<br>$EC_{50}$: 9.3 mg/l | Li, 2009 in RIVM 2010 |
| | | *Dugesia japonica* / 96 hr<br>$LC_{50}$: 18 mg/l (geometric mean of two values) | Li, 2008 and Li, 2009 in RIVM 2010 |

| | | | |
|---|---|---|---|
| | | *Physa acuta* / 96 hr<br>$LC_{50}$: 165 mg/l | Li, 2009 in RIVM 2010 |
| | | *Unio complamatus* / 96 hr<br>$LC_{50}$: 59 mg/l | Environment Agency,2004<br>OECD, 2002 in RIVM 2010 |
| | **Marine** | *Mysid shrimp (Americamysis bahia)* / 96 h<br>$EC_{50}$ : 3.6mg/l | Environment Agency,2004<br>OECD, 2002 in RIVM 2010 |
| | | *Brine shrimp (Artemia spp)* / 48hr<br>$LC_{50}$: 8.9 mg/l | Environment Agency,2004 |
| | | *Artemia* spp / 48 hr<br>$LC_{50}$: 8.3 mg/l | OECD, 2002 in RIVM 2010 |
| | | *Crassostrea virginica (Eastern oyster)* 96hr EC50 >3.0mg/l (Shell deposition) | Wildlife international (2000) referenced in OECD 2002 |
| | **Sediment** | No data | |
| **Fish**<br>**(mg.l$^{-1}$)** | **Freshwater** | *Fathead minnow (Pimephales promelas* /96 h<br>$EC_{50}$ : 4.7mg/l *** | Environment Agency,2004 |
| | | *Fathead minnow (Pimephales promelas*/96h<br>LC50: 9.5mg/l | Environment Agency,2008 |
| | | *Pimephales promelas* / 96 h<br>$LC_{50}$: 6.6 mg/l (geometric mean of two values) | OECD, 2002 in RIVM 2010 |
| | | *Bluegill sunfish (Lepomis macrochirus)* / 96 h<br>$LC_{50}$: 6.9 mg/l | Environment Agency,2004 |
| | | *Lepomis macrochirus* / 96 h<br>$LC_{50}$: 6.4 mg/l | OECD, 2002 in RIVM 2010 |
| | | *Oncorhynchus mykiss* / 96h<br>$LC_{50}$: 7.8mg/l | Environment Agency,2008 |
| | | *Oncorhynchus mykiss* / 96 h<br>$LC_{50}$: 13 mg/l (geometric mean of two values) | OECD, 2002 in RIVM 2010 |
| | **Marine** | *Sheepshead minnow (Cyprinodon variegatus*/ 96hr<br>$EC_{50}$ : >15mg/l | Environment Agency,2004 |

| | | | |
|---|---|---|---|
| | | *Oncorhynchus mykiss* / 96h<br>LC50: 13.7mg/l | Environment Agency,2004<br>OECD, 2002 in RIVM 2010 |
| **Other taxonomic groups** | | | |

* Noted that this study should be considered with care as it is based on nominal concentrations and the study duration is longer than the recommended test duration.

** This value was generated in a static system with nominal concentrations and therefore the data should be treated with care.

*** This study was conducted in a static system with nominal test concentrations and should therefore be treated with care.

| CHRONIC EFFECTS | | | Master reference |
|---|---|---|---|
| Algae & aquatic plants ($mg.l^{-1}$) | Freshwater | *Selenastrum capricornutum*/96h<br>$EC_{10}$: 5.3mg/l * | Environment Agency, 2008 |
| | | *Lemna gibba*/7d<br>NOEC: 15.1mg/l | Environment Agency,2004 |
| | | *Lemna gibba*/42d<br>$EC_{10}$: 0.2mg/l ** | Environment Agency,2008 |
| | | *Chlorella vulgaris* / 96h<br>$EC_{10}$: 8.2mg/l | Environment Agency,2008<br>Boudreau et al, 2003 in RIVM, 2010 |
| | | *Navicula pelliculosa* / 96 h<br>NOEC: 44mg/l | Environment Agency,2004<br>OECD, 2002 in RIVM 2010 |
| | | *Rhapidocelis subcapitata* /96h<br>$EC_{10}$: 53mg/l | OECD, 2002 in RIVM, 2010 |
| | | *Anabaena flos-aqua* /96h<br>NOEC: 44mg/l | OECD, 2002 in RIVM, 2010 |
| | | *Lemna gibba*/7d<br>$EC_{10}$: 6.6mg/l | Environment Agency,2008<br>Boudreau et al., 2003 in RIVM, 2010 |
| | | *Myriophyllum sibiricum* / 42 d<br>NOEC: 0.092mg/l | Hanson et al, 2005 in RIVM 2010 |
| | | *Myriophyllum spicatum* / 42 d<br>NOEC: 3.2mg/l | Hanson et al, 2005 in RIVM, 2010 |
| | Marine | *Skeletonema costatum* /96h<br>NOEC : >3.2mg/l | Environment Agency,2004<br>OECD, 2002 in RIVM, 2010 |
| Invertebrates ($mg.l^{-1}$) | Freshwater | *Daphnia magna* / 21 d<br>NOEC : 12 mg/l | Environment Agency,2004 |
| | | *Daphnia magna*/28d<br>NOEC: 7mg/l *** | Environment Agency,2004 |
| | | *Daphnia magna*/21d<br>NOEC: 5.3mg/l *** | Environment Agency,2004 |
| | | *Daphnia magna* / 21/28 d<br>NOEC: 7.0 mg/l (geomean of 4 values) | Boudreau et al, 2003, OECD, 2002 and Ji et al, 2008 in RIVM, 2010 |
| | | *Moina macrocopa / 7 d*<br>EC10: 0.40mg/l | Ji et al, 2008 in RIVM 2010 |

| | | | |
|---|---|---|---|
| | | *Chironomus tentans* / 10d<br>NOEC: 0.049mg | Environment Agency,2008 |
| | | *Chironomus tentans* / 36d<br>NOEC: 0.049mg <0032mg/l<br>LOEC with 32% effect | MacDonald et al, 2004 in RIVM, 2010 |
| | | *Chironomus tentans* / 36d<br>NOEC: <0.002mg<br>LOEC 0.002mg/l | MacDonald et al, 2004 in RIVM, 2010 |
| | | *Enallagma cyathigerum* / 120 d<br>NOEC: <0.01mg/l<br>LOEC with 18% effect | Bots et al, 2010 in RIVM 2010 |
| | **Marine** | *Mysidopsis bahia* / 35 d<br>NOEC：0.25mg/l | Environment Agency,2004<br>OECD, 2002 in RIVM 2010 |
| | **Sediment** | No data | |
| **Fish**<br>**(mg.l$^{-1}$)** | **Freshwater** | Fathead minnow (*Pimephales promelas* / 42d<br>NOEC：0.3mg/l | Environment Agency,2004 |
| | | Fathead minnow (*Pimephales promelas*) / 21d<br>NOEC: 0.028mg/l | Environment Agency,2008<br>Ankley et al, 2005 in RIVM, 2010 |
| | | *Oryzias latipes* / 14 d<br>NOEC: <0.01mg/l<br>LOEC with 80% effect | Ji et al, 2008 in RIVM, 2010 |
| | | Bluegill sunfish (*Lepomis macrochirus* / 62d<br>NOEC: <0.87mg/l | |
| | **Marine** | No data | |
| **Other taxonomic groups** | | *Xenopus leavis* / 96 h<br>NOEC: 5.0mg/l | |

*Noted that the algal study needs to be treated with care as based on nominal concentrations and also of 96hr duration rather than the test recommendation of 72hrs.

** Noted that this data generated in an outdoor microcosm study and the study details are incomplete

*** Noted that these studies were undertaken with nominal concentrations and therefore should be treated with care. Lowest valid datapoint is 12mg/l.

## 7.2 DERIVATION OF THE MAC-QS$_{WATER,ECO}$

Short term toxicity data are available for five taxonomic groups including algae, amphibians, crustaceans, fish and molluscs (Environment Agency, 2008). According to the TGD-EQS (EC 2011) freshwater and saltwater data can be pooled unless there is evidence that sensitivity of organisms differs between freshwater and saltwater environments. The available dataset is insufficient to enable a statistical comparison of the freshwater and saltwater data to identify whether there is a significant difference. The available data however do not point to a difference in sensitivity, and therefore the freshwater and saltwater data for PFOS have been pooled. This approach has also been taken in other existing reviews of the data on PFOS, eg RIVM (2010).

### 7.2.1 Freshwater MAC-QS$_{freshwater,eco}$

Although acute data was available for a number of species, the range of taxonomic groups covered was insufficient to enable use of the Species Sensitivity Distribution approach to derive the MAC-QS. The assessment factor approach has therefore been used.

Acute toxicity data was available for a number of taxonomic groups including algae, crustaceans, molluscs and fish. The lowest reliable acute toxicity study from the available dataset for PFOS is a 96hr LC50 study on the marine invertebrate Mysidopsis bahia. The 96hr LC50 was 3.6mg/l. The TGD-EQS (EC 2011) notes that an assessment factor of 100 should be applied to the lowest reliable acute endpoint if acute data is available for the three trophic levels, ie fish, invertebrate and algae. An assessment factor of 100 was therefore applied to the lowest acute effect concentration of 3.6mg/l. This gives a MAC-QS for the freshwater environment of 0.036mg/l (36µg/l).

### 7.2.2 Saltwater MAC-QS$_{saltwater,eco}$

As noted above the lowest reliable acute toxicity study from the available dataset for PFOS is a 96hr LC50 study on the marine invertebrate Mysidopsis bahia. The 96hr LC50 was 3.6mg/l. In the case of the freshwater value an assessment factor of 100 was applied to derive the QS. The AFs for use in the derivation of QS$_{saltwater, eco}$ however are generally higher than for the freshwater environment as outlined in the TGD-EQS (EC 2011). The guidance notes this is justified by the need to account for the additional uncertainties associated with the extrapolation for the marine ecosystem, especially the general under representation in the experimental dataset of specific marine taxa and possibly a greater species diversity. An additional AF of 10 is therefore proposed for saltwater in the TGD-EQS, which can be lowered if data is available for additional marine taxonomic groups. The dataset for PFOS includes a reliable acute toxicity study for the marine mollusc Crassostrea virginica. The availability of this study enables the additional assessment factor to be reduced to 5 rather than 10. This results in an assessment factor of 500 being applied to the acute study on Mysidopsis bahia of 96hr LC50 3.6mg/l. This gives a proposed MAC-QS of 0.0072mg/l (ie 7.2µg/l).

## 7.3 DERIVATION OF THE AA-QS$_{WATER,ECO}$

Long term data are available for seven taxonomic groups including algae, cyanophyta, crustaceans, insects, fish, macrophytes, and amphibians. The lowest effect concentrations are noted in Section 7.1. Although chronic data was available for a number of species the range of taxonomic groups covered was insufficient to enable use of the Species Sensitivity Distribution approach to derive the AA-QS. The assessment factor approach has therefore been used.

### 7.3.1 Freshwater AA-$QS_{freshwater,eco}$

The lowest chronic NOECs for a number of invertebrates and fish are in a similar order of magnitude with a number of NOECs being reported in the range of 0.01 – 0.095mg/l. The lowest chronic NOECs however have been reported for the invertebrates Chironomus tentans and Enallagma cyathigerium. A NOEC for total emergence of Chironomus tentans (MacDonald et al 2004) indicated a NOEC of <0.0023mg/l. A NOEC for Enallagma cyathigerium (Bots et al 2009) for effects on metamorphosis indicated effects at concentrations of <0.01mg/l. Both of these NOECs relate to the study of the effect of PFOS on the emergence of invertebrates. This looks to be a particularly sensitive endpoint. In terms of the Chironomus tentans study the EC10 for total emergence was reported as 0.0893mg/l which is considerably higher than the NOEC of <0.0023mg/l. The paper by Mac Donald et al (2004) however does not indicate any reason to not consider the NOEC for this endpoint.

As chronic data is available for three trophic levels an assessment factor of 10 can be applied to the lowest reliable NOEC or EC10 value. Applying an assessment factor of 10 to the lowest NOEC of 2.3µg/l gives a AA-$QS_{freshwater,eco}$ of 0.23µg/l. It is recognised that the endpoint which has been used to derive the AA-QS is an unbounded NOEC and therefore there is uncertainty associated with the QS derived. The $QS_{biota,hh}$ however is the key driving QS for PFOS based on the available information.

### 7.3.2 Saltwater AA-$QS_{saltwater,\ eco}$

Chronic data was available for algae, invertebrates and fish. Data was not available for an additional marine taxonomic group and therefore, as explained in the TGD-EQS (EC 2011), an additional factor of 10 was applied to derive the AA-$QS_{saltwater,eco}$. This results in the application of an assessment factor of 100 to the lowest NOEC value of 2.3µg/l to give a AA-$QS_{saltwater,eco}$ of 0.023µg/l.

## 7.4 DERIVATION OF THE $QS_{SEDIMENT}$

The criteria for triggering the development of a $QS_{sediment}$ are identified in the TGD-EQS (EC 2011). The criteria include log Koc and log Kow properties, toxicity to benthic organisms and evidence of accumulation of PFOS in sediment.

A log Kow is not able to be calculated for PFOS and therefore this information is not available. Reported log Koc values for PFOS are 1.8 (RIVM, 2010) and 2.57 (EFSA, 2008). Both these values are below the threshold of 3. No data is available on the toxicity of PFOS to sediment dwelling organisms and therefore it is not possible to determine whether PFOS is of high toxicity to benthic organisms.

The final criterion relates to evidence of accumulation of PFOS in sediments. Reports have been obtained of the presence of PFOS in sediment. Monitoring data collated for the review of the Priority Substances list included data for sediment from 2 Member States which gave a PEC1 of 3.12µg/kg dw and a PEC 2 of 1.98µg/kg dw. The data was for 62 analyses within the 2 Member States of which 22 were below the limit of detection. Studies have reported rapid adsorption of PFOS to soil, sediment and sludge. Desorption studies showed that desorption took place rapidly and that river sediment s displayed the most desorption at 39% after 48hrs (Environment Canada, 2006). If released to water the distribution was expected to have 4.2% distribution to sediment and 83.18% in water (Environment Agency, 2004).

Based on the above it is felt that insufficient information is available to support a decision to derive a sediment threshold for PFOS. The lack of sediment toxicity data would mean that if a $QS_{sediment}$ was to be derived for PFOS the Equilibrium Partitioning (EqP) approach would need to be used. The validity of this approach for a substance such as PFOS has been questioned. Work undertaken by the OECD (2002) noted that for an anionic surfactant such as PFOS it is likely that interaction with inorganic substrate as well as organic substrate will be important. As a result Kp soil/sediment data was noted to be more relevant than Koc data which assumes that only the organic components of sediment or soil are important. The OECD report also noted that whilst for all substances extrapolation of PNEC from aquatic data to the terrestrial or sediment compartment is subject to uncertainty that uncertainty is compounded when the mode of uptake is different for organisms present in different environmental compartments. The mode of toxic action and the mechanism of uptake of surfactants such as PFOS were noted to be complex and therefore the use of the EqP approach is subject to considerable doubt. The OECD report concluded that on the basis of the presently available data for PFOS that the equilibrium partitioning theory can not be applied to determine a PNEC for PFOS. The following reasons were given:-

- the nature of the adsorption process can not be assumed to be linearly dependent upon concentration
- the adsorption is likely to be highly independent upon soil composition, particularly the inorganic component
- the rate at which equilibrium might be achieved is unknown.

In summary it is therefore proposed that there is insufficient data available to confirm the need for a $QS_{sediment}$ for PFOS and that in addition there would be insufficient data to derive such a threshold for PFOS.

| Tentative $QS_{water}$ | Relevant study for derivation of QS | Assessment factor | Tentative QS | Reference |
|---|---|---|---|---|
| $MAC_{freshwater, eco}$ * | Mysidopsis bahia/ 96hr LC50: 3.6mg/l | 100 | 36µg/l | Environment Agency (2004) |
| $MAC_{marine\ water, eco}$ | | 500 | 7.2µg/l | |
| $AA\text{-}QS_{freshwater, eco}$ | *Chironomus tentans* / 36d NOEC : <0.0023mg.$l^{-1}$ | 10 | 0.23 µg.$l^{-1}$ * | McDonald et al 2004 |
| $AA\text{-}QS_{marine\ water, eco}$ | | 100 | 0.023 µg.$l^{-1}$ * | |

## 7.5 DERIVATION OF A QS FOR SECONDARY POISONING ($QS_{BIOTA, SECPOIS}$)

The available toxicity data for PFOS has been collated and reviewed by a number of organisations, eg OECD (2002), EFSA (2008). Details of a number of the lowest reported effect concentrations are noted in the table below.

| Secondary poisoning of top predators | | Master reference |
|---|---|---|
| Mammalian oral toxicity | Rat / Gavage / gestation studies (AF 90) / gestation length and pup viability<br>NOAEL : 0.37mg.kg$^{-1}_{bw}$.d$^{-1}$<br>NOEC : 7.4 mg.kg$^{-1}_{feed}$ (CF = 20) | Luebker et al, 2005 in RIVM, 2010 |
| | Rat / diet / 90-d (AF 90) / Body weight<br>NOAEL : >1.5-2 mg.kg$^{-1}_{bw}$.d$^{-1}$<br>NOEC : 30 mg.kg$^{-1}_{feed}$ (CF 15 and 13.3 from studies) | Seacat et al, 2003 and Goldenthal et al, 1978a in RIVM, 2010 |
| | Rat / Diet / Chronic (AF 30) / Carcinogenicity<br>NOAEL : 0.14 mg.kg$^{-1}_{bw}$.d$^{-1}$<br>NOEC : 2 mg.kg$^{-1}_{feed}$ (CF 14.3from study) | Thomford, 2002 and Christian et al, 1999 in RIVM, 2010 |
| | Rat / Gavage / two generations (AF 30) / birth weight F2 generation<br>NOAEL : 0.1 mg.kg$^{-1}_{bw}$.d$^{-1}$<br>NOEC : 2 mg.kg$^{-1}_{feed}$ (CF 20) | |
| | Mouse / Gavage / gestation studies (AF 90) / malformations (sternal defects)<br>NOAEL : 1 mg.kg$^{-1}_{bw}$.d$^{-1}$<br>NOEC : 8.3 mg.kg$^{-1}_{feed}$ (CF = 8.3) | Thibodeaux et al, 2003 in RIVM 2010 |
| | Rabbit / Gavage / gestation studies (AF 90) / maternal weight gain<br>NOAEL : 0.1 mg.kg$^{-1}_{bw}$.d$^{-1}$<br>NOEC : 3.33 mg.kg$^{-1}_{feed}$ (CF = 33.3) | Case et al, 2001 |
| | Rhesus monkey / Gavage / 90-d (AF 90) / Severe gastrointestinal effects<br>NOAEL : 0.5 mg.kg$^{-1}_{bw}$.d$^{-1}$<br>NOEC : 10 mg.kg$^{-1}_{feed}$ (CF = 20) | Goldenthal et al, 1978b in RIVM, 2010 |
| | Cynomolgus monkey / Intubation / 26-w (AF 30) / Body weight, survival<br>NOAEL : 0.15 mg.kg$^{-1}_{bw}$.d$^{-1}$<br>NOEC : 3 mg.kg$^{-1}_{feed}$ (CF = 20) | Seacat et al, 2002 |
| Avian oral toxicity | Mallard duck / Diet / 21-w (AF 30) / Body weight, reproduction<br>NOAEL : 1.49 mg.kg$^{-1}_{bw}$.d$^{-1}$<br>NOEC : 10 mg.kg$^{-1}_{feed}$ (CF = 6.7 from study) | Newsted et al 2007 in RIVM 2010 |

| | | |
|---|---|---|
| | Mallard duck / Diet / 21-w (AF 30) / Body weight, reproduction<br>NOAEL : 0.77 $mg.kg^{-1}_{bw}.d^{-1}$<br>NOEC : 10 $mg.kg^{-1}_{feed}$ (CF = 13 from study) | Newsted et al 2007 in RIVM 2010 |

Both mammalian and avian toxicity data were considered. The available data indicated that mammalian species were more sensitive than avian species and therefore the QS has been based on mammalian data.

Several studies have reported NOAEL values around the 0.1mg/kg bw/day. These include:-

| Species | Test Duration | Endpoint | Effect concentration | Reference |
|---|---|---|---|---|
| Rat | 2 generation | Pup weight | NOAEL 0.1mg/kg bw | Christian et al 1999 |
| Rabbit | Gestation day 6-20 | Maternal weight gain | NOAEL 0.1mg/kg | Case et al 2001 |
| Cynomologus monkey | 183day | Body weight<br>Hormone | NOAEL 0.15mg/kg<br>NOAEL 0.03mg/kg | Seacat et al 2002 |

A two generation study in rats (Christian et al 1999) showed high sensitivity for PFOS. A NOAEL of 0.1mg/kg bw/day was reported based on significant reductions in mean pup body weight. The NOAEL for the F0 generation male and female parents was 0.1mg/kg based on reductions in body weight gain and food consumption – this was the same NOAEL for the F1 females. In addition a NOAEL of 0.1mg/kg was noted for the F2 generation offspring based on significant reductions in mean pup body weight.

Case et al (2001) administered PFOS to pregnant New Zealand white rabbits from gestation day 6-20. The NOAEL of 0.1mg/kg bw/day related to maternal toxicity (reduced weight gain).

The study by Seacat et al (2002) on the Cynomologus monkey was a 6 month study (183days) and was reported as a subchronic study. The original paper by Seacat et al (2002) noted a NOAEL of 0.15mg/kg bw day. This was due to the fact that they noted that there was uncertainty concerning the significance of the lowered HDL observed in females at 0.15mg/kg bw day. EFSA (2008) recently reviewed this study . They considered the observed changes in thyroid hormones and HDL to be treatment related and therefore concluded it was justified to consider the NOAEL of 0.03mg/kg bw/day to be valid. This endpoint was used by EFSA as the basis of the derivation of the Tolerable Daily Intake (TDI) for PFOS (EFSA, 2008). The NOAEL of 0.03mg/kg bw/day has been used by the US EPA to derive their provisional health advisory value for PFOS (2009) and has also been quoted by other regulatory bodies, eg the UK Health Protection Agency. The question arises as to the relevance of the effects observed at the NOAEL endpoint of 0.03mg/kg in relation to population level effects. Following consideration and discussion at meetings of the EU Sub-Group on the Review of Priority Substances it is proposed that the NOAEL of 0.15mg/kg should be considered in terms of the derivation of a $QS_{biota,secpois}$ due to the uncertainty around the population effects of the changes seen in relation to hormone levels.

Based on the above the lowest reported NOAEL for PFOS is therefore 0.1mg/kg bw/day which was derived in both the study by Christian et al (1999) and Case et al (2001). It is proposed that the NOAEL derived from the 2 generation rat study undertaken by Christian et al (1999) is used as the basis of the derivation of the $QS_{biota,secpois}$. This was a 2 generation study with the NOAEL of 0.1mg/kg being reported for effects observed in the F0, F1 and F2 generation. The study by Case et al (2001) on the other hand related to exposure during gestation day 6-20 and the NOAEL related solely to maternal toxicity (reduced weight gain). The NOAEL of 0.1mg/kg can be converted to a NOEC using the conversion factor of 20 taken from the REACH guidance and included in the EC TGD-EQS. This gives a NOEC of 2mg/kg. To derive a $QS_{biota,secpois}$ based on this NOEC an assessment factor of 30 has been applied to this chronic study as identified in the TGD-EQS. This gives a $QS_{biota,secpois}$ of 0.067mg/kg bw.

However it is recognised that the Cynomologus monkey study by Seacat et al (2002) is a subchronic study based on the lifespan of this species and that the chronic effects are therefore not known. A lower NOAEL of 0.03mg/kg has been reported for this study however as noted above it was proposed that the NOAEL of 0.15mg/kg should be considered in terms of the derivation of a $QS_{biota,secpois}$ due to the uncertainty around the population effects of the changes seen in relation to hormone levels. Applying a conversion factor of 20 to this NOAEL gives a NOEC of 3mg/kg food. An assessment factor of 90 is applied as this study is of 183days duration and is reported to be a subchronic study. Application of an assessment factor of 90 gives a $QS_{biota,secpois}$ of 0.033mg/kg bw.

Due to the fact that this is a subchronic study rather than a chronic study and effects have been reported at lower levels (NOAEL 0.03mg/kg for hormone changes) it is proposed that the lower value ie that derived from the Cynomologus study is used for the $QS_{biota,secpois}$ rather than that derived based on the rat study undertaken by Christian et al 1999. This gives a $QS_{biota,secpois}$ of 0.033mg/kg bw.

Conversion of the $QS_{biota,secpois}$ to a concentration in water is undertaken using the formula proposed in the TGD-EQS (see below).

$$QS_{freshwater} = QS_{biota,secpois}/(BCF \times BMF)$$

$$QS_{saltwater} = QS_{biota,secpois}/(BCF \times BMF1 \times BMF2)$$

A range of BCF values have been reported for PFOS ranging from information on accumulation in specific fish organs/tissues, eg liver, through to BCF values for the whole organism. Information on BCFs for the whole organism are required for the above calculation. The highest, reliable BCF value for whole fish was noted to be 2796. This has been used to calculate the water concentration.

In terms of BMF1 and BMF2 values, default values are provided in the TGD-EQS (EC 2011). The default values used depend on both the log Kow and the BCF values for fish. The default values therefore apply to lipophilic, hydrophobic substances. PFOS is not lipophilic but instead binds to proteins. A log Kow cannot be derived for PFOS. Use of the default values for BMF1 and BMF2 are therefore not appropriate for PFOS. RIVM (2010) and Environment Canada (2006) have both produced reviews on PFOS which have included information on BMF values. The RIVM report notes BMF1 values in the range of 0.77 – 6 but that the reliability of these studies is either 3 or 4. In terms of BMF2 values these are reported in the range of 1.4 – 4.6 although again the reliability of the studies is noted as either 3 or 4. RIVM used values of 5 for both BMF1 and BMF2 in their derivation of risk limits for secondary poisoning. Environment Canada (2006) reported BMF values in the range of 0.4 – 5.88. This is a similar range to that reported by RIVM (2010).

As noted above RIVM note that the reliability of the studies from which the BMF values are reported is low, ie 3 or 4. Although each individual study has a low reliability score the weight of evidence may be used to determine a BMF1 for PFOS. If the BMF1 values for PFOS are averaged this gives a BMF1 value of approximately 5. It is therefore proposed that a BMF1 value of 5 is applied. In terms of the BMF2 value the values range from 1.4 – 4.6. If the same approach is applied, ie the data is used as a weight of evidence

and an average is derived it gives a BMF2 value of approximately 2. Due to the uncertainties associated with the data available in relation to BMF2 however and evidence of detection of PFOS in higher trophic levels it is proposed to use the same value as the BMF1, ie 5 for BMF2.

Using the formula shown above from the TGD-EQS a $QS_{biota,secpois}$ in water is derived. The BCF value used is 2796, the BMF value of 5 and a $QS_{biota,secpois}$ of 0.033mg/kg bw. This gives a freshwater concentration of 0.000002mg/l (0.002µg/l). For saltwater a QS of 0.00000047mg/l is derived (0.00047µg/l).

| Tentative $QS_{biota}$ | Relevant study for derivation of QS | Assessment factor | Tentative QS | Source |
|---|---|---|---|---|
| Biota | Cynomolgus monkey 183d NOAEL 0.15mg/kg (NOEC 3.3mg/kg food) | 90 | 0.033mg/kg<br>0.002µg/l (freshwater)<br>0.00047µg/l (saltwater) | Seacat et al 2002 |
| | | | | |

## (37) Dioksini in njim podobne spojine



# 5 ENVIRONMENTAL BEHAVIOUR

## 5.1 ENVIRONMENTAL DISTRIBUTION

Values reported in the table below are either estimated or calculated/extrapolated from experimental values.

| | | | Master reference |
|---|---|---|---|
| Water solubility ($mg.l^{-1}$) | PCDDs | | US-EPA, 2003 |
| | 2,3,7,8-$T_4$CDD | $1.93\ 10^{-5}$ (25°C) | |
| | 1,2,3,7,8-$P_5$CDD | — | |
| | 1,2,3,4,7,8-$H_6$CDD | $4.42\ 10^{-6}$ (25°C) | |
| | 1,2,3,6,7,8-$H_6$CDD | — | |
| | 1,2,3,7,8,9-$H_6$CDD | — | |
| | 1,2,3,4,6,7,8-$H_7$CDD | $2.40\ 10^{-6}$ (20°C) | |
| | 1,2,3,4,6,7,8,9-$O_8$CDD | $7.40\ 10^{-8}$ (25°C) | |
| | PCDFs | | |
| | 2,3,7,8-$T_4$CDF | $4.19\ 10^{-4}$ (22.7°C) | |
| | 1,2,3,7,8-$P_5$CDF | — | |
| | 2,3,4,7,8-$P_5$CDF | $2.36\ 10^{-4}$ (22.7°C) | |
| | 1,2,3,4,7,8-$H_6$CDF | $8.25\ 10^{-5}$ (22.7°C) | |
| | 1,2,3,6,7,8-$H_6$CDF | $1.77\ 10^{-4}$ (22.7°C) | |
| | 1,2,3,7,8,9-$H_6$CDF | — | |
| | 2,3,4,6,7,8-$H_6$CDF | — | |
| | 1,2,3,4,6,7,8-$H_7$CDF | $1.35\ 10^{-5}$ (22.7°C) | |
| | 1,2,3,4,7,8,9-$H_7$CDF | — | |
| | 1,2,3,4,6,7,8,9-$O_8$CDF | $1.16\ 10^{-5}$ (25°C) | |
| | DL-PCBs | | |
| | 3,3',4,4'-$T_4$CB [77] | $1.0\ 10^{-3}$ (25°C) | |
| | 3,3',4',5-$T_4$CB [81] | $2.92\ 10^{-3}$ (25°C) | |
| | 2,3,3',4,4'-$P_5$CB [105] | $1.90\ 10^{-3}$ (25°C) | |
| | 2,3,4,4',5-$P_5$CB [114] | $2.58\ 10^{-3}$ (20°C) | |
| | 2,3',4,4',5-$P_5$CB [118] | $1.59\ 10^{-3}$ (20°C) | |
| | 2,3',4,4',5'-$P_5$CB [123] | $1.64\ 10^{-3}$ (25°C) | |
| | 3,3',4,4',5-$P_5$CB [126] | $1.03\ 10^{-3}$ (25°C) | |
| | 2,3,3',4,4',5-$H_6$CB [156] | $4.10\ 10^{-4}$ (20°C) | |
| | 2,3,3',4,4',5'-$H_6$CB [157] | $3.61\ 10^{-4}$ (25°C) | |
| | 2,3',4,4',5,5'-$H_6$CB [167] | $3.61\ 10^{-4}$ (25°C) | |
| | 3,3',4,4',5,5'-$H_6$CB [169] | $3.61\ 10^{-5}$ (25°C) | |
| | 2,3,3',4,4',5,5'-$H_7$CB [189] | $6.26\ 10^{-5}$ (25°C) | |

| | | | Master reference |
|---|---|---|---|
| **Volatilisation** | Given the high potential of accumulation in organic tissues and the high potential to adsorb on particulate matter (see below), volatilisation and evaporation are not major processes of dissipation of DL-compounds from the water phase | | |
| **Vapour pressure** (Pa) | <u>PCDDs</u> | | US-EPA, 2003 |
| | 2,3,7,8-$T_4$CDD | $2.0\ 10^{-7}$ | |
| | 1,2,3,7,8-$P_5$CDD | $5.9\ 10^{-8}$ | |
| | 1,2,3,4,7,8-$H_6$CDD | $5.1\ 10^{-9}$ | |
| | 1,2,3,6,7,8-$H_6$CDD | $4.8\ 10^{-9}$ | |
| | 1,2,3,7,8,9-$H_6$CDD | $6.5\ 10^{-9}$ | |
| | 1,2,3,4,6,7,8-$H_7$CDD | $7.5\ 10^{-10}$ | |
| | 1,2,3,4,6,7,8,9-$O_8$CDD | $1.1\ 10^{-10}$ | |
| | <u>PCDFs</u> | | |
| | 2,3,7,8-$T_4$CDF | $2.0\ 10^{-6}$ | |
| | 1,2,3,7,8-$P_5$CDF | $2.3\ 10^{-7}$ | |
| | 2,3,4,7,8-$P_5$CDF | $3.5\ 10^{-7}$ | |
| | 1,2,3,4,7,8-$H_6$CDF | $3.2\ 10^{-8}$ | |
| | 1,2,3,6,7,8-$H_6$CDF | $2.9\ 10^{-8}$ | |
| | 1,2,3,7,8,9-$H_6$CDF | — | |
| | 2,3,4,6,7,8-$H_6$CDF | $2.7\ 10^{-8}$ | |
| | 1,2,3,4,6,7,8-$H_7$CDF | $4.7\ 10^{-9}$ | |
| | 1,2,3,4,7,8,9-$H_7$CDF | $1.4\ 10^{-8}$ | |
| | 1,2,3,4,6,7,8,9-$O_8$CDF | $5.0\ 10^{-10}$ | |
| | <u>DL-PCBs</u> | | |
| | 3,3',4,4'-$T_4$CB [77] | $5.96\ 10^{-5}$ | |
| | 3,3',4',5-$T_4$CB [81] | $1.05\ 10^{-4}$ | |
| | 2,3,3',4,4'-$P_5$CB [105] | $1.10\ 10^{-4}$ | |
| | 2,3,4,4',5-$P_5$CB [114] | $5.57\ 10^{-5}$ | |
| | 2,3',4,4',5-$P_5$CB [118] | $4.19\ 10^{-5}$ | |
| | 2,3',4,4',5'-$P_5$CB [123] | $1.17\ 10^{-4}$ | |
| | 3,3',4,4',5-$P_5$CB [126] | $3.95\ 10^{-5}$ | |
| | 2,3,3',4,4',5-$H_6$CB [156] | $1.96\ 10^{-5}$ | |
| | 2,3,3',4,4',5'-$H_6$CB [157] | $7.29\ 10^{-6}$ | |
| | 2,3',4,4',5,5'-$H_6$CB [167] | $2.60\ 10^{-5}$ | |
| | 3,3',4,4',5,5'-$H_6$CB [169] | $2.41\ 10^{-5}$ | |
| | 2,3,3',4,4',5,5'-$H_7$CB [189] | $1.75\ 10^{-6}$ | |

| | | | Master reference |
|---|---|---|---|
| **Henry's Law constant** ($Pa.m^3.mol^{-1}$) | <u>PCDDs</u> | | US-EPA, 2003 |
| | 2,3,7,8-$T_4$CDD | 3.33 | |
| | 1,2,3,7,8-$P_5$CDD | — | |
| | 1,2,3,4,7,8-$H_6$CDD | 1.08 | |
| | 1,2,3,6,7,8-$H_6$CDD | — | |
| | 1,2,3,7,8,9-$H_6$CDD | — | |
| | 1,2,3,4,6,7,8-$H_7$CDD | 1.28 | |
| | 1,2,3,4,6,7,8,9-$O_8$CDD | 0.684 | |
| | <u>PCDFs</u> | | |
| | 2,3,7,8-$T_4$CDF | 1.46 | |
| | 1,2,3,7,8-$P_5$CDF | — | |
| | 2,3,4,7,8-$P_5$CDF | 0.505 | |
| | 1,2,3,4,7,8-$H_6$CDF | 1.45 | |
| | 1,2,3,6,7,8-$H_6$CDF | 0.741 | |
| | 1,2,3,7,8,9-$H_6$CDF | — | |
| | 2,3,4,6,7,8-$H_6$CDF | — | |
| | 1,2,3,4,6,7,8-$H_7$CDF | 1.43 | |
| | 1,2,3,4,7,8,9-$H_7$CDF | — | |
| | 1,2,3,4,6,7,8,9-$O_8$CDF | 0.190 | |
| | <u>DL-PCBs</u> | | |
| | 3,3',4,4'-$T_4$CB [77] | 1.72 | |
| | 3,3',4',5-$T_4$CB [81] | 13.0 | |
| | 2,3,3',4,4'-$P_5$CB [105] | 10.1 | |
| | 2,3,4,4',5-$P_5$CB [114] | 6.99 | |
| | 2,3',4,4',5-$P_5$CB [118] | 8.61 | |
| | 2,3',4,4',5'-$P_5$CB [123] | 17.6 | |
| | 3,3',4,4',5-$P_5$CB [126] | 5.47 | |
| | 2,3,3',4,4',5-$H_6$CB [156] | 88.2 | |
| | 2,3,3',4,4',5'-$H_6$CB [157] | 58.8 | |
| | 2,3',4,4',5,5'-$H_6$CB [167] | 11.2 | |
| | 3,3',4,4',5,5'-$H_6$CB [169] | 6.61 | |
| | 2,3,3',4,4',5,5'-$H_7$CB [189] | 6.74 | |

| | | Master reference |
|---|---|---|
| **Adsorption** | The value of $K_{sed-water}$ depends on several factors, including the type of sediment (e.g. grain size) and its organic carbon content (illustrated by $K_{OC}$ values) and the chlorine content of the chemical. Therefore, a large variability can be expected. **For dioxins and DL-compounds, the range can be as wide as 30 – 7.9 $10^6$.** | |
| **log Organic carbon – water partition coefficient (log $K_{OC}$) ($l.kg^{-1}$)** | <u>PCDDs</u><br>2,3,7,8-$T_4$CDD 3.06–8.50<br>1,2,3,4,7,8-$H_6$CDD 5.02–7.10<br><u>PCDFs</u><br>2,3,7,8-$T_4$CDF 5.20–7.50<br>1,2,3,4,7,8-$H_6$CDF 7.40<br>1,2,3,4,7,8,9-$H_7$CDF 5.00–6.70<br>1,2,3,4,6,7,8,9-$O_8$CDF 6.00–7.40<br><u>DL-PCB</u><br>3,3',4,4'-$T_4$CB [77] 4.41–5.75<br>A study from Tanaka et al. provides useful information for predicting the fates and toxicities of polychlorinated dibenzo-*p*-dioxins in the environment, actually it proves that $K_{OC}$ values of hydrophobic organic pollutants such as DL-compounds are significantly related to the polarity and/or hydrophobicity of the humic substances (Tanaka *et al.*, 2005). This can be a reason for the wide range of log $K_{OC}$ reported here. | US-EPA, 2003 |
| **Sediment – water partition coefficient ($K_{sed-water}$) ($m^3.m^{-3}$)** | Calculated values based on the above $K_{OC}$ values from US-EPA, 2003, using the equation recommended in the draft Technical Guidance for deriving EQS (E.C., 2010) $K_{sed-water}$ = 0,8+(0,2*((0,05*Koc)/1000)*2500)<br><u>PCDDs</u><br>2,3,7,8-$T_4$CDD 30 – 7.9 $10^6$<br>1,2,3,4,7,8-$H_6$CDD 2 619 – 3.1 $10^5$<br><u>PCDFs</u><br>2,3,7,8-$T_4$CDF 3 963 – 7.9 $10^5$<br>1,2,3,4,7,8-$H_6$CDF 6.3 $10^5$<br>1,2,3,4,7,8,9-$H_7$CDF 2 501 – 1.3 $10^5$<br>1,2,3,4,6,7,8,9-$O_8$CDF 25 001 – 6.3 $10^5$<br><u>DL-PCB</u><br>3,3',4,4'-$T_4$CB [77] 643 – 14 059 | US-EPA, 2003<br>E.C., 2010 |

| | | | Master reference |
|---|---|---|---|
| **Bioaccumulation / Biomagnification** | According to the values reported thereafter, the BCF values for fish range from around 1 700 – 186 000 (log BCF range ~ 3.2 – 5.3). The range of value is very large depending on the congener considered. Therefore, **it is chosen to use the geometrical mean of the BCF values for derivation of quality standards: 41 540.** Whatever the choice made on the BCF value, it corresponds to **default $BMF_1$ and $BMF_2$ values of 10** according to the Technical Guidance for deriving EQS (E.C., 2011). | | |
| **Octanol-water partition coefficient (log Kow)** | <u>PCDDs</u> | | US-EPA, 2003 |
| | 2,3,7,8-$T_4$CDD | 6.80 | |
| | 1,2,3,7,8-$P_5$CDD | 6.64 | |
| | 1,2,3,4,7,8-$H_6$CDD | 7.80 | |
| | 1,2,3,6,7,8-$H_6$CDD | — | |
| | 1,2,3,7,8,9-$H_6$CDD | — | |
| | 1,2,3,4,6,7,8-$H_7$CDD | 8.00 | |
| | 1,2,3,4,6,7,8,9-$O_8$CDD | 8.20 | |
| | <u>PCDFs</u> | | |
| | 2,3,7,8-$T_4$CDF | 6.1 | |
| | 1,2,3,7,8-$P_5$CDF | 6.79 | |
| | 2,3,4,7,8-$P_5$CDF | 6.5 | |
| | 1,2,3,4,7,8-$H_6$CDF | 7.0 | |
| | 1,2,3,6,7,8-$H_6$CDF | — | |
| | 1,2,3,7,8,9-$H_6$CDF | — | |
| | 2,3,4,6,7,8-$H_6$CDF | — | |
| | 1,2,3,4,6,7,8-$H_7$CDF | 7.4 | |
| | 1,2,3,4,7,8,9-$H_7$CDF | — | |
| | 1,2,3,4,6,7,8,9-$O_8$CDF | 8.0 | |
| | <u>DL-PCBs</u> | | |
| | 3,3',4,4'-$T_4$CB [77] | 6.5 | |
| | 3,3',4',5-$T_4$CB [81] | 6.36 | |
| | 2,3,3',4,4'-$P_5$CB [105] | 6.0 | |
| | 2,3,4,4',5-$P_5$CB [114] | 6.65 | |
| | 2,3',4,4',5-$P_5$CB [118] | 7.12 | |
| | 2,3',4,4',5'-$P_5$CB [123] | 6.74 | |
| | 3,3',4,4',5-$P_5$CB [126] | 6.89 | |
| | 2,3,3',4,4',5-$H_6$CB [156] | 7.16 | |
| | 2,3,3',4,4',5'-$H_6$CB [157] | 7.19 | |
| | 2,3',4,4',5,5'-$H_6$CB [167] | 7.09 | |
| | 3,3',4,4',5,5'-$H_6$CB [169] | 7.46 | |
| | 2,3,3',4,4',5,5'-$H_7$CB [189] | 7.71 | |
| **log BCF** | Log BCF values for PCDD and PCDF congeners measured in fish (Guppy) | | US-EPA, 2003 |

| | | | Master reference |
|---|---|---|---|
| | PCDDs | | |
| | 2,3,7,8-$T_4$CDD | 5.24 | |
| | 1,2,3,7,8-$P_5$CDD | 5.27 | |
| | 1,2,3,4,7,8-$H_6$CDD | 5.01 | |
| | 1,2,3,6,7,8-$H_6$CDD | 4.94 | |
| | 1,2,3,7,8,9-$H_6$CDD | 4.93 | |
| | 1,2,3,4,6,7,8-$H_7$CDD | 4.68 | |
| | 1,2,3,4,6,7,8,9-$O_8$CDD | 4.13 | |
| | PCDFs | | |
| | 2,3,4,7,8-$P_5$CDF | 5.14 | |
| | 1,2,3,6,7,8-$H_6$CDF | 4.95 | |
| | 1,2,3,4,6,7,8-$H_7$CDF | 4.46 | |
| | 1,2,3,4,6,7,8,9-$O_8$CDF | 3.90 | |
| | Log BCF value measured in various fish species | | |
| | DL-PCB | | |
| | 3,3',4,4'-$T_4$CB [77] | 3.24–4.15 | |

## 5.2 ABIOTIC AND BIOTIC DEGRADATIONS

Literature data indicate that PCDDs and PCDFs, particularly the tetra- and higher chlorinated congeners, are extremely stable compounds under most environmental conditions. The only environmentally significant transformation processes for these congeners are believed to be atmospheric photo-oxidation and photolysis of non-sorbed species in the gaseous phase or at the soil or water-air interface (US-EPA, 2003).

| | | | Master reference |
|---|---|---|---|
| **Hydrolysis** | There is no available evidence indicating that hydrolysis would be an operative environmental process for degradation of dioxin-like compounds | | US-EPA, 2003 |
| **Photolysis** | | *Half-life (days)* | |
| | 2,3,7,8-$T_4$CDD | 0.255–0.78 (water/organic solvent mixtures) | |
| | 2,3,7,8-$T_4$CDF | 0.25–1.2 (natural waters) | |
| | 2,3,4,7,8-$P_5$CDF | 0.19 (natural waters) | |
| **Biodegradation** | Several studies have indicated that certain ligninolytic fungi can degrade these higher-chlorinated congeners and that anaerobic degradation in sediment may occur at a slow rate. To a large extent, these degradation processes involve dechlorination to less-chlorinated (and possibly more toxic) congeners | | |

The degradation of PCDDs, PCDFs, and dioxin-like compounds in the environment depends largely on their chemical properties and the environmental media and conditions in consideration. For instance, photodegradation may determine the persistence of the aforesaid compounds in soil by processes predominantly occurring in the topsoil layer. Factors such as the degree of chlorination and the position of the chlorine atoms in the molecule may strongly affect the rate of decomposition (the persistence increases as the degree of chlorination increases). In addition, processes involving transport by wind or water (e.g. runoff) can influence the persistence of the chemicals in soil where they would be otherwise immobile. Reported half-lives in soil vary considerably. For instance, a half-life for 2,3,7,8-$T_4$CDD in soil of one up to 10 years has been reported, although a range of 10–12 years is viewed as most probable (UNEP, 2003).

# 7 EFFECTS AND QUALITY STANDARDS

## 7.1 ACUTE AND CHRONIC AQUATIC ECOTOXICITY

### 7.1.1 Organisms living in the water column

| ACUTE EFFECTS | | | Master reference |
|---|---|---|---|
| Algae & aquatic plants ($mg.l^{-1}$) | Freshwater | No data available | |
| | Marine | No data available | |
| Invertebrates ($mg.l^{-1}$) | Freshwater | Crustacean, unknown species / unknown duration / most probably mixtures of PCB 118 and non-DL-PCBs<br>$EC_{50\ -\ crustaceans} = 2\ 10^{-3}$ | FHI, as cited in FHI, 1999 |
| | Marine | No data available | |
| | Sediment | No data available | |
| Fish ($mg.l^{-1}$) | Freshwater | *Oncorhynchus mykiss* / 56 days / 2,3,7,8-$T_4$CDD<br>$EC_{60} = 4.6\ 10^{-8}$ | Ritter *et al.*, 1995 |
| | Marine | No data available | |
| | Sediment | No data available | |
| Other taxonomic groups | | No data available | |

| CHRONIC EFFECTS | | | Master reference |
|---|---|---|---|
| Algae & aquatic plants ($mg.l^{-1}$) | Freshwater | *Oedogonium cardiacum* / 33d / 2,3,7,8-$T_4$CDD<br>$NOEC = 3.1\ 10^{-9}$ | Yockim *et al.*, 1978 |
| | Marine | No data available | |
| Invertebrates ($mg.l^{-1}$) | Freshwater | *Daphnia magna* / 32d / 2,3,7,8-$T_4$CDD<br>$NOEC = 3.1\ 10^{-9}$ | Yockim *et al.*, 1978 |
| | Marine | No data available | |
| Fish ($mg.l^{-1}$) | Freshwater | *Oncorhynchus mykiss* / 28d / 2,3,7,8-$T_4$CDD<br>$NOEC = 1.1\ 10^{-9}$ | Mehrle *et al.*, 1998 |
| | | *Oncorhynchus mykiss* / 56d / 2,3,7,8-$T_4$CDD<br>$NOEC_{growth\ and\ mortality} = 3.8\ 10^{-8}$ | Ritter *et al.*, 1995 |
| | Marine | No data available | |
| | Sediment | No data available | |
| Other taxonomic groups | | No data available | |

*Acute exposure*

Based on information on the knowledge of possible sources of dioxins and dioxin-like compounds (e.g. mainly unintentionally formed and released origins) long term or continuous releases into the aquatic environment are more likely than episodic releases of high concentrations, except in accidents cases. Chronic exposure of aquatic organisms is therefore expected rather than acute exposure and the need for a quality standards corresponding to short-term exposure may be questioned and is not felt appropriate at this stage based on the available dataset.

*Chronic exposure*

Valid toxicity data available for organisms living in the water column have been reported in the tables above for acute and chronic exposures for information. However, because of their hydrophobic nature, the majority of dioxins and dioxin-like compounds released into aquatic systems ultimately become associated with particulate matter and/or bioaccumulate in aquatic organisms. Given these considerations, uncertainties and difficulties of setting standards for the pelagic community based on waterborne exposure are substantial and it was recommended by the Scientific Committee on Health and Environmental Risks (SCHER, 2011) that biomarkers and other biological monitoring tools should be recommended rather than single chemical analysis in the case of dioxins assessment for water and sediment matrices (cf. section 7.1.3).

### 7.1.2 Sediment-dwelling organisms

Although sediment is a relevant matrix for Dioxins and DL-PCBs, there are no acute or chronic tests on exposure of sediment-dwelling to dioxins or DL-compounds (single or in mixtures) through true spiked sediment/water systems which allow determination of true $L(C)_{50}$, NOEC or $EC_{10}$ values. There are however some sediment quality guidelines/criteria derived by NOAA (Buchman, 2008) or the Canadian Council of Ministers of the Environment (2001) and which are considered as screening/interim values. These are reported in the table below.

| | |
|---|---|
| Freshwater sediment value – Upper Effect Treshold (UET) = 8.8 $ng_{TE}.kg^{-1}_{dw}$<br>(lowest reliable value among AET tests, on 1% total organic carbon basis and based on *Hyalella Azteca* exposed to 2,3,7,8-$T_4$CDD) | Buchman, 2008 |
| Marine sediment value – Apparent Effect Treshold (AET) = 3.6 $ng_{TE}.kg^{-1}_{dw}$,<br>(lowest reliable value among AET tests, based on *Neanthes* exposed to 2,3,7,8-$T_4$CDD) | |
| Interim Sediment Quality Guideline (ISQG) = 0.85 $ng_{TE}.kg^{-1}_{dw}$,<br>based on benthic Invertebrates exposure exposed | Buchman, 2008<br>Canadian Council of Ministers of the Environment, 2001 |

However, these values are qualified as "screening tools" or "interim guidelines" by their authors and can therefore hardly be taken into account to derive legally-binding quality standards such as EQS without a "*clear analysis of the data and methodologies applied by the other bodies, and without a proper assessment of their applicability regarding WFD objectives*" (SCHER, 2011).

### 7.1.3 Relevance of biomarkers and other biological monitoring tools as alternative to single chemical analysis for deriving water and sediment quality standards

Data reported here above for direct ecotoxicity of water as well as toxicity to sediment-dwelling organisms are reported for illustration of the available dataset for these protection objective but can reasonably not be used to derive any $QS_{water, eco}$ nor $QS_{sediment}$ given the uncertainties, difficulties and low relevance of setting EQS for the pelagic community based on waterborne exposure.

However, the possibility for using effect-based monitoring tools for monitoring purposes should be noted here as alternatives to classical EQS compliance check. In this context, the use of *in vitro* cell-based bioassays to assess dioxin-like activities in organic extracts of sediments or water appears as a useful alternative methodology. This tool allows detecting substances characterized by a common mechanism of action: interaction with the Ah receptor. The direct measurement of the biological responses associated to the Ah receptor in water and sediment samples may provide a proper and rapid quantification of the overall potency of dioxin and dioxin-like compounds in the sample, that can be easily expressed as 2,3,7,8-TCDD TEQ. Hence, the results provide a global evaluation of environmental sample contamination by dioxin-like substances (Brack *et al.*, 2005; Brack *et al.*, 2007; Louiz *et al.*, 2008; Kinani *et al.*, 2010) conversely to chemical analysis. The joint effects can be considered as additive, and therefore quantified on the basis of their relative potencies using the TEF approach.

Several methods based on a similar mechanism are commercially available (e.g. DR-CALUX, PLHC 1-EROD) and are used to assess dioxin-like contamination in environmental samples. Some examples are given in the table thereafter for the sediments.

| Bioassays | Sites location | Relative potencies expressed as ng TCDD-TEQ.$g^{-1}_{dw}$ | Master reference |
|---|---|---|---|
| PLHC 1-EROD | *North of France area (France)* | 0.67 – 48.38 | Kinani *et al.*, 2010 |
| | *Bay of Kvarner area (Croatia)* | 6.0 – 132.1 | Traven *et al.*, 1998 |
| DR-CALUX | *UK estuaries (United Kingdom)* | 1.1 – 154 | Hurst *et al.*, 2004 |
| RTL-W1 | *Forellemback creek (Germany)* | 0.01 – 70.06 | Brack *et al.*, 2005 |

These methods can also be used to assess dioxin-like contamination in biota (Thomas *et al.*, 2006).

In biota, biomarker responses and particularly responses linked to cytochrome P450 1A (CYP1A; i.e. gene expression, protein or catalytic activity inductions) could be used to derive a QS for a specific mechanism of action. Indeed, CYP1A induction is due to activation of Ah receptor by dioxin-like substances and is described as a relevant biomarker of dioxin-like exposure (for review, see Whyte *et al.*, 2000). However, many chemicals such as heavy metals or estrogens are known to inhibit CYP1A activity and many biotic and biological factors are also documented as confounding factors. Hence, in a context of multi-contamination, application of a single biomarker such as CYP1A cannot be a relevant methodology to define accurately a QS which is by definition substance-specific. Gene expression/array systems also provide a sensitive measure of early changes but enzyme induction and results from gene expression arrays would only be considered as possible early indicators for potential adverse effects if they are demonstrated to be obligate precursors to an adverse effect and appropriate consideration is given to mechanisms of repair and homeostasis (EFSA, 2004).

As a conclusion, the direct measurement of the biological responses associated to the Ah receptor in water and sediment samples may provide a proper and rapid quantification of the overall potency of dioxin and dioxin-like compounds in the sample. Therefore, screening of ecotoxicological effects may rather be considered using biological responses together with classical EQS compliance check.

## 7.2 SECONDARY POISONING

The effects of dioxins and dioxin-like compounds have been extensively reviewed recently by some authors, (e.g. Bursian *et al.*, 2011) who conclude that these are numerous in humans, mammals and some avian species. These effects notably include female reproductive effects (e.g. reduction in women fecundity, increased preimplantation embryomortality in mammals, presence of endometrial glands and stroma outside the women uterus, reduced ovarian weight, declined fertility and persistent vaginal estrous in mammals, placental hypoxia and delayed maturation of the mammary gland which could increase the incidence of breast cancer due to increase susceptibility of the gland to carcinogens in rats) and male reproductive effects (e.g. decreased testis and accessory organ weight, abnormalities testicular morphology, decreased spermatogenesis and reduce fertility) when given to adult animals in doses sufficient to reduce feed intake and/or body weight. On the overall, these effects occurring at the lowest doses in animal studies result from *in utero* exposures.

Further to its Scientific Colloquium in 2004, EFSA concluded that "the neurological development may also be affected and neurobehavioural endpoints may be a future area for investigation. Also, they added that "non-developmental effects in laboratory animals include immune effects, endometriosis and cancer" (EFSA, 2004).

It is to be noted that the majority of the available toxicological studies on mammals involve acute bolus dosing, and therefore require extrapolation for long term dietary exposure.

| **Secondary poisoning of top predators** | | **Master reference** |
|---|---|---|
| **Mammalian oral toxicity** | Females Wistar rat / Oral / Reproductive study<br>Exposure to 2,3,7,8 TCDD<br>Initial subcutaneous loading doses (2 weeks prior to mating): 25, 60, or 300 $ng.kg^{-1}_{bw}$<br>Weekly maintenance doses: 5, 12, or 60 $ng.kg^{-1}_{bw}$<br>Observation of male offsprings on PND70 and PND170<br>Effects: Decreased sperm production and altered sexual behaviour in male offspring<br>Uncertainties: no clear dose-effect response (E.C., 2001; Bell *et al.*, 2010)<br>LOAEL = 2.5 $10^{-5}$ $mg.kg^{-1}_{bw}.d^{-1}$<br>corresponding to a maternal body burden of 4 $10^{-5}$ $mg.kg^{-1}_{bw}.d^{-1}$ at steady state following subchronic daily administration (E.C., 2001).<br>NOAEL = 1.3 $10^{-5}$ $mg.kg^{-1}_{bw}.d^{-1}$ ($CF_{LOAEL->NOAEL}$=3)<br>NOEC = 1.1 $10^{-4}$ $mg.kg^{-1}_{feed\ ww}$ (CF=8.33, E.C., 2010, to be considered with caution since administration route is subcutaneous) | Faqi *et al.*, 1998 |
| | Females Holtzman rat / Oral / Reproductive study<br>Exposure to 2,3,7,8 TCDD<br>Single doses – GD15: 0, 12.5, 50, 200, 800 $ng.kg^{-1}_{bw}$<br>Observation of male offsprings on PND49 or PND120<br>Effects:<br>- no changes seen on testicular or epididymal weights nor in daily sperm production or sperm reserve at any of the doses used<br>- no apparent dose-dependent changes in levels of either serum testosterone or luteinizing hormone | Ohsako *et al.*, 2001 |

| Secondary poisoning of top predators | | Master reference |
|---|---|---|
| | - significant reduction of the urogenital complex weight, including the ventral prostate, at 200 and 800 ng.kg$^{-1}_{bw}$ doses on PND 120<br>- significant decrease of anogenital distance on PND 120 at 50 ng.kg$^{-1}_{bw}$ doses or higher<br>Uncertainties: effects observed on prostate at PND49 not observed at PND120 (E.C., 2001)<br>NOAEL = 1.25 $10^{-6}$ mg.kg$^{-1}_{bw}$.d$^{-1}$<br>corresponding to a maternal body burden of 3.1 $10^{-5}$ mg.kg$^{-1}_{bw}$.d$^{-1}$, corresponding to a maternal body burden of 2 $10^{-5}$ mg.kg$^{-1}_{bw}$.d$^{-1}$ at steady state following subchronic daily administration (E.C., 2001).<br>NOEC = 1.7 $10^{-4}$ mg.kg$^{-1}_{feed\ ww}$ (CF=8.33, E.C., 2010) | |
| | Other studies available but which, according to E.C. (2001):<br>- exert less stringent effects on rats (Gray et al., 1997;Mably et al., 1992) or body burdens deemed too low to affect fertility of the male offsprings rats (Murray et al., 1979)<br>- did not address the sensitive endpoints included the above cited studies,<br>- did address other effects than effects on rats reproductive system (e.g. immune system, Nohara *et al.*, 2000) but at higher dose.<br>- did address effects on monkey but studies included too much uncertainties (e.g. Rier *et al.*, 1993)<br>For all these reasons, the above cited studies were not considered as pivotal in the derivation of a threshold level for secondary poisoning. | |
| **Avian oral toxicity** | *Gallus domesticus* / Oral / 21 d<br>NOAEL = 1 $10^{-4}$ mg$_{TE}$.kg$^{-1}_{bw}$.d$^{-1}$<br>NOEC = 8 $10^{-4}$ mg.kg$^{-1}_{biota\ ww}$ (CF=8) | Schwetz *et al.*, 1973 |

In its opinion on the risk assessment of dioxins and dioxin-like PCBs in food, the scientific committee on food (E.C., 2001) recognized that the Wistar rats as used in the study by Faqi et al. (1998) might be the most sensitive rat strain and concluded that the value issued from this study should be considered as a tolerable intake for 2,3,7,8-TCDD. For comparison purpose, a conversion factor of 8.33 for converting NOAELs (dose) from mammalian toxicity studies into NOECs (concentration) according to TGD-EQS (E.C., 2011). This factor however may not be appropriate for this study where animals have been administered subcutaneously. For the back calculation of $QS_{biota,\ sec.pois.}$ into water, the BCF values of 41 540 is used as well as equal default $BMF_1$ and $BMF_2$ values of 10 (cf. section 5.1).

| Tentative $QS_{biota,\ sec.pois.}$ | Relevant study for derivation of QS | Assessment factor | Tentative QS |
|---|---|---|---|
| **Biota** | NOEC = 1.1 $10^{-4}$ mg.kg$^{-1}_{feed\ ww}$<br>(using a provisional conversion factor of 8.33) | 90[(1)] | For comparison purpose only:<br>1.2 $10^{-3}$ µg.kg$^{-1}_{biota\ ww}$<br>corresponding to<br>2.8 $10^{-9}$ µg.l$^{-1}$ (freshwater)<br>2.8 $10^{-10}$ µg.l$^{-1}$ (marine waters) |

*[(1)] proposal made for the purpose of this dossier, according to REACH guidance on information requirements and chemical safety assessment (ECHA, 2008) and the draft technical guidance on deriving Environmental Quality Standards (E.C., 2010) estimating the study considered to be a "reproductive study".*

***Quality of the data set and uncertainties associated***

According to a number of authors (e.g. Bell *et al.*, 2010; Foster *et al.*, 2010), the decreased sperm count observed in some publications as the most sensitive effect failed to be reproduced and that the although animal studies available provide clear evidence of an adverse effect of in utero dioxins exposure on epididymal sperm count, no clear link could be made with possible adverse effects on spermatogenesis. Foster *et al.* (2010) conclude that the mechanisms underlying decreased epididymal sperm count are not unknown but postulate that epididymal structure and/or function as well as developmental abnormalities of the male reproductive tract might be the key target of the adverse effects of dioxins.

Bell and its collaborator (2010), add that maternal doses of <1 µg TCDD/kg that produced adverse effects reported in offspring are "frequently within the range of historical variation seen in other laboratories" and that "the potency of TCDD to induce these effects appears to be much greater after chronic dosing, compared with acute dosing". They note as this regards that "maternal pharmacokinetics of TCDD vary considerably between acute and chronic dosing, and that these two differing dosing regimens have been shown to impact upon the potency of TCDD at inducing adverse effects" (Bell *et al.*, 2010).

Given these considerations and associated uncertainties, the proposed $QS_{biota,\ sec.pois.}$ has to be considered with caution and the $QS_{biota,\ human\ health}$ should be preferred.

## (43) Heksabromociklododekan (HBCDD)

# 5 ENVIRONMENTAL BEHAVIOUR

## 5.1 ENVIRONMENTAL DISTRIBUTION

| | | Master reference |
|---|---|---|
| **Water solubility** ($mg.l^{-1}$) | 0.066 at 20°C<br>(sum of α-, β-, γ-HBCDD)<br>0.0488 (α-HBCDD)<br>0.0147 (β-HBCDD)<br>0.0021 (γ-HBCDD) | MacGregor and Nixon (2004)<br>Cited in EU-RAR (2008) |
| **Volatilisation** | | |
| **Vapour pressure** (Pa) | $6.3*10^{-6}$ Pa at 21°C | Stenzel and Nixon (1997)<br>Cited in EU-RAR (2008) |
| **Henry's Law constant** ($Pa.m^3.mol^{-1}$) | 0.75 (calculated from vapour pressure and water solubility) | EU-RAR (2008) |
| **Adsorption** | **The Koc value 45709 is used for derivation of quality standards.** | |
| **Organic carbon – water partition coefficient ($K_{OC}$)** | $K_{OC}$ = 45709<br>(Log $K_{oc}$= 4.66, QSAR equation<br>Log $K_{oc}$= 0.81 Log $K_{ow}$ + 0.10) | EU-RAR (2008) |
| **Suspended matter – water partition coefficient ($K_{ced-water}$)** | 1143.7 | Calculated from the Koc according to the methodology described in the TGD for deriving EQS (2010) |
| **Bioaccumulation** | **The BCF value 18100 for fish is used for derivation of quality standards.** | |
| **Octanol-water partition coefficient (Log Kow)** | 5.62 (technical product) | MacGregor and Nixon (1997)<br>Cited in EU-RAR (2008) |
| | 5.07±0.06 α-HBCDD<br>5.12±0.09 β-HBCDD<br>5.47±0.10 γ-HBCDD | Hayward *et al.* (2006)<br>Cited in EU-RAR (2008) |
| **BCF (measured)** | 18100 (*Pimephales promelas*, steady state)<br>8974-21940 (*Oncorhynchus mykiss*, whole fish, BCF differ depending on exposure concentration and calculation method) | Veit *et al.* (1979) and Drottar and Krueger (2000)<br>Evaluated in EU-RAR (2008) |
| | BAFs, various fish species:<br>310-6000 ΣHBCDD<br>1200-23000 α-HBCDD<br>250-3500 β-HBCDD<br>110-3200 γ-HBCDD<br>(L/ng lw) | Harrad *et al.* (2009a)<br>Harrad *et al.* errata (2010) |

| | | |
|---|---|---|
| | 105000 ΣHBCDD (average)<br>(L/kg fw) | |
| | Only α-HBCDD found in eggs of guillemot, white-tailed sea eagle and peregrine falcon, whereas γ-HBCDD made up 25-33% of total HBCDD in herring. Highest concentrations were found in eggs of the two top-predators. | Janak *et al.* (2008) |
| | BMF of α-HBCDD, ringed seal (blubber) to polar bear (adipose tissue: 1.7 | Letcher *et al.* (2009) |
| | Arctic marine food web (beluga whale, narwhal, walrus, cod, shrimp, clams, deepwater redfish and zooplankton), eastern Canada.<br>Trophic magnification factor (TMF) of 2.1 for α-HBCDD. Dilution of γ-HBCDD with trophic level. Determined using stable N-isotopes. | Tomy *et al.* (2008) |
| | Fresh water food web (snail, prawn, carps, snakehead, water snake), southern China.<br>TMF of 1.8 and 2.2 (ΣHBCDD and α-HBCDD, respectively) | Wu *et al.* (2010) |
| | BMFs for *Oncorhynchus mykiss* fed fortified food.<br>9.2 (α-HBCDD)<br>4.3 (β-HBCDD)<br>7.2 (γ-HBCDD) | Law *et al.* (2006a) |
| | Fresh water food web (zooplankton, mussels and various fish species), Lake Winnipeg, Canada.<br>TMF of 1.8 (ΣHBCDD)<br>BMFs (predator/prey):<br>0.1-8.2 (α-HBCDD)<br>0.3-5.0 (β-HBCDD)<br>0.3-6.3 (γ-HBCDD) | Law *et al.* (2006b)<br>Law *et al.* (2007) |
| | Fresh water food web (plankton, various invertebrates and fish species), Lake Ontario, Canada.<br>TMF of 6.3 (ΣHBCDD)<br>BMFs (predator/prey):<br>0.4-10.8 (α-HBCDD)<br>0.2-9.9 (β-HBCDD) | Tomy *et al.* (2004) |
| | Arctic marine food web (beluga, ringed seal, cod, herring, cisco), western Canada<br>No significant TMF found<br>BMFs (predator/prey):<br>0.1-1.7 (α-HBCDD)<br>Results suggest accumulation in lower TL animals, but metabolic depletion in higher | Tomy *et al.* (2009) |

| | | |
|---|---|---|
| | TL animals. | |
| | Food chain scenarios based on median concentrations of monitoring data (marine mammals/fish).<br>Baltic Sea: 61 and 5.8<br>Western Scheldt: 187 and 11<br>UK Harbour porpoise: 1859 and 44<br>(wet weight basis and lipid weight basis respectively) | EU-RAR (2008) |

## 5.2 ABIOTIC AND BIOTIC DEGRADATIONS

| | | Master reference |
|---|---|---|
| **Hydrolysis** | Hydrolysis considered to be of low significance | EU-RAR (2008) |
| **Photolysis** | | |
| | Shift in diastereomer composition caused by exposure to light, predominantly from γ to α. Estimated half-life in indoor dust: 12.2 weeks in presence of light, 26 weeks in absence of light. | Harrad *et al.* (2009b) |
| **Biodegradation** | Degradation half-lives based on 2 simulation studies<br>Aer. fresh. sed: 11 & 101 days (20°C), 21 & 191 days (12°C)<br>Anaer. fresh. sed: 1.5 & 66 days (20°C), 2.8 & 125 days (12°C)<br>Method of scaling measured half-lives from 20°C to 12°C questioned by Arnot *et al.* (2009) | EU-RAR (2008)<br>Arnot *et al.* (2009) |

# 7. EFFECTS AND QUALITY STANDARDS

## 7.1 ACUTE AND CHRONIC AQUATIC ECOTOXICITY

| ACUTE EFFECTS | | | Val. score[**]/Comments given in EU-RAR | Master reference |
|---|---|---|---|---|
| Algae & aquatic plants ($mg.l^{-1}$) | Freshwater | *Selenastrum capricornutum* / 72 h<br>$EC_{50}$ : > 0.0025 (measured highest tested concentration) | Considered valid. | Roberts and Swigert (1997)<br>Evaluated in EU-RAR (2008) |
| | Marine | *Chlorella sp.*/ 96 h<br>$EC_{50}$ : > above water solubility | Study not performed according to guideline. Results used as supportive data in EU-RAR | Walsh *et al.* (1987)<br>Evaluated in EU-RAR (2008) |
| | | *Thallassiosira pseudonana* / 72 h<br>$EC_{50}$ : 0.040 | | |
| | | *Skeletonema costatum* / 72 h<br>$EC_{50}$ : 0.009 | | |
| | | *Skeletonema costatum* / 72 h<br>$EC_{50}$ : 0.052 | Considered valid | Desjardins *et al.* (2005)<br>Evaluated in EU-RAR (2008) |
| Invertebrates ($mg.l^{-1}$) | Freshwater | *Daphnia magna* / 48 h<br>$EC_{50}$ : > 0.0032 (mean of measured values at the highest tested concentration) | Considered valid | Graves and Swigert (1997a)<br>Evaluated in EU-RAR (2008) |
| | Marine | *Gender species* / d or h<br>$EC_{50}$ : No data available | | |
| | Sediment | *Gender species* / d or h<br>$EC_{50}$ : No data available | | |
| Fish ($mg.l^{-1}$) | Freshwater | *Oncorhynchus mykiss* / 96 h<br>$EC_{50}$ : > 0.0068 (no effects observed at highest tested concentration, with a mean measured value of 0.0025 mg/l) | Considered valid | Graves and Swigert (1997b)<br>Evaluated in EU-RAR (2008) |
| | | *Leuciscus idus* / 96 h<br>$EC_{50}$ : > 10000 (no effects observed at any tested concentartion) | Considered to be of low reliability | Kirsch and Munk (1988)<br>Evaluated in EU-RAR (2008) |

[**] Klimisch, H. J., M. Andreae, et al. (1997). "A Systematic Approach for Evaluating the Quality of Experimental Toxicological and Ecotoxicological Data." Regulatory Toxicology and Pharmacology 25: 1-5.

| | | | | |
|---|---|---|---|---|
| | | *Lepomis macrochirus* / 96 h<br>$EC_{50}$ : > 100 (no effects observed at any tested concentration) | Considered to be of low reliability | Calmbacher (1978)<br>Evaluated in EU-RAR (2008) |
| | | *Danio rerio* / 96 hpf<br>Effects on survival rate and heart rate at 0.05 mg/l.<br>Effects on malformation rate, body length, apoptotic cells and ROS formation at 0.1 mg/l | 2 | Deng *et al.* (2009) |
| | **Marine** | *Gender species* / d or h<br>$EC_{50}$ : No data available | | |
| | **Sediment** | *Gender species* / d or h<br>$EC_{50}$ : No data available | | |
| **Other taxonomic groups** | | *Gender species* / d or h<br>$EC_{50}$ : No data available | | |

| CHRONIC EFFECTS | | | Val. score/Comments given in EU-RAR | Master reference |
|---|---|---|---|---|
| Algae & aquatic plants ($mg.l^{-1}$) | Freshwater | *Selenastrum capricornutum* / 72 h<br>NOEC : > 0.0025 (measured highest tested concentration) | Considered valid | Roberts and Swigert (1997)<br>Evaluated in EU-RAR (2008) |
| | Marine | *Sceletonema costatum* / 72 h<br>NOEC : > 0.010 | Considered valid | Desjardins *et al.* (2005)<br>Evaluated in EU-RAR (2008) |
| | | *Sceletonema costatum* / 72 h<br>NOEC : ≤ 0.040 | Considered valid | Desjardins *et al.* (2004)<br>Evaluated in EU-RAR (2008) |
| Inver tebrates ($mg.l^{-1}$) | Freshwater | *Daphnia magna* / 21 d<br>NOEC : 0.0031 | Considered valid | Drottar and Krueger (1998)<br>Evaluated in EU-RAR (2008) |
| | Marine | *Macoma baltica* / 50 d / nuclear and nucleolar abnormalities<br>NOEC : < 0.1 (static experiment, nominal water concentration, exposure also through food) | 2 | Smolarz and Berger (2009) |
| | Sediment | *Hyalella azteca* / 28 d<br>NOEC : ≥ 1000 mg/kg dw (2% and 5% organic carbon) | Considered valid | Thomas *et al.* (2003a) and Thomas *et al.* (2003b)<br>Evaluated in EU-RAR (2008) |
| | | *Lumbriculus variegatus* / 28 d<br>NOEC : 8.6 mg/kg dw (total number of worms, normalised to 5% organic carbon) | Considered valid | Oetken *et al.* (2001)<br>Evaluated in EU-RAR (2008) |
| | | *Chironomus riparius* / 28 d<br>NOEC : 37.8 mg/kg dw<br>(number of eggs from F1 generation, normalised to 5% organic carbon) | Considered valid | Oetken *et al.* (2001)<br>Evaluated in EU-RAR (2008) |
| Fish ($mg.l^{-1}$) | Freshwater | *Oncorhynchus mykiss* / 88 d (27 d hatching, 61 d post-hatch)<br>NOEC : > 0.0037 (no effects on hatching success, time to swim-up, larvae and fry survival or growth, at highest measured tested concentration) | Considered valid | Drottar *et al.* (2001)<br>Evaluated in EU-RAR (2008) |

| | | | | |
|---|---|---|---|---|
| | | *Gobiocypris rarus* / 42 d<br>SOD activity, ROS and protein carbonyl formation in brain, DNA damage (Oliver tail movement) in erythrocytes.<br>NOEC: 0.001<br>EROD and PROD activity in liver, lipid peroxidation (TBARS) in brain.<br>NOEC: 0.01 | 2 | Zhang *et al.* (2008) |
| | | *Salmo salar* / 30 d, peak smoltification period / decreased olfactory sensitivity, effects on thyroid hormone levels<br>Exposure conc: 0.000011 | 3 | Lower and Moore (2007) |
| | | *Oncorhynchus mykiss* / 56 d / altered thyroid hormone levels and deiodinase activity.<br>Exposure to α-, β- & γ-HBCDD separately through fortified food. Exposure concentrations were 29, 11, and 23 ng/g lw, respectively. | 2 | Palace *et al.* (2008) |
| | **Marine** | | | |
| | **Sediment** | *Platichthys flesus* / 78 d / thyroid hormones, histology, enzyme activities.<br>No effects seen at the highest tested doses;<br>800 µg/g TOC (0.24 mg/kg dw) + 300 µg/g lipid in food, or<br>8000 µg/g TOC (2.4 mg/kg dw) | 2 | Kuiper *et al.* (2007) |
| **Other taxonomic groups** | | *Gender species* / d<br>NOEC : No data available | | |

There are acute toxicity data for nine species representing algae, crustaceans and fish. Chronic toxicity data are available for 11 species representing algae, crustaceans, molluscs, annelids and fish.

Most of the studies have been evaluated in the EU-RAR (2008), but in the EU-RAR no Klimisch codes are presented. For these studies, it is indicated if they are considered valid in the EU-RAR.

The tentative AA-QSs for fresh and marine water for direct ecotoxicity were calculated from the chronic toxicity NOEC of 0.0031 mg.l$^{-1}$ derived from a 21-day study with *Daphnia magna*, and the assessment factors 10 and 100, in accordance with the TGD for deriving EQS (2010). There are two studies available reporting lower effect concentrations (Zhang *et al.*, 2008; Lower and Moore, 2007). However, the relevance of the endpoints used in these studies is not easily assessed. Further, the study by Lower and Moore (2007) is considered to be of low reliability due to the lack of true replicates and only one exposure concentration. For the tentative MAC-QSs for direct ecotoxicity, the $EC_{50}$ value derived from a toxicity study with *Sceletonema costatum* is used and assessment factors of 100 and 1000 are applied for freshwater and marine waters, respectively. The limited acute and chronic toxicity data do not provide convincing evidence that the sensitivity of marine organisms is covered by the sensitivity of freshwater species. Thus, in accordance with the TGD for deriving EQS (European Commission 2011) larger assessment factors are applied to derive the marine QSs.

Tentative QSs for sediment were calculated from the lowest chronic NOEC of three, from studies with sediment dwelling species with different feeding regimes. No marine benthic toxicity data on relevant endpoints has been identified. In accordance with chapter 5.2 of the TGD for deriving EQS (European Commission 2011), an assessment factor of 10 was used for the $QS_{freshwater, sed.}$, whereas for the $QS_{marine\ water, sed.}$ the assessment factor was 50.

The TGD for deriving EQS (2011) recommend the adoption of PNECs derived in risk assessments under Regulation (EC) No. 793/93 as QSs, if new data do not alter the evaluation undertaken. The resulting tentative QSs are the same as the PNECs derived in the EU-RAR (2008).

| Tentative $QS_{water}$ | Relevant study for derivation of QS | Assessment factor | Tentative QS |
|---|---|---|---|
| $MAC_{freshwater, eco}$ | *Sceletonema costatum* / 72 h<br>$EC_{50}$ : 0.052 mg.l$^{-1}$ | 100 | 0.52 µg.l$^{-1}$ |
| $MAC_{marine\ water, eco}$ | | 1000 | 0.052 µg.l$^{-1}$ |
| $AA\text{-}QS_{freshwater, eco}$ | *Daphnia magna* / 21d<br>NOEC : 0.0031 mg.l$^{-1}$ | 10 | 0.31 µg.l$^{-1}$ |
| $AA\text{-}QS_{marine\ water, eco}$ | | 100 | 0.031 µg.l$^{-1}$ |
| $AA\text{-}QS_{freshwater, sed.}$ | *Lumbriculus variegatus* / 28 d<br>NOEC : 8.6 mg/kg dw (total number of worms, 5% organic carbon) | 10 | 0.86 mg/kg dw |
| $AA\text{-}QS_{marine\ water, sed.}$ | *Lumbriculus variegatus* / 28 d<br>NOEC : 8.6 mg/kg dw (total number of worms, 5% organic carbon) | 50 | 0.17 mg/kg dw |

## 7.2 SECONDARY POISONING

| Secondary poisoning of top predators | | Master reference |
|---|---|---|
| Mammalian oral toxicity | Rat / Oral / 28 days / liver weight<br>NOAEL : 22.9 mg.kg$^{-1}_{bw}$.d$^{-1}$<br>NOEC : 229 mg.kg$^{-1}_{feed}$ (CF= 10) | van der Ven *et al.* (2006)<br>Evaluated in EU-RAR (2008) |
| | Rat / Oral / 2-generation / decrease in fertility-index and reduced number of primordial follicles, increased pup mortality during lactation in F2.<br>NOAEL : 10 mg.kg$^{-1}_{bw}$.d$^{-1}$<br>NOEC : 150 mg.kg$^{-1}_{feed}$ | Ema *et al.* (2008)<br>Evaluated in EU-RAR (2008) |
| | Mouse / Oral / single dose postnatal day 10 / spontaneous behaviour, learning and memory<br>LOAEL: 0.9 mg.kg$^{-1}_{bw}$.d$^{-1}$<br>(indicative, results need to be confirmed) | Eriksson *et al.* (2006)<br>Evaluated in EU-RAR (2008) |
| | Rat / Oral / 1-generation / thyroid related parameters and brain morphometry in offspring<br>NOAEL: 8-21 mg.kg$^{-1}_{bw}$.d$^{-1}$<br>NOEC: 100 mg.kg$^{-1}_{feed}$ | Saegusa *et al.* (2009)<br>Evaluated in CHL Report for hexabromocyclododecane (2009) |
| | Rat / Oral / 1-generation / various endocrine and immunological endpoints<br>BMDLs : 0.056-8.6 mg.kg$^{-1}_{bw}$.d$^{-1}$<br>NOEC: 0.56-86 mg.kg$^{-1}_{feed}$ (CF= 10, CF in the study varied from 8 to 15) | van der Ven *et al.* (2009)<br>Evaluated in CHL Report for hexabromocyclododecane (2009) |
| | Rat / Oral / 1-generation / cataleptic behaviour and BAEP<br>BMDLs : 0.6-6 mg.kg$^{-1}_{bw}$.d$^{-1}$<br>NOEC : 6-60 mg.kg$^{-1}_{feed}$ (CF= 10, same study as by van der Ven *et al.* (2009)) | Lilienthal *et al.* (2009)<br>Evaluated in CHL Report for hexabromocyclododecane (2009) |
| Avian oral toxicity | *Coturnix coturnix japonica* (Japanese quail) / Oral / 6 weeks / survival of hatched chicks<br>NOAEL : 0.7 mg.kg$^{-1}_{bw}$.d$^{-1}$<br>NOEC : 5 mg.kg$^{-1}_{feed}$ | MOEJ (2009) |
| | *Falco sparverius* / Oral / 3 wks prior pairing until 2 days before hatching<br>LOAEL: 0.8 mg.kg$^{-1}_{bw}$.d$^{-1}$<br>Reduced weight and growth rate of nestlings | Marteinson *et al.* (2009) |

In the EU-RAR on HBCDD, there are mainly three studies considered for the risk characterization. From an oral 28-days study on rats, conducted by van der Ven *et al.* (2006), a NOAEL of 22.9 mg.kg$^{-1}_{bw}$.d$^{-1}$ has been derived. The study found increased liver, thyroid, and pituitary weights. A 2-generation rat study conducted by Ema *et al.* (2008) resulted in a NOAEL of 10 mg.kg$^{-1}_{bw}$.d$^{-1}$, effects found included a decrease in fertility-index, a reduced number of primordial follicles, and an increased pup mortality during lactation in F2. There is also a study on developmental neurotoxicity effects (seen as changes in spontaneous behaviour, learning and memory defects) conducted by Eriksson *et al.* (2006). It resulted in an indicative LOAEL of 0.9 mg.kg$^{-1}_{bw}$.d$^{-1}$. In the EU-RAR it is concluded that the study by Eriksson *et al.* (2006) is well performed, but the results need to be confirmed by other laboratories.

Since the EU-RAR on HBCDD was finalised in 2008, some new toxicity studies of relevance for the derivation of $QS_{biota}$ have been published. Two studies not included in the EU-RAR are reviewed in the ongoing European Chemicals Agency (ECHA) evaluation for harmonisation of classification and labelling (CHL Report for hexabromocyclododecane, 2009). A rat 1-generation study performed by Saegusa *et al.* (2009) found effects on the thyroid system (thyroid weight, T3 and TSH levels), the liver (weight), and also brain morphometry (impaired oligodendroglial development) in offspring, resulting in a of NOAEL of 8-21 $mg.kg^{-1}_{bw}.d^{-1}$. The study was not conducted according to any guideline. The ECHA-evaluation also presents the study presented by van der Ven *et al.* (2009) and by Lilienthal *et al.* (2009). The experimental set up was based on the OECD415 guideline, but modified to fit a Benchmark Design. In addition, it was enhanced according to the OECD407 guideline for endocrine and immunological endpoints (results reported in van der Ven *et al.*, 2009), and also for assessments on cataleptic behaviour and brainstem auditory evoked potentials (BAEP) (reported in Lilienthal *et al.*, 2009). The results are reported as benchmark dose lower bounds (BMDLs). Reported BMDLs for several parameters are low, in the same range as the indicative LOAEL presented by Eriksson *et al.* (2006). The lowest value, 0.056 $mg.kg^{-1}_{bw}.d^{-1}$, is for trabecular bone mineral density. In the ECHA-evaluation it is however stated that the BMDLs derived in the articles by Lilienthal *et al.* (2009) and van der Ven *et al.* (2009) should be viewed with caution.

There are also two recent avian toxicity studies available. An avian reproduction study on Japanese quail, sponsored by the Japan Ministry of the Environment, has been performed by the Research Institute for Animal Science in Biochemistry & Toxicology (MOEJ, 2009). Statistically significant effects on young bird survival and reproductive ability index were seen in the 15 ppm and higher exposure groups. The study reports a NOEC of 5 ppm (0.7 mg/kg/day). These low effect concentrations are supported by a study conducted by Marteinson *et al.* (2009) presented as an abstract. Marteinson *et al.* (2009) exposed American kestrels (*Falco sparverius*) to HBCDD (0.8 mg/kg/day) for three weeks prior pairing until two days before hatching. Reduced weight and growth rates of nestlings were observed.

The tentative $QS_{biota}$ was derived based on the results from the Quail study, using the reported NOEC 5 mg/kg food and an assessment factor of 30. It should be noted that some studies have reported effects at exposure levels lower or in the same range as this NOEC, see above.

The corresponding tentative QS for freshwater and marine waters were calculated with the following formulas according to the TGD for deriving EQS (2010):

$$QS_{freshwater}\,(\mu g/l) = QS_{biota}\,((\mu g/kg) / BCF\,(l/kg) * BMF_1)$$

$$QS_{marine\ waters}\,(\mu g/l) = QS_{biota}\,((\mu g/kg) / BCF\,(l/kg) * BMF_1 * BMF_2)$$

For the calculation, the BCF 18100 was used, see Chapter 5.1. Based on the results from a dietary accumulation study, studies on food chains and food chain scenarios based on monitoring data, the EU-RAR (2008) concluded that HBCDD biomagnifies with a $BMF_1 > 1$ and $BMF_2 > 10$. However, no definite BMFs could be determined and the default values for substances with BCF>5000 ($BMF_1$: 10, $BMF_2$: 10) were used in the risk assessment.

Since the EU-RAR, some new studies presenting BMFs and TMFs have been published, see section 5.1.

The available BMFs vary between 0.1 and 10.8, whereas the TMFs are in the range 1.8-6.3, most values approximately 2. For the food chain scenarios based on monitoring data given in the EU-RAR, ratios between marine mammals and fish in the range 61-1859 based of fresh weight and 5.8-44 based lipid weight are presented. Thus, for the extrapolation between the tentative $QS_{biota}$ and water concentrations, most of the avaliable TMFs indicate that a factor of 2 for $BMF_1$ and $BMF_2$ could be used, whereas some of the BMFs and also the food chain scenarios based on monitoring data indicate a higher biomagnification potential. There are however drawbacks to the use of both the TMF studies and the food chain scenarios presented in the EU-RAR in setting definitive BMFs. Drawbacks include e.g. sampling over several years, lack of TMFs for ΣHBCDD, and the use of trophic levels assigned based on previous studies. Further, for $BMF_1$ the inclusion of higher trophic level animals potentially metabolising HBCDD may result in TMFs that underestimate the biomagnification potential in fish.

$BMF_1$ can also be estimated by triangulation with BAFs. In the study by Harrad *et al.* (2009) BAFs expressed on a lipid weight basis are presented. However, in an errata Harrad *et al.* (2010) estimate an average BAF (30 samples, several species) for ΣHBCDD of 105000 L/kg fw assuming a total body lipid content of 5 % to derive the average BMF based on fresh weight. The range for individual data would be 15500-300000 L/kg fw (using same assumptions regarding lipid content as in the errata). By triangulation with the BCF 18100, this result in an average BMF of 5.8, range 0.86-17. BAFs can also be derived from reported concentrations in water and fish in the study by Wu *et al.* (2010). This data results in BAFs (L/kg fw) of 78045, 415139 and 46438, for carp, mud carp and northern snakehead. By triangulation with the BCF 18100, these values result in BMFs of 4.3, 29 and 2.6, respectively.

For $BMF_1$ the average value of 5.8 derived by triangulation with the BAF presented by Harrad *et al.* (2010) is used.

To illustrate the higher metabolism of HBCDD in higher trophic level animals suggested by several studies (see e.g. Letcher *et al.,* 2009 and Tomy *et al.,* 2009), a $BMF_2$ of 2 is used for the calculation of corresponding water concentrations.

| Tentative $QS_{biota}$ | Relevant study for derivation of QS | Assessment factor | Tentative QS |
|---|---|---|---|
| Biota | NOEC : 5 $mg.kg^{-1}_{feed}$ | 30 | 167 $\mu g.kg^{-1}_{biota\ ww}$ corresponding to 0.0016 $\mu g.L^{-1}$ (freshwater) 0.00080 $\mu g.L^{-1}$ (marine waters) |

## (44) Heptaklor in heptaklorepoksid

# 5 ENVIRONMENTAL BEHAVIOUR

## 5.1 ENVIRONMENTAL DISTRIBUTION

| | | Master reference |
|---|---|---|
| **Water solubility** ($mg.l^{-1}$) | [1] 0.06<br>[2] 0.3 at 25°C | WHO, 1984<br>ATSDR, 2007 |
| **Volatilisation** | Heptachlor and heptachlor epoxide are volatile substances (half-life of 0.73 days in distilled water without agitation). | HSDB, 2001 |
| **Vapour pressure** (Pa) | $5.3.10^{-2}$ at 20°C [1]<br>$3.5.\ 10^{-5}$ at 25°C [2] | Verschueren, 2001<br>Verschueren, 2001 |
| **Henry's Law constant** ($Pa.m^3.mol^{-1}$) | [1] 29.8 at 20°C<br>[2] 3.2 | HSDB, 2001<br>HSDB, 2001 |
| **Adsorption** | Heptachlor and heptachlor epoxide are likely to be strongly adsorbed to suspended and bottom sediment. | HSDB, 2001 |
| **Organic carbon – water partition coefficient ($K_{OC}$)** | $K_{OC}$ = 10 000 – 661 000<br>Log $K_{OC}$ = 4 – 5.82 | HSDB, 2001 |
| **Sediment – water partition coefficient ($K_{sed-water}$)** | 250 – 16 525 | *Calculated from $K_{OC}$* |

| | | Master reference |
|---|---|---|
| **Bioaccumulation** | | |
| **Octanol-water partition coefficient (Kow)** | [1] log $K_{OW}$ = 5.44 – 6.10<br>[2] log Kow = 5.40 | Verschueren, 2001 ; HSDB, 2001<br>Verschueren, 2001 |
| **BCF (measured)** | Heptachlor and heptachlor epoxide are very lipophilic substances and as a fact have a high bioconcentration potential.<br>Many BCF values are available for several fish, molluscs and other aquatic species, ranging from rather low to high values, but few of them were considered valid after assessment [1].**The BCF value of 14 400 for *Pimephales promelas* is used for derivation of quality standards.** | Veith *et al.*, 1979 |
| **BMF (measured)** | According to the available literature, whole food web trophic magnification factors for heptachlor, including heptachlor epoxide range around a value of 6 or 7 (Hoekstra *et al.*, 2003a; Hoekstra *et al.*, 2003b, Fisk *et al.*, 2001).<br>Single biomagnification factors values are also available in these articles but it is to be noted that as long as they are not normalised to trophic level, these are less reliable parameters to take into consideration. Moreover, there are some errors in the equations used by these authors to calculate single BMF values.<br>In a study lead by Kelly *et al.*, 2007b for which supporting material is available (Kelly *et al.*, 2007a) heptachlor and heptachlor epoxide biomagnification was also studied. Trophic magnification factors were not calculated but data were reported that allow the calculation of worst case BMF values for heptachlor and heptachlor epoxide. Resulting values are low for the aquatic food chain (1.11 and 2.26 for heptachlor and heptachlor epoxide, respectively) while they are high when considering the upper levels of the food chain (11.5 and 19.8 for heptachlor and heptachlor epoxide, respectively), i.e. fish to mammals level.<br>As a conclusion, as this latter study on biomagnification is the only reliable one reported up to date[2], it is proposed to rely on worst case BMF values found for heptachlor epoxide: BMF1= 2.26 and BMF2=19.8" | Fisk *et al.*, 2001 ; Hoekstra *et al.*, 2003a; Hoekstra *et al.*, 2003b ; Kelly *et al.*, 2007b; Kelly *et al.*, 2007a |

[1] The value of BCF of 56 000 for crustaceans (Perez-Ruzafa *et al.*, 2000) comes from a study in which measurements were made in water and in various aquatic organisms representing different trophic levels. The samples were taken in a natural environment. The BCF of 56 000 is for crustaceans that have been contaminated not only by water but also by food. The value provided in the report cannot be interpreted as a BCF or a BAF, and these two factors cannot be recalculated from the information contained in the report. Another BCF value of 21 300 for *Cyprinodon variegatus* (Schimmel *et al.*, 1976) was not validated because fish were exposed to technical grade heptachlor, corresponding to a purity of 65% only. Hence, it is not possible to address with certainty how the remaining 35% affect bioaccumulation.. Moreover, the 37 000 value of BCF for fish could not be used either, because not enough information is available on the study reporting this value (Hansen and Parrish, 1977) at the time this assessment is made. Therefore, valid study reporting values of BCF ranging from 9 500 to 14 400 (Veith *et al.*, 1979) are used for the derivation of $QS_{biota}$.

[2] Data from Hoekstra et al., 2003a; Hoekstra et al., 2003b, Fisk et al., 2001 are not considered reliable. Some other studies on biomagnification of persistent organic pollutants in the aquatic food web are available in the literature but they are mostly reporting BMF values for the sum of chlordanes and/or not reporting BMF values as such (Ikemoto *et al.*, 2008; Jarman *et al.*, 1996; Kidd *et al.*, 1998; Ricca *et al.*, 2008; Roche *et al.*, 2009; Strandberg *et al.*, 1998). Therefore, these studies can not be use to evaluate heptachlor and heptachlor epoxide BMF values.

## 5.2 ABIOTIC AND BIOTIC DEGRADATIONS

| | | Master reference |
|---|---|---|
| **Hydrolysis** | [1] Heptachlor rapidly undergoes hydrolysis to 1-hydrochlordene ($DT_{50\text{-hydrolysis}}$ = 4.5 at pH7) which is then readily converted by microorganisms into heptachlor epoxide.<br>[2] On the contrary, hydrolysis is not environmentally significant to heptachlor epoxide ($DT_{50\text{-hydrolysis}}$ = 4 years). | ATSDR, 2007; HSDB, 2001 |
| **Photolysis** | [1] Direct and photosensitized photolysis of unabsorbed heptachlor may occur in the environment.<br>[2] photolysis would only be significant in surface waters in the presence of photosensitizers for heptachlor epoxide. | HSDB, 2001 |
| **Biodegradation** | [1] Heptachlor is not readily biodegradable: 0% of biodegradation after 28 days but it is metabolised in heptachlor epoxide by many living organisms and may be degraded partly by adapted bacterial strains. In this case, main degradation products are 1-hydroxy-2,3-epoxychlordene and heptachlor epoxide.<br>[2] Heptachlor epoxide is a very persistent compound, notably in trophic chain. | MITI, 1992<br>US-EPA, 1980<br>HSDB, 2001<br>US-EPA, 1980<br>WHO, 1984 |

# 7 EFFECTS AND QUALITY STANDARDS

As a reminder, [1] refers to heptachlor and [2] refers to heptachlor epoxide in the tables below.

## 7.1 ACUTE AND CHRONIC AQUATIC ECOTOXICITY

Ecotoxicological databases publicly available such as the US-EPA AQUIRE database (US-EPA, 2007) were browsed in order to collate as far as possible an exhaustive dataset of acute and chronic toxicity data on aquatic organisms. Also, a number of other sources such as scientific reports (e.g. US-EPA Reregistration Eligibility Decision, US-EPA, 1992) were investigated. All studies considered were assessed for their relevancy and reliability. These studies are numerous, in particular acute ecotoxicity studies, but they most often refer to bioassays which were realised under static conditions and for which the concentrations are expressed as nominal concentrations. Given the high hydrophobicity and potential volatility of heptachlor and heptachlor epoxide, in the cases above described, there was a risk of underestimation of the toxicity and data were discarded because of a reliability index considered as low (≥3). Indeed, it was observed that many studies among those assessed which were realised under static conditions led to effects concentrations which were significantly higher than those reported from studies realised under continuous flow or renewal, and/or with analytical measurement of the substance. As a consequence, only continuous flow or renewal assays were validated and reported in the tables hereunder. The reliability was assessed according to Klimisch code (Klimisch *et al.*, 1997) which are specified as well in the tables below.

| **ACUTE EFFECTS** | | | **Reliability** | **Master reference** |
|---|---|---|---|---|
| **Algae & aquatic plants ($mg.l^{-1}$)** | **Freshwater** | *Selenastrum capricornutum* / 96 h<br>[1] $EC_{50}$ = 0.028 | 2 | Call *et al.*, 1983 |
| | **Marine** | No available information | | |
| **Invertebrates ($mg.l^{-1}$)** | **Freshwater** | No available information | | |
| | **Marine** | *Penaeus duorarum* / 96 h<br>[1] $LC_{50}$ = 3 $10^{-5}$<br>[2] $LC_{50}$ = 4 $10^{-5}$ | 1 | Schimmel *et al.*, 1976 |
| | **Sediment** | No available information | | |
| **Fish ($mg.l^{-1}$)** | **Freshwater** | No available information | | |
| | **Marine** | *Leiostomus xanthurus* / 96 h<br>[1] $LC_{50}$ = 8.6 $10^{-4}$ | 1 | Schimmel *et al.*, 1976 |

| **CHRONIC EFFECTS** | | | **Reliability** | **Master reference** |
|---|---|---|---|---|
| **Algae & aquatic plants ($mg.l^{-1}$)** | **Freshwater** | No available information | | |
| | **Marine** | No available information | | |
| **Invertebrates ($mg.l^{-1}$)** | **Freshwater** | No available information | | |
| | **Marine** | No available information | | |
| | **Sediment** | No available information | | |
| **Fish ($mg.l^{-1}$)** | **Freshwater** | No available information | | |
| | **Marine** | *Cyprinodon variegatus* / 28 d<br>[1] NOEC = 7.9 $10^{-4}$ | 2 | Goodman *et al.*, 1978 |

As already noted above, numerous data are available for heptachlor [1] but a number of them were discarded because of their low reliability. According to the acute dataset available in the tables above, crustaceans appear to be more sensitive than fish and a lot more sensitive than algae. The lowest ecotoxicological data is a 96h-$LC_{50}$ for *Penaeus duorarum*. It can be noted that for this individual test assessing the effects of both heptachlor and heptachlor epoxide, there is no apparent difference of toxicity between the two substances. Also, there are no valid ecotoxicological data available for algae and crustaceans in the chronic dataset. Therefore, the acute data is used for deriving both the MAC-$QS_{water}$ and the AA-$QS_{water}$ values.

Finally, although $QS_{water}$ values below are derived from a marine data on *Penaeus duorarum*, it should be stressed that the additional marine assessment factor (AF) 10 is applicable for both the MAC-$QS_{water}$ and the AA-$QS_{water}$ values. In fact, this AF addresses the higher uncertainty in derivation of marine QS compared to freshwater QS because of the higher biodiversity of marine ecosystems and the fact that marine ecosystems include specific taxonomic groups not represented in the dataset (e.g. echinoderms).

| Tentative $QS_{water}$ | Relevant study for derivation of QS | Assessment factor | Tentative QS |
|---|---|---|---|
| $MAC_{freshwater, eco}$ | *Penaeus duorarum* / 96 h $LC_{50}$ : 3 $10^{-5}$ mg.$l^{-1}$ | 100 | 3 $10^{-4}$ µg.$l^{-1}$ |
| $MAC_{marine\ water, eco}$ | | 1 000 | 3 $10^{-5}$ µg.$l^{-1}$ |
| $AA\text{-}QS_{freshwater, eco}$ | | 1 000 | 3 $10^{-5}$ µg.$l^{-1}$ |
| $AA\text{-}QS_{marine\ water, eco}$ | | 10 000 | 3 $10^{-6}$ µg.$l^{-1}$ |
| $AA\text{-}QS_{freshwater, sed.}$ | - | EqP[(1)] | 5.8 $10^{-3}$ µg.$kg^{-1}_{ww}$<br>1.5 $10^{-2}$ µg.$kg^{-1}_{dw}$ |
| $AA\text{-}QS_{marine\ water, sed.}$ | - | EqP | 5.8 $10^{-4}$ µg.$kg^{-1}_{ww}$<br>1.5 $10^{-3}$ µg.$kg^{-1}_{dw}$ |

(1) The worst case was applied to establish the $QS_{sediment}$, that is to use the lowest $K_{OC}$ value (10 000) to calculate the QS. As this lowest $K_{OC}$ corresponds to a log $K_{OC}$ of 4, the additional security factor of 10 was not deemed necessary.

## 7.2 SECONDARY POISONING

| Secondary poisoning of top predators | | Master reference |
|---|---|---|
| **Mammalian oral toxicity** | [2] Dog / Oral / Chronic, 2 years / 0-1-3-5-7-10 ppm<br>Hepatic effects (Increased relative liver weight, histologic changes)<br><br>[2] Dog / Oral / F0, 4 females & 2 males F1 / Reproductive study / 0-1-3-5-7-10 ppm<br>Developmental effect (increased mortality in pups)<br><br>For both studies:<br>NOAEL : 0.025 mg.$kg^{-1}_{bw}$.$d^{-1}$<br>NOEC : 1 mg.$kg^{-1}_{feed\ ww}$ (CF=40) | Wazeter *et al.*, 1971a; Wazeter *et al.*, 1971b<br>as cited *in* WHO, 2008 |
| | [1] Mink / Oral / reproductive study / 181d<br>Reduced pup growth<br>LOAEL = 6.25 mg.$kg^{-1}_{bw}$.$d^{-1}$<br>NOAEL = 2.08 mg.$kg^{-1}_{bw}$.$d^{-1}$ ($CF_{LOAEL->NOAEL}$=3[(1)])<br>NOEC = 609 mg.$kg^{-1}_{food}$ ($CF_{NOAEL->NOEC}$=8.77, study specific) | Crum *et al.*, 1994<br>as cited *in* Ritter *et al.*, undated |