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A literature review

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A search for peer-reviewed literature relating to sediment-spiked toxicity data for plant protection products (pesticides) and freshwater and marine benthic organisms was performed. In addition, publicly available review documents of regulatory authorities in the EU were consulted for toxicity data on the insect *Chironomus riparius* and the oligochaete worm *Lumbriculus variegatus*, since these species currently are a data requirement to assess the effects of sediment exposure to plant protection products. The toxicity data for sediment organisms thus obtained are discussed within the context of a possible prospective tiered effect assessment procedure for insecticides, fungicides and herbicides and sediment-dwelling organisms.

Keywords: Pesticides; benthic organisms; sediment exposure; sediment ecotoxicology; Regulation 1107/2009/EC.

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Contents

Samenvatting

In dit rapport worden de resultaten van een literatuurstudie gepresenteerd over de gevoeligheid van sediment-bewonende (benthische) organismen voor blootstelling aan gewasbeschermingsmiddelen via het sediment. Vooral voor hydrofobe èn relatief persistente gewasbeschermingsmiddelen die in oppervlatewater terecht komen is de kans op chronische blootstelling via het sediment aanwezig.

In de openbare literatuur werden voor benthische organismen sediment toxicteitsgegevens gevonden voor dertien orchanochloor insecticiden, veertien pyrethroide insecticiden, veertien acteyl-cholinesterase remmers, zestien insecticiden met een overig werkingsmechanisme, 24 fungiciden en achttien herbiciden. De gegevens uit de wetenschappelijke literatuur zijn vooral acute (testduur ≤ 4d) en semi-chronische (testduur 10-13d) toxiciteitsgegevens voor *Hyalella azteca* (een kreeftachtige uit Amerika), *Chironomus dilutus* (een chironomide insect uit Amerika) en in mindere mate *Chironomus riparius* (een chironomide uit Europa). Voor *Chironomus riparius* zijn ook chronische (testduur 28 dagen) sediment toxiciteitsgegevens beschikbaar omdat bij de Europese risicobeoordeling *Chironomus riparius* een standaard testorganisme is. Voor de sediment-bewonende worm *Lumbriculus variegatus* kon slechts voor één gewasbeschemingsmiddel een acute toxiciteitswaarde gevonden worden die betrekking had op blootstelling via sediment. Sinds kort is een sediment toxiciteitstest met *Lumbriculus variegatus* een datavereiste bij de Europese risicobeoordeling. In een beperkt aantal wetenschappelijke publikaties worden sediment toxiciteitsgegevens voor andere benthische dieren uit zoete en mariene wateren gerapporteerd. Per individueel gewasbeschermingsmiddel zijn voor maximaal vijf verschillende sediment-bewonende evertebraten toxiciteitsgevens gevonden. Over het algemeen zijn voor insecticiden meer sedimenttoxiciteitgegevens beschikbaar dan voor herbiciden en fungiciden. Sediment-toxiciteitsgevens voor een wortelende waterplant (*Myriophyllum*) zijn voor slecht drie herbiciden gerapporteerd.

In acute en semi-chronische sediment-testen met pyrethroiden en enkele organofosfaten blijkt de kreeftachtige *Hyalella azteca* over het algemeen gevoeliger dan het insect *Chironomus dilutus/riparius*. *Chironomus* soorten zijn echter gevoeliger dan *Hyalella* in sediment-toxiciteitstesten met organochloor verbindingen en overige insecticiden. In acute en semi-chronische sedimenttesten blijkt het verschil in gevoeligheid tussen *Chironomus dilutus* (Amerikaanse soort) en *Chironomus riparius* (Europese soort) klein, alhoewel deze vergelijking slechts gebaseerd is op testen met drie middelen. Het beperkt aantal sediment-toxiciteitsgegevens voor andere benthische soorten dan *Hyalella* en *Chironomus* lijkt er op te wijzen dat arthropoden (insecten en kreeftachtigen) niet de gevoeligste soorten behoeven te zijn voor fungiciden en herbiciden. De gevoeligste benthische soort gerapporteerd voor het fungicide triphenyltin acetaat is een slak. Voor enkele herbiciden en blootstelling via het sediment is de wortelende waterplant *Myriophyllum* het gevoeligst.

Een redelijk goede correlatie kan worden aangetoond tussen 28d NOEC-waarden voor *Chironomus riparius* verkregen uit 'OECD sediment-spiked' en die uit 'OECD water-spiked' toxiciteitstesten, maar de voorspellende waarde van de 'water spiked' test voor de effectbeoordeling van blootstelling via sediment is waarschijnlijk met een relatief grote onzekerheid omgeven. Momenteel kunnen beide testen aangeleverd worden voor de effectbeoordeling van gewasbeschermingsmiddelen als potentiële risico's voor sediment organismen getriggered worden. De sediment-toxiciteit voor insecticiden en *Chironomus* (en *Hyalella*) is niet op een eenvoudige manier te voorspellen op basis van de hydrofobiciteit (K_{ow}) van het middel, hetgeen aantoont dat een voorspelling van de toxicteit op basis van de K_{ow} waarde van de stof (o.a. gebruikelijk bij QSAR-methoden) geen oplossing is voor het invullen van ontbrekende gegevens.

De huidige kennis over verschillende opnameroutes van gewasbeschermingsmiddelen door benthische organismen suggereert dat toxiciteitsgegevens (effectconcentraties) niet alleen uitgedrukt moeten worden in termen van totale concentraties in het sediment maar ook in termen van concentraties in het poriewater. Bij de risicobeoordeling van benthische organismen en blootstelling via sediment lijkt

speciale aandacht nodig voor effecten van langdurige blootstelling. De korte-termijn risico's van sediment-bewonende organismen worden hoogstwaarschijnlijk afgedekt met de risicobeoordeling voor gevoelige waterorganismen en blootstelling via water.

In dit rapport wordt voorgesteld om voor insecticiden en de eerste trap van de sediment beoordeling voor 'edge-of-field' oppervlaktewater te kiezen voor de benthische standaard test organismen *Chironomus riparius* (of een andere OECD soort zoals *Chironomus dilutus*) en een Europese benthische kreeftachtige (of de Amerikaanse kreeftachtige *Hyalella azteca*). Als beschikbare toxiteitsgegevens voor typische waterorganismen en het insecticide (of insecticiden met een overeenkomstig werkingsmechanisme) aantonen dat insecten en kreeftachtigen niet wezenlijk in gevoeligheid verschillen, of dat insecten relatief gevoeliger zijn, kan volstaan worden met het testen van de standaard soort *Chironomus*.

Voor de effectbeoordeling van blootstelling aan fungiciden via het sediment worden de volgende eerste trap standaard testorganismen voorgesteld: (1) het insect *Chironomus riparius* (of *C. dilutus*) en de worm *Lumbriculus variegatus* als de toxiciteitsgegevens voor typische waterorganismen niet duiden op een mogelijke herbicide werking van het fungicide, (2) het insect *Chironomus riparius* of de worm *Lumbriculus variegatus* (de laatste soort indien de terrestrische standaard worm *Eisenia* relatief gevoelig is) en een wortelende waterplant (bijvoorbeeld *Myriophyllum*) als toxiciteitsgegevens voor typische waterorganismen wel duiden op een mogelijke herbicide werking van het fungicide.

Een optie voor benthische standaard testsoorten voor blootstelling aan herbiciden via sediment is de combinatie van een wortelende waterplant (bijvoorbeeld *Myriophyllum*) en een evertebraat (*Chironomus* of *Lumbriculus*). De uiteindelijke keuze kan ingeperkt worden op basis van beschikbare dossierinformatie voor de gevoeligheid van typische waterorganismen en terrestrische bodemorganismen voor het herbicide (of de stofgroep met een overeenkomstig werkingsmechanisme).

Als toxiciteitgevens voor additionele benthische soorten beschikbaar zijn kan een hogere trap beoordeling overwogen worden op basis van de 'Geometric mean' en 'Species Sensitivity Distribution' methode zoals beschreven voor waterorganismen in het EFSA Aquatic Guidance Document. Bij deze methoden kunnen toxiciteitsgegevens voor zoetwater en mariene benthische organismen van dezelfde taxonomische groep gebruikt worden. De te gebruiken veiligheidsfactoren voor het afleiden van $RAC_{sed;ch}$ waarden (=Regulatory Acceptable Concentration voor het compartiment sediment) zijn nog onvoldoende gecalibreerd/gevalideerd met veld- en semi-veldgegevens met een focus op benthische organismen en blootstelling via sediment.

In dit rapport wordt aan mogelijke effecten van gewasbeschermingsmiddelen op microorganismen in het sediment geen aandacht besteed omdat in het kader van de Europese regelgeving hiervoor nog geen datavereisten geformuleerd zijn.

Summary

This report presents the results of a literature review on sediment-spiked toxicity data for plant protection products (PPPs) and benthic organisms. In the open literature, and publicly available review reports, sediment toxicity data for thirteen organochlorine compounds, fourteen pyrethroid insecticides, forteen acetyl-chlinesterase inhibiting insecticides, sixteen other types of insecticides, 24 fungicidal substances and eighteen herbicides could be found. Most open literature papers deal with acute (≤ 4 days) and semi-chronic (10-13 days) toxicity data relating to either the amphipod *Hyalella azteca*, the chronomid *Chironomus dilutus* or the chironomid *Chironomus riparius*, although some of the papers consider other benthic species as well, including estuarine and marine invertebrates. A few herbicide studies only, quantified effects on the rooted macrophyte *Myriophyllum* in standardized sediment exposure experiments. Chronic (test duration 28 days) NOEC data derived from sediment-spiked toxicity tests are available for *Chironomus riparius* in particular. In the literature (including regulatory documents), results of sediment-spiked sediment toxicity test for *Lumbriculus variegatus* are very scarce (one report for one compound found).

In acute and semi-chronic tests the crustacean *Hyalella azteca* appears to be overall more sensitive than the insect *Chironomus dilutus* (or *C. riparius*) for pyrethroid and organophosphorus insecticides, while *Chironomus* overall is more sensitive than *Hyalella* to insecticides belonging to organochlorines and several insecticides with another mode-of-action. In acute (≤ four days) and semi-chronic (ten – thirteen days) tests the American species *Chironomus dilutus* and the European species *Chironomus riparius* seem to be of similar sensitivity, although the number of substances for which this comparison could be made is limited (three substances).

Herbicides and fungicidal compounds overall appear to be much less toxic to *Hyalella azteca* and *Chironomus* species than insecticidal compounds. The relatively few sediment toxicity data available for test species other than *Hyalella* and *Chironomus* seem to suggest that for fungicides arthropod species not necessarily are the most sensitive. In the few available tests with sediment-spiked herbicides the 10-13d EC50 values for the macrophyte *Myriophyllum aquaticum* (sediment contact tests) overall were lower than those for benthic arthropods.

The toxicity of insecticidal compounds to *Hyalella* and *Chironomus* appears not to be related to the hydrophobicity of these chemicals in a simple fashion. This suggests that QSAR methods that primarely use K_{ow} information to predict sediment toxicity may not be the way forward. A fairly good correlation could be demonstrated between the 28d NOEC for *Chironomus riparius* derived from the sediment-spiked OECD toxicity test and that of the corresponding water-spiked OECD toxicity test. Nevertheless, the predictive value of the water-spiked test for the effect assessment of sediment exposure most probably is surrounded by a relatively high uncertainty.

Current knowledge on the role and importance of several possible uptake routes of PPPs by benthic organisms suggests that test results, i.e. effect concentrations, should not only be expressed on the basis of total content but also on the basis of total and dissolved concentrations in pore water. Emphasis should be on chronic exposure testing, since it is expected that sediment toxicity will be most important for compounds which, due to their physico-chemical properties, result in long-term exposures. Most likely the risks of short-term exposure of sediment-dwelling organisms to PPPs is covered by the effect assessment scheme for sensitive water column organisms.

On basis of the available sediment toxicity data it is proposed to select *Chironomus riparius* (or another OECD chironomid such as *Chironomus dilutus*) and a benthic crustacean indigenous for Europe (or the American amphipod *Hyalella azteca*) as Tier 1 test species for insecticides. An option is to request a toxicity value for a representative benthic crustacean only if the toxicity data for the type of insecticide under evaluation and typical water column arthropods indicate that crustaceans overall are more sensitive than insects.

To assess the effects of sediment exposure to fungicides the following combinations of Tier 1 test species may be an option: (1) the insect *Chironomus riparius* (or *C. dilutus*) and the oligochaet worm *Lumbriculus variegatus* if the toxicity data for typical water column organisms do not indicate herbicidal properties, (2) either *Chironomus riparius* or *Lumbriculus variegatus* (the latter if e.g. the terrestrial worm and Tier 1 test species *Eisenia* is relatively sensitive) and a rooted macrophyte (e.g. *Myriophyllum*) if the toxicity data for typical water column organisms indicate herbicidal properties of the fungicide.

An option for the effect assessment of herbicides for benthic organisms is to select as Tier 1 standard test species a rooted macrophyte (e.g. *Myriophyllum*) and either the insect *Chironomus riparius* or the oligochaet worm *Lumbriculus variegatus*. The final selection of the two Tier 1 test species may be informed and motivated by the available information on sensitivity of water (column) and soil organisms for the same herbicide and related substances with a similar toxic mode-of-action (read across).

When additional toxicity data for sediment-dwelling organisms are available the Geometric mean and Species Sensitivity Distribution approaches seem to be promising and in these approaches sediment toxicity data for freshwater and marine species of the same taxonomic group may be combined. The proposed approaches, and the size of the AF for $RAC_{sed;ch}$ (= Regulatory Acceptable Concentration for sediment compartment) derivation, however, need to be calibrated with field data or results of appropriate semi-field experiments in which the responses of benthic populations are expressed in terms of PPP concentrations in the sediment compartment.

The validity of most conclusions in this review report is probably hampered by the limited size of the available data set. Furthermore, it needs to be decided whether the performance of the microbial community in sediments and the upper debris/litter layer needs to be evaluated in the prospective risk assessment for sediment organisms and PPPs, although no microbial tests are currently mentioned as data requirement.

1 Introduction

In the early phases of aquatic risk assessment suspended and settled solids were considered to be safe repositories of sorbed contaminants. Such assessments were therefore mostly limited to the water column (Maki et al., 1987). However, as concerns about sediment-bound chemicals became more widespread in the late 1970's the toxicity and bioconcentration of sediment-bound metals and hydrophobic chemicals was met with growing interest (Burton Jr., 1991).

For hydrophobic organic chemicals one of the most important steps in standardizing sediment toxicity tests, and understanding the results they yield, was the realization that the binding of organic chemicals to sediments is governed to a large extent by the amount of organic material present, resulting in the use of 'organic carbon standardized' sorption coefficients (Gschwend and Wu, 1985). Initially this was interpreted as evidence that the concentration of the compound in the interstitial water was the driving factor for uptake and effects, and that interstitial water was the dominant route of uptake (e.g. Adams et al., 1985; Adams, 1987). However, the current theory is that exposure of benthic organisms may comprise uptake routes from phases like interstitial and overlying water as well as from different sediment fractions that e.g. may be selectively consumed by benthic organisms. In the often used 'Equilibrium Partition Theory', where equilibrium of contaminant concentrations between the various phases is assumed, the experimental distinction between the various possible routes of uptake receives less emphasis (Bierman Jr., 1990; Di Toro et al., 1991).

Retrospective sediment toxicity testing has been widely used in evaluations of dredged materials (Burton Jr., 1991). Due to the nature of the sorption processes it is understandable that the emphasis of establishing sediment quality criteria and toxicity values for benthic organisms has been on contaminants like metals, polycyclic aromatic hydrocarbons, polychlorinated biphenyls, dioxins and chlorinated plant protection products (PPPs) like endrin, dieldrin and DDT. The focus on these compounds appears to continue until today (see e.g. Burgess et al., 2013), with the possible exception of synthetic pyrethroids. This latter group of PPPs, encompassing some of the most hydrophobic organic pesticides still in use today, has received more attention than most other PPPs.

Due to their rapid disappearance from the water column as a result of their sorption to sediments many pyrethroids are believed to predominantly pose short-term risks to aquatic life in the water column at concentrations resulting from proper agricultural use (Maund et al., 2001). However, pyrethroid-contaminated sediments have been demonstrated to cause toxicity in the environment (see e.g. Amweg et al., 2005; Amweg et al., 2006; Holmes et al., 2008; Trimble et al., 2009). Recent studies demonstrate that other hydrophobic insecticides like benzoylurea substances (e.g. lufenuron and teflubenzuron) may as well pose long-term risks to sediment-dwelling organisms via sediment exposure (e.g. Brock et al., 2010; Tassou and Schulz, 2011).

Tests establishing the toxicity of less hydrophobic PPPs towards benthic organisms are still much less common, and relatively little is known about the toxicity of such compounds to benthic organisms, their tendency to sorb to sediments, and their subsequent bioconcentration in benthic organisms. This awareness has sparked interest in sediment-related behaviour and toxicity of other types of PPP, and compounds like pharmaceuticals, to benthic organisms (see e.g. Ding et al., 2011; Ho et al., 2013). This has resulted in the observation that for many classes of organic compounds much work remains to be done in the field of sediment toxicity (Di Toro, 2013).

The present report aims to summarize data from recent literature on the sediment-related toxicity of plant protection products in benthic organisms. In addition, on basis of these data, this report aims to provide building blocks for the development of a prospective effect assessment procedure for plant protection products and sediment-dwelling organisms inhabiting edge-of-field surface waters, and in support of Regulation 1107/2009/EC.

2 Literature search

A literature search was performed in Scopus, using the following key words:

Sediment* AND toxic* AND (pestic* OR protect*)
Sediment* AND Bioavail* AND toxic*
Sediment* AND concentrat* AND (toxic* OR effect*) AND (plant* OR pestic* OR PPP)
Sediment* AND concentrat* AND (toxic* OR effect*) AND benth*
(Sediment* OR benth*) AND (lc50 OR ec50)
Chironomus AND sediment AND (“plant protect*” OR pestic*)
Hyalella AND sediment AND (“plant protect*” OR pestic*)
Lumbriculus AND sediment AND (“plant protect*” OR pestic*)
Myriophyllum AND sediment AND (“plant protect*” OR pestic*)
Glyceria AND sediment AND (“plant protect*” OR pestic*)

The search focussed on peer-reviewed literature dealing with the sediment-related toxicity to benthic organisms of plant protection products (PPPs). On the basis of the titles found, a more detailed inspection of some of the papers was made, including their lists of references. Papers reporting the results of experimental determinations of acute or chronic toxicity data for benthic species, including review papers, were selected. Data on toxicity for non-benthic species were not included, nor were the results of studies with benthic species in test systems containing no sediments, i.e. using water-only exposures, or expressing the toxicity values in terms of water exposure only. However, 28d toxicity values for *Chironomus riparius* and PPPs in water-spiked water-sediment test systems were considered if for the same PPP also a sediment-spiked test with this species was performed. This enabled the investigation of the correlation of 28d NOEC values for *C. riparius* between the OECD water-spiked and sediment-spiked *Chironomus* test (OECD, 2004 a and b; OECD, 2010).

Within the EU aquatic effect assessment procedure for PPPs, chronic toxicity data on basis of OECD *Chironomus* tests (OECD, 2004 a and b; OECD, 2010) and/or the *Lumbriculus variegatus* test (OECD, 2007) have to be submitted if potential risks of exposure for benthic organisms are identified. Consequently, 28d NOEC values for PPPs and *Chironumus riparius* were retrieved from EU draft assessment reports (DARs), review reports of the European Food Safety Authority and public databases (e.g. IUPAC footprint; http://sitem.herts.ac.uk/aeru/iupac/). Unfortunately, toxicity data for *Lumbriculus variegatus* on basis of sediment spiked toxicity tests hardly could be found in these databases. The same appeared to be the case for the availability of toxicity data for rooted macrophytes on basis of sediment spiked toxicity tests.

3 Toxicity data for PPPs and benthic test species

3.1 Species used in sediment toxicity tests

Experimental results for various test organisms were found, but by far the most results are reported for the amphipod *Hyalella azteca* (especially in papers originating in North America, where *H. azteca* is the primary crustacean in sediment toxicity testing) and larvae of the midges *Chironomus dilutus* (previously known as *Chironomus tentans*) and *Chironomus riparius*. A few papers consider toxicity towards other benthic invertebrates, especially when dealing with marine or estuarine sediments, or the rooted macrophyte *Myriophyllum*, especially when dealing with herbicides. Table 1 gives an overview of species used in the various papers.

Table 1
Overview of species for which relevant toxicity data were found.

Species	Taxonomic group	Environment
Ampelisca abdita	Amphipod, Crustacea	Estuarine
Amphiascus tenuiremis	Copepod, Crustacea	Estuarine
Asellus aquaticus	Isopod, Crustacea	Fresh
Chironomus dilutus (tentans)	Chironomid, Insecta	Fresh
Chironomus riparius	Chironomid, Insecta	Fresh
Corophium volutator	Amphipod, Crustacea	Marine
Eohaustorius estuarius	Amphipod, Crustacea	Estuarine
Ephoron virgo	Trichopteran; Insecta	Fresh
Hyalella azteca	Amphipod, Crustacea	Fresh / estuarine
Jappa kutera	Ephemeropteran, Insecta	Fresh
Leptocheirus plumosus	Amphipod, Crustacea	Estuarine
Lumbriculus variegatus	Worm, Oligochaeta	Fresh
Mercenaria mercenaria	Bivalve, Mollusca	Marine
Microarthridion littorale	Copepod, Crustacea	Estuarine
Myriophyllum aquaticum	Rooted macrophyte	Fresh
Myriophyllum spicatum	Rooted macrophyte	Fresh
Neanthes arenaceodentata	Worm, Polychaeta	Marine
Nereis diversicolor	Worm, Polychaeta	Marine
Nereis virens	Worm. Polychaeta	Marine
Potamopyrgus antipodarum	Snail, Mollusca	Fresh
Paronychocamptus wilsoni	Copepod, Crustacea	Marine
Tubifex tubifex	Worm, Oligochaeta	Fresh

Although test protocols for many more species than *Hyalella and Chironomus* exist (for an overview see e.g. Diepens et al., 2013; Sheahan and Fisher, 2012), there was only very little open literature found using them to assess the toxicity of PPPs. The fact that hardly no sediment toxicity data (expressed in terms of total sediment or sediment organic matter concentration) could be found for PPPs and the oligochaete *Lumbriculus variegatus* is not surprising, since toxicity data for this species is a data requirement for PPP registration only since recently. Most data on PPPs and *Lumbriculus variegatus* found in the open literature concerned bioaccumulation studies or the toxicity values were derived from water-only test systems.

The experimental toxicity values for benthic organisms that were found in the open literature were not equally distributed over different types of PPPs. Most papers dealt with either chlorinated compounds, synthetic pyrethroids and acetyl-cholinesterase inhibiting insecticides, and only relatively few gave experimental results for other types of PPPs. For this reason, results are discussed in separate sections for organochlorine compounds, synthetic pyrethroids, actyl-cholinesterase inhibitors, ‘other insecticides’, fungicides and herbicides.

In the Sections below a distinction is made in acute toxicity tests (test duration ≤ 4 d), semi-chronic toxicity tests (test duration 10-13 d), and chronic toxicity tests (test duration of ≥ 21 d). Note, however, that several long-term tests (≥ 21 days) considered mortality only, while this may not be the most sensitive chronic endpoint. Furthermore, not all long-term toxicity tests covered the whole life-cycle of the test organisms. Tests that cover several succeeding generations of the test species are rare. Tassou and Schulz (2011) describe a 2-generation study with *C. riparius* (lasting 56 days).

The current OECD sediment test protocols (Guidelines 218, 219, 225, 233; OECD 2004a, 2004b, 2007, 2010 resp.) advocate the use of artificial sediments, containing 4 - 5% peat, but EPA OPPTS 850.173.5 (US EPA, 1996) advocates the use of clean natural sediments. All protocols require the determination of organic carbon content of the sediment, enabling the recalculation of effect concentrations on the basis of organic carbon (OC) content. In toxicity tests derived from the open literature different types of sediments varying in OC were used, hampering a direct comparison of test results. To allow a comparison of sediment toxicity data from different sources, in this report, where possible and relevant, sediment toxicity data were standardized to concentrations expressed on the basis of sediment organic carbon content.

3.2 Organochlorine compounds

Table 2 gives acute (duration ≤ 4 d) and semi-chronic (10-12 d) toxicity data found for organochlorine compounds, some of which were previously given by Di Toro et al. (1991). The acute and semi-chronic LC50 values for different species tested with the same organochlorine compound are further summarized in Table 3 and chronic toxicity data (duration ≥ 21 days) are presented in Table 4.

Not surprisingly, the organochlorine compounds were among the first pesticides for which sediment toxicity was investigated, the earlier of the papers summarized in Table 2 being published before 1990. However, there are also some papers of later date addressing these compounds, reflecting that they are still of concern because of their ensuing presence in the environment, and sediments in particular.

Most of the tests used *Hyalella azteca* or *Chironomus dilutus*. The 3-12 d toxicity data for the species mentioned in Table 2 range from 0.96 – 2000 µg/g OC, reflecting a high variability in toxicity for the combination of different organochlorine compounds, test species, endpoints and test conditions.

A comparison in sensitivity between different test species for the same organochlorine compound is presented in Table 3. Data for six test species can be used for this comparison and for only one compound (endosulfan) semi-chronic toxicity data for five species are available. Overall, of the species tested *Chironomus dilutus* seems to be amongst the most sensitive, but the reported value for the marine polychaete *Nereis virens* is low as well, suggesting that arthropods may not be the only sensitive taxonomic group for organochlorine compounds. The geometric mean acute toxicity value for *C. dilutus* and all organochlorine compounds is on average a factor of 11 lower than that for *Hyallella azteca*. For the compound alpha-endosulfan *C. dilutus* is a factor of 54 more sensitive than *H. azteca.* Note, however, that the reported variability in 10 d acute toxicity values for the same test species and test compound may also be relatively high (up to a factor of 19 for the compound endosulfan and *C. dilutus*). The mollusc *M. mercenaria* is on average a factor of 4 less sensitive to DDT than the amphipod *H. azteca*. The sensitivity of the amphipod *L. plumulosus* and the ephemeropteran *J. kutera* for endosulfan is intermediate between that of *H. azteca* and *C. dilutus*.

Table 2

Acute and semi-chronic (duration ≤ 12 d) sediment toxicity data for organochlorine compounds.

Compound	Species	Effect endpoint	LC50/EC50/NOEC (µg/g OC) Mean (Range)	endpoint	References
Kepone	*C. dilutus*	Mortality	584 (293 – 1000)	10d LC50	Adams et al., 1985; Di Toro et al., 1991
Kepone	*C. dilutus*	Growth/ weight	495 (311 – 662)	10d EC50	Adams et al., 1985; Di Toro et al., 1991
DDT	*H. azteca*	Mortality	420 (367 – 473)	10d LC50	Nebeker et al., 1989
DDT	*H. azteca*	Mortality	121 (101 – 140)	10d LC50	Schuytema et al., 1989
DDT	*H. azteca*	Mortality	135 (128 – 142)	10d LC50	Amweg and Weston, 2007
DDT	*H. azteca*	Mortality	259 (221 – 296)	10d LC50	Weston et al., 2009
DDT	*M. mercenaria*	Mortality	829	10d LC50	Chung et al., 2007
DDD	*H. azteca*	Mortality Length	260 240	10d LC50 10d EC50	Ingersoll et al., 2005
Dicofol	*H. azteca* *C. dilutus* *C. dilutus*	Mortality Mortality Growth	>573[a] 915 630	10d LC50 10d LC50 10d NOEC	Ding et al., 2011
Dieldrin	*C. dilutus*	Mortality	57 (35-78)	10d LC50	US EPA 1993
Dieldrin	*H. azteca*	Mortality	2000 (1100-3700)	10d LC50	US EPA 1993
Endrin	*C. dilutus*	Mortality	4.22	10d LC50	Weston et al. 2004 You et al. 2004
Endrin	*H. azteca*	Mortality	100 (54 – 147)	10d LC50	Nebeker et al., 1989
Endrin	*H. azteca*	Mortality	153 (136 – 170)	10d LC50	Schuytema et al., 1989
Endosulfan (sulfate)	*C. dilutus*	Mortality	5.22	10d LC50	Weston et al. 2004 You et al. 2004
Endosulfan (sulfate)	*C. dilutus*	Mortality	100	10d LC50	Sappington, 2013
Endosulfan (sulfate)	*L. plumulosus*	Mortality	144	10d LC50	Sappington, 2013
Endosulfan (sulfate)	*H. azteca*	Mortality	873	10d LC50	Weston et al. 2004 You et al. 2004
Endosulfan (sulfate)	*J. kutera*	Mortality	324[b]	10d LC50	Leonard et al. 2001
Endosulfan (sulfate)	*N. virens*	Mortality	17	12-d LC50	McLeese et al., 1982
Alpha-endosulfan	*C. dilutus*	Mortality	0.96	10d LC50	Weston et al. 2004 You et al. 2004
Alpha-endosulfan	*H. azteca*	Mortality	51.7	10d LC50	Weston et al. 2004 You et al. 2004
Beta-endosulfan	*C. dilutus*	Mortality	3.24	10d LC50	Weston et al. 2004 You et al. 2004
Lindane	*T. tubifex*	Lethality Avoidance Autotomy	>1000 224 200	3d LC50 3d EC50 3d EC50	Meller et al., 1998
Alpha-chlordane	*H. azteca*	Lethality	516	10d LC50	Trimble et al., 2009
Gamma-chlordane	*H. azteca*	Lethality	889	10d LC50	Trimble et al., 2009
Methoxychlor	*C. dilutus* *H. azteca*	Mortality Mortality	36.7 85.8	10d LC50 10d LC50	Weston et al. 2004 You et al. 2004

[a] Range of values given as >1230, >274 and >215 µg/g OC for three sediments.

[b] Recalculated on basis of 95% moisture content and 1% OC content of sediment used.

Table 3

Comparison of 10-12 d sediment toxicity data for organochlorine compounds between the amphipods Hyalella azteca and Leptocheirus plumulosus, the insects Chironomus dilutus and Jappa kutera, the polychaete Nereis virens and the mollusc Mercenaria mercenaria on basis of the endpoint mortality (background data,see Table 2).

Compound	Geometric mean 10-12 LC50 of values reported in Table 2 (µg/g OC)					
	H. azteca	*L. plumulosus*	*C. dilutus*	*J. kutera*	*N. virens*	*M. mercenaria*
DDT	205					829
Dicofol	>573		915			
Dieldrin	2000		57			
Endrin	124		4.22			
Endosulfan (sulfate)	873	144	23	324	17	
Alpha-endosulfan	51.7		0.96			
Methoxychlor	85.8		36.7			

Chronic sediment toxicity data, here defined as toxicity tests with a duration of ≥ 21 days, are very scarce for organochlorine compounds (Table 4). A comparison of 10d L(E)C50 data and chronic L(E)C50 data is possible only for DDD and *H. azteca* (Tables 2 and 4), indicating similar toxicity values for test periods of 10, 28 and 42 days when considering the same assessment endpoint (mortality and length). The 42d EC50 for DDD and the endpoint reproduction of *H. azteca* was approximately a factor of 2 lower than the corresponding 42 d EC50 for the endpoint length.

The reported 120d NOECreproduction for DDT and the marine polychaete *Neanthes arenaceodentata* (17100 µg/g OC; Table 4), suggests that this species is relatively insensitive to DDT (see also reported 10d toxicity data in Table 2).

Table 4
Chronic sediment toxicity data for organochlorine compounds.

Compound	**Species**	**Effect endpoint**	**L(E)C50/NOEC (µg/g OC)**		**References**
			Mean	**Toxicity endpoint**	
DDD	*Hyalella azteca*	Mortality	250	28d LC50	Ingersoll et al., 2005
		Length	240	28d EC50	
		Length	250	42d EC50	
		Reproduction	120	42d EC50	
DDT	*Neanthes arenaceodentata*	Reproduction	17100	120d NOEC	Murdoch et al. 1997

3.3 Synthetic pyrethroids

Table 5 summarizes semi-chronic sediment toxicity data (test duration ten days) for synthetic pyrethroids to benthic organisms. Table 6 further summarises the semi-chronic sediment data found for different test species and the same pyrethroid. In Table 7 the 28d sediment-spiked chronic toxicity data for *Chironomus riparius* are reported.

Most of the literature found for synthetic pyrethroids is relatively recent, being published in 1999 or later, with the exception of the paper by Chandler et al. (1994), dealing with the toxicity of fenvalerate to the estuarine copepod *Amphiascus tenuiremis*.

Most of the 10d toxicity values published refer either to *Hyalella azteca* (26 of 49 values in Table 5), *Chironomus dilutus* (12 values) or the marine amphipod species *Eohaustorius estuarium* (4 values) or *Ampelisca abdita* (3 of 49 values).

For some of the compounds, 10d toxicity data for lethal and sublethal effects are available, but the ratio between 10d LC50 and 10d $NOEC_{growth}$ is within a factor 5. The 10d toxicity data for lethal and sublethal effect concentrations for the species mentioned in Table 5 ranged from 0.11 – 1143 µg/g OC, again reflecting a high variability in toxicity for the combination of different pyrethroids, test species, measurement endpoints and test conditions. Within the group of pyrethroids the reported sediment toxicity data for permethrin are relatively high.

Synthetic pyrethroids are known to be susceptible to metabolic degradation in many species, and their metabolic fate and hence toxicity can be influenced by the presence of other compounds, nutritional status and environmental conditions like temperature. Surprisingly little information about such effects, specifically relating to benthic organisms was found, although Amweg and Weston (2007) reported their findings on the toxicity-enhancing effect of the presence of piperonyl butoxide, and Weston et al. (2009) found enhanced toxicity of pyrethroids to *H. azteca* at reduced temperature. This prompted Fojut et al. (2012) to conclude that laboratory tests, due to the relatively high temperatures usually employed, may well underestimate the toxicity of pyrethroids in field situations.

For eight synthetic pyrethroids 10d LC50 values could be found for more than one test species (Table 6). All the test species mentioned in Table 6 are arthropods, so belonging to the potential sensitive taxonomic group for pyrethroids (Maltby et al., 2005). The maximum number of 10d LC50 toxicity data for different test species and the same pyrethroid was five (permethrin and cypermethrin). For bifenthrin 10d LC50 data were found for four different species.

Table 5
Semi-chronic sediment toxicity data for synthetic pyrethroids.

Compound	Species	Effect endpoint[a]	L(E)C50/NOEC (µg/g OC)		References
			Mean (Range)	Toxicity endpoint	
Bifenthrin	*H. azteca*	Mortality Growth	0.52 (0.37-0.63) 0.17 (0.11-0.34)	10 d LC50 10 d NOEC	Amweg et al., 2005 (erratum x 2.86)
Bifenthrin	*H.azteca*	Mortality	0.26	10 d LC50	Amweg&Weston, 2007
Bifenthrin	*H. azteca*	Mortality	0.11	10 d LC50	Maul et al., 2008a
Bifenthrin	*H. azteca*	Mortality	0.99	10 d LC50	Weston et al., 2009
Bifenthrin	*H. azteca*	Mortality	25.7 (18.3-29.8)	10 d LC50	Xu et al., 2007
Bifenthrin	*C. dilutus*	Mortality Growth rate	6.2 1.5	10 d LC50 10 d EC50	Maul et al., 2008b
Bifenthrin	*A. abdita* *E. estuarius*	Mortality	122 1.0	10 d LC50 10 d LC50	Anderson et al., 2008
Cyfluthrin	*H. azteca*	Mortality Growth	1.08 (1.07-1.09) 0.36 (0.28-0.46)	10 d LC50 10 d NOEC	Amweg et al., 2005
Cyfluthrin	*H. azteca*	Mortality	2.34 (2.21-2.43)	10 d LC50	Xu et al., 2007
Cyfluthrin	*E. estuarius*	Mortality	0.33	10 d LC50	Lao et al., 2012
Cypermethrin	*H. azteca*	Mortality	0.38	10 d LC50	Hintzen et al., 2009
Cypermethrin	*H. azteca*	Mortality Growth	0.34 (0.18-0.60) 0.09 (0.014-0.18)	10 d LC50 10 d NOEC	Maund et al., 2002
Cypermethrin	*C. dilutus*	Mortality Growth	1.34 (0.48-2.23) 0.44 (0.11-0.83)	10 d LC50 10 d NOEC	Maund et al., 2002
Cypermethrin	*C. dilutus*	Mortality	0.82	10 d LC50	Mehler et al., 2011
Cypermethrin	*A. abdita* *E. estuarius*	Mortality	60 1.4	10 d LC50 10 d LC50	Anderson et al., 2008
Cypermethrin	*C. volutator*	Mortality	0.313	10 d LC50	Mayor et al., 2008
Deltamethrin	*H. azteca*	Mortality Growth	0.79 (0.71-0.87) 0.12	10 d LC50 10 d NOEC	Amweg et al., 2005
Esfenvalerate	*H. azteca*	Mortality Growth	1.54 (1.27-1.75) 0.34 (0.29-0.50)	10d LC50 10d NOEC	Amweg et al., 2005 (erratum x 1.72)
Esfenvalerate	*H. azteca*	Mortality	2.0	10d LC50	Weston et al., 2009
Etofenprox	*C. riparius*		0.152 [a]	10d NOEC	Footprint
Fenpropathrin	*H. azteca*	Mortality	1.1	10d LC50	Ding et al., 2010
Fenpropathrin	*H. azteca*	Mortality	1.6 (1.1-2.2)	10d LC50	Ding et al., 2011
Fenpropathrin	*H. azteca*	Mortality	2.36 (2.23-2.50)	10d LC50	Xu et al., 2007
Fenpropathrin	*C. dilutus*	Mortality Growth	8.9 1.7	10d LC50 10d NOEC	Ding et al., 2011
Fenvalerate	*A. tenuiremis* *P. wilsoni*	Mortality	84 74	10d LC25 10d LC50	Chandler et al., 1994
Lambda-cyhalothrin	*H. azteca*	Mortality Growth	0.45 (0.43-0.46) 0.11 (0.08-0.14)	10d LC50 10d NOEC	Amweg et al., 2005
Lambda-cyhalothrin	*H. azteca*	Mortality	0.42	10d LC50	Weston et al., 2009
Lambda-cyhalothrin	*C. dilutus*	Mortality Growth rate	2.8 1.9	10d LC50 10d EC50	Maul et al., 2008b
Permethrin	*H. azteca*	Mortality Growth	10.83 (11.1-18.0) 7.1(<1.6 – 7.1)	10d LC50 10d NOEC	Amweg et al., 2005 (erratum x 2.22)
Permethrin	*H. azteca*	Mortality	17.4	10d LC50	Weston et al., 2009
Permethrin	*C. riparius*	Mortality	21.9	10d LC50	Conrad et al., 1999
Permethrin	*C. dilutus*	Mortality Growth rate	24.5 27.5	10d LC50 10d EC50	Maul et al., 2008b
Permethrin	*A. abdita* *E. estuarius*	Mortality	1143 18	10d LC50 10d LC50	Anderson et al., 2008
Tefluthrin	*H. azteca*	Mortality	2.9	10d LC50	Ding et al., 2010

Table 6
Comparison of 10d sediment LC50 data for pyrethroid insecticides between the amphipods Hyalella azteca, Eohautorius estuarius and Ampelica abdita, the copepods Amphiascus tenuiremis and Paronychocamptus wilsoni and the insects Chironomus dilutus and Chironomus riparius (for background data see Table 5).

Compound	Geometric mean of 10d LC50 in Table 5 (µg/g OC)							
	H. azteca	*E. estuarius*	*A. abdita*	*C. volutator*	*A. tenuiremis*	*P. wilsoni*	*C. dilutus*	*C. riparius*
Bifenthrin	0.82	1.0	122				6.2	
Cyfluthrin	1.59	0.33						
Cypermethrin	0.36	1.4	60	0.313			1.05	
Fenpropathrin	1.61						8.9	
Fenvalerate					84	74		
L-cyhalothrin	0.43						2.8	
Permethrin	13.7	18.0	1143				24.5	21.9

The toxicity data presented in Table 6 do not indicate a fundamental difference in the toxicity distribution between freshwater and marine arthropods. For five of the pyrethroid compounds 10d LC50 values for both *H. azteca* and *C. dilutus* are available, from which it appears that in short-term tests the latter species is approximately 2 to 8 times less sensitive to synthetic pyrethroids than *H. azteca*. The geometric mean 10d LC50 value for the amphipod *Hyallella azteca* and all pyrethroids is on average a factor of 4 lower than that for *C. dilutus.* The amphipod *A. abdita* appears to be much less sensitive to synthetic pyrethroids than either *H. azteca* or *C. dilutus*. In contrast, the 10d LC50 values for the amphipod *E. estuarius* fall in the ranges of those reported for *H. azteca* and *C. dilutus.* For the compound permethrin the 10d LC50 values are remarkably similar for the chironomids *C. dilutus* and *C. riparius*.

Chronic sediment toxicity data (tests duration ≥ 21 days) are available for five synthetic pyrethroids only and all data concern toxicity values for *C. riparius* (Table 7). For gamma-cyhalothrin the observed difference in 28d EC50 and 28d NOEC values for emergence of *C. riparius* was approximately a factor of 4. A comparison of 10d L(E)C50 data and chronic L(E)C50/NOEC data for the same species and pyrethroid is possible only for *C. dilutus* and permethrin (Tables 5 and 7). The difference in reported 10d LC50 (24.5 µg/g OC; endpoint mortality) and the 56d EC50 (0.838 µg/g OC; endpoint emergence) for *C. dilutus* is approximately a factor of 30, at least in part due to different types of test sediments used and associated differences in bioavailability of permethrin. For lambda-cyhalothrin, however, the reported 10d LC50 (2.8 µg/g OC) does not deviate much from, and even is somewhat lower than, the 28d NOEC of *C. riparius*.

Table 7
Chronic sediment toxicity data for synthetic pyrethroids and Chironomus riparius.

Compound	Species	Effect endpoint[a]	28 d L(E)C50/NOEC (µg/g OC)		References
			Mean	Toxicity endpoint	
Beta-cypermethrin	*Chironomus riparius*	Emergence?	2.4 [a]	28d NOEC	Footprint
Deltamethrin	*Chironomus riparius*	Mortality	0.60	28d LC50	Akerblom et al., 2008
Gamma-cyhalothrin	*Chironomus riparius*	Emergence	1.948 [a] 0.512 [a]	28d EC50 28d NOEC	EU DAR
Lambda-cyhalothrin	*Chironomus riparius*		6.8	28d EC50	Weston et al. 2004
Lambda-cyhalothrin	*Chironomus riparius*	Emergence	4.2 [a]	28d NOEC	Footprint/EFSA review report
Permethrin	*Chironomus dilutus*	Emergence	0.838 0.016	56 d EC50 56 d EC5	Du et al. (2013)
Tau-fluvalinate	*Chironomus riparius*	Emergence	8.0 [a]	28d NOEC	EU DAR

[a] Assuming 2.5% organic carbon content in OECD 218 standard sediment.

3.4 Acetyl-cholinesterase inhibiting insecticides

Table 8 summarises acute (≤ 4d) and semi-chronic (test duration 10d) sediment toxicity data for acetyl-cholinesterase inhibiting (organophosphorous and carbamate) insecticides. In Table 9 an overview of these sediment data for different benthic test species and the same acetyl-cholinesterase inhibiting insecticide is given. Unfortunately, chronic sediment toxicity data (tests with a duration ≥ 21d) for benthic organisms could not be found in the open literature and EU data bases.

Most of the toxicity data in Table 8 refer to *C. riparius* (11 of the 28 values), *C. dilutus* (7) and *H. azteca* (5). The marine taxon *Amphiascus tenuiremis* is represented by two values and *Eohaustorius estuarius*, *Ampelisca abdita* and *Microarthridion littorale* by one value each.

For diazinon and methyl-parathion and the test species *C. dilutus* both a 10d LC50 and a 10d NOEC value are available differing less than a factor of 4.

Amweg and Weston (2007) investigated the influence of piperonyl butoxide (PBO) on the toxicity of chlorpyrifos to *H. azteca*, and found that the increased metabolism of this insecticide due to the presence of PBO decreased its toxicity in a 10-day toxicity test. The 10-d LC50 in the absence of PBO was 1.77 µg/g OC, which is slightly lower than the value given by Hintzen et al. (2009) for *H. azteca* of 4.4 µg/g OC.

The effect of temperature on the toxicity of chlorpyrifos to *H. azteca* was found to be negligible by Weston et al. (2009), whereas Harwood et al. (2009) found a two-fold decrease of toxicity, i.e. a doubling of the 10-d LC50, to *C. dilutus* upon decreasing the temperature from 23^{o}C to 13^{o}C. This was attributed to a decrease in the rate of metabolism and the slower formation of toxic metabolites at lower temperature.

For five acetyl-cholinesterase inhibiters acute and semi-chronic LC50 values for more than one test species were found (Table 9). All test species mentioned in Tables 8 and 9 are arthropods, a taxonomic group that can be considered as potentially sensitive to insecticides (Maltby et al., 2005). The maximum number of acute and semi-chronic LC50 values for different test species and the same acetyl-cholinesterase insecticide is five (chlorpyrifos) and structural differences in sensitivity between freshwater and saltwater species are not apparent.

For carbamate and organophosphorus insecticides the acute LC50 values of H. azteca are within the range of the values found for *C. riparius* and *C. dilutus.* Overall, the test species *C. riparius, C. dilutus* and *H. azteca* seem to be representative sensitive arthropods for acetyl-cholinesterase inhibitors. The value found for azinphos-methyl and the marine copepod *M. littorale* is relatively high, as well as the value found for methyl-parathion and *C. dilutus.*

Table 8

Acute and semi-chronic sediment toxicity data for organophosphorous and carbamate insecticides.

Compound	Species	Effect endpoint	L(E)C50/NOEC (µg/g OC)		References
			Mean (Range)	Toxicity endpoint	
Azinphos-methyl	*M. littorale* *A. tenuiremis*	Mortality Mortality	370 21.8	4d LC50 4d LC50	Klosterhaus et al., 2003
Carbaryl	*C. riparius*	Mortality	14.7	1d LC50	Fisher et al., 1993
Carbofuran	*C. riparius*	Mortality	0.26	1d LC50	Fisher et al., 1993
Carbofuran	*C. dilutus*	Mortality	0.43	10d LC50	Douglas et al., 1993
Chlorpyrifos	*H. azteca*	Mortality	1.77	10d LC50	Amweg & Weston, 2007
Chlorpyrifos	*H. azteca*	Mortality	4.4	10d LC50	Hintzen et al., 2009
Chlorpyrifos	*H. azteca*	Mortality	4.1 (4.1-4.2)	10d LC50	Weston et al., 2009
Chlorpyrifos	*C. dilutus*	Mortality	7.74 (5.51-9.96)	10d LC50	Ankley et al., 1994
Chlorpyrifos	*C. dilutus*	Mortality	6.68	10d LC50	Harwood et al., 2009
Chlorpyrifos	*A. abdita* *E. estuarius*	Mortality Mortality	15.9 13.2	10d LC50	Anderson et al., 2008
Chlorpyrifos	*A. tenuiremis*	Mortality (adult)	1.74	4d LC50	Green et al., 1996
Diazinon	*H. azteca* *C. dilutus* *C. dilutus*	Mortality Mortality Growth	15.4 (2.8-24.4) 54.3 15.9	10d LC50 10d LC50 10d NOEC	Ding et al., 2011
Dichlorvos	*C. riparius*	Mortality	0.56	1d LC50	Fisher et al., 1993
Ethion	*C. riparius*	Mortality	13.1	1d LC50	Fisher et al., 1993
Leptophos	*C. riparius*	Mortality	>167	1d LC50	Fisher et al., 1993
Malathion	*C. riparius*	Mortality	0.22	1d LC50	Fisher et al., 1993
Methyl-parathion	*C. riparius*	Mortality	0.13	1d LC50	Fisher et al., 1993
Methyl-parathion	*H. azteca* *C. dilutus* *C. dilutus*	Mortality Mortality Growth	6.9 (2.8-12.7) 318 115	10d LC50 10d LC50 10d NOEC	Ding et al., 2011
Mevinphos[x]	*C. riparius*	Mortality	0.88	1d LC50	Fisher et al., 1993
Mexacarbate	*C. riparius*	Mortality	0.85	1d LC50	Fisher et al., 1993
Parathion	*C. riparius*	Mortality	2.4	1d LC50	Fisher et al., 1993
Propoxur	*C. riparius*	Mortality	3.6	1d LC50	Fisher et al., 1993

[x] In the original paper denoted as Phosdrin.

Table 9

Comparison of acute and semi-chronic sediment toxicity data for organophosphorous and carbamate insecticides between the amphipods Hyalella azteca, Eohaustorius estuarius and Ampelisca abdita, the copepods Amphiascus tenuiremis and Microarthridion littorale and the insect Chironomus dilutus and Chironomus riparius (for background data see Table 8).

Compound	Geometric mean of acute LC50 values in Table 8 (µg/g OC)						
	H. azteca	*E. estuarius*	*A. abdita*	*A. tenuiremis*	*M. littorale*	*C. dilutus*	*C. riparius*
Azinphos-methyl				21.8 [b]	370 [b]		
Carbofuran						0.43 [a]	0.26 [c]
Chlorpyrifos	2.8 [a]	13.2 [a]	15.9 [a]	1.74 [b]		7.2 [a]	
Diazinon	15.4 [a]					54.3 [a]	
Methyl-parathion	6.9 [a]					318 [a]	0.13 [c]

[a] 10d LC50; [b] 4d LC50; [c] 1d LC50

3.5 Other insecticides

Sediment toxicity data for insecticides, other than organochlorine, pyrethroid and acetyl-cholinesterase inhibiting substances, are relatively scarce in the open literature. The experimental toxicity data for these insecticides, including the acaricides etoxazole and propargite and tebufenpyrad, are summarized in Tables 10 (semi-chronic toxicity data) and Table 13 (chronic toxicity data).

The acute toxicity values summarised in Table 10 refer to the insects *C. dilutus* (7 of 17) and *C. riparius* (5) and the crustaceans *H. azteca* (4) and *E. estuarius* (1).

For several compounds (abamectin, indoxacarb and propargite) both 10d LC50 and 10d NOEC values for *C. dilutus* are available, but the difference in these LC50s and NOECs is not more than a factor of 2 to 4.

The semi-chronic toxicity values for the acaricides reported in Table 10 are relatively high when compared with those of the other insecticides in this table.

For the compounds abamectin, fipronil, indoxacarb and propargite acute LC50 for both *C. dilutus* and *H. azteca* are available. For all these compounds, except the acaricide propargite, the insect *C. dilutus* is substantially more sensitive than the crutacean *H. azteca*.

Table 10
Semi-chronic sediment toxicity data for insecticides, other than organochlorines, pyrethroids and acetyl-cholinesterase inhibitors.

Compound	Species	Effect endpoint	EC50/LC50/NOEC (µg/g OC)		References
			Mean (Range)	Toxicity endpoint	
Biopesticides					
Abamectin	*H. azteca* *C. dilutus* *C. dilutus*	Mortality Mortality Growth	19.9 (11.3-26.2) 0.18 0.10	10d LC50 10d LC50 10d NOEC	Ding et al., 2011
Emamectin (benzoate)	*E. estuarius*	Mortality	>29	10d LC50	Kuo et al., 2010
Emamectin (benzoate)	*C. volutator* *N. diversicolor*	Mortality Mortality	9.56 85.5	10 d LC50 10 d LC50	Mayor et al., 2008
Benzoylureas					
Lufenuron	*C. riparius*	Wet weight Mortality	0.6 [b] 1.2 [b]	10d NOEC 10d NOEC	Hooper et al. 2005
Teflubenzuron	*C. riparius parents* *C. riparius offspring*	Emergence	4.0 [a] 2.48 [a]	10d NOEC 10d NOEC	Tassou & Schulz, 2011
Other insecticides					
Fipronil	*H. azteca*	Mortality	4.1	10d LC50	Hintzen et al., 2009
Fipronil	*C. dilutus*	Mortality Growth	0.13 0.12	10d LC50 10d EC50	Maul et al., 2008b
Imidacloprid	*L. variegatus*	Mortality Avoidance Growth	>925.9 <9.3 <9.3	10d LC50 10d EC50 10d NOEC	Sardo and Soares, 2010
Indoxacarb	*H. azteca* *C. dilutus* *C. dilutus*	Mortality Mortality Growth	>1419 [c] 11.3 3.2	10d LC50 10d LC50 10d NOEC	Ding et al., 2011
Metaflumizone	*C. riparius*	AFDW	48.0 [a] 10.4 [a]	10d EC50 10d NOEC	EU DAR
Acaricides					
Etoxazole	*C. riparius*	Growth rate	1000 [a]	10d NOEC	EU DAR
Propargite	*H. azteca* *C. dilutus* *C. dilutus*	Mortality Mortality Growth	576 [e] 964 633	10d LC50 10d LC50 10d NOEC	Ding et al., 2011

[a] Assuming 2.5% organic carbon content in OECD 218 standard sediment.

[b] Assuming 5% organic carbon in OECD 207 standard sediment.

[c] Range of values given as >2630, >1010 and >616 µg/g OC for three sediments.

[e] Range of values given as 576, >408 and >416 µg/g OC for three sediments.

For the individual insecticides mentioned in Table 10 the maximum number of species for which semi-chronic sediment toxicity data could be found was two.

Tassou and Schulz (2011) observed that in 10d toxicity tests the first-generation offspring of *C. riparius* was somewhat more sensitive to the chitin synthesis inhibitor teflubenzuron than the parent generation, the 10d $NOEC_{emergence}$ being 2.48 µg/g OC for F1 and 4.0 µg/g OC for the P generation (Table 10). Similar findings were reported for the effects of pyriproxyfen to parent and first offspring, but in these studies the exposure was via water and not sediment (Tassou and Schulz, 2012).

Chronic sediment toxicity data (test duration ≥ 21 d) for benthic organisms predominantly are available for *Chironomus riparius* (Table 11). For several compounds mentioned in Table 11 (emamectine benzoate, lufenuron, chlorantranilprole) both EC50 and NOEC values are reported but the NOEC are not more than a factor of 2-3 lower. For a few compound 10d LC50/NOEC values for *C. dilutus* (Table 10) and 28/29d NOEC values for *C. riparius* (Table 11) are available (abamectine, fipronil, lufenuron, teflubenzuron). Assuming a similar sensitivity of *C. dilutus* and *C. riparius,* these toxicity data suggest that the 10d LC50/NOECs do not deviate more than a factor of 2 when compared with the corresponding endpoint of the 28/29d toxicity data.

Table 11
Chronic sediment toxicity data for insecticides other than organochlorines, pyrethroids and acetyl-cholinesterase inhibitors.

Compound	Species	Effect endpoint[a]	LC50/EC50/NOEC (µg/g OC)		References
			Mean (Range)	Toxicity endpoint	
Biopesticides					
Abamectine	*Chironomus riparius*	Emergence	0.132 [a]	28d NOEC	Scheepmaker, 2008a
Emamectine benzoate	*Chironomus riparius*	Emergence	0.096 [a] 0.05 [a]	29d EC50 29d NOEC	EU DAR
Benzoylureas					
Lufenuron	*Chironomus riparius*	Emergence	3.26 [a] 1.6 [a]	28d EC50 28d NOEC	EU DAR
Lufenuron	*Asellus aquaticus*	Mortality	6.59	21d LC50	Internal info Alterra
Teflubenzuron	*Chironomus riparius*	Emergence	2.0 [a]	28d NOEC	Scheepmaker, 2008b
Other insecticides					
Buprofezin	*Chironomus riparius*	Emergence	108.8 [a]	28d NOEC	Footprint
Chlorantranilprole	*Chironomus riparius*	Emergence	0.52 [a] 0.2 [a]	28d EC50 28d NOEC	EU DAR
Chromafenozide	*Chironomus riparius*	Emergence	2.9 [a]	28d NOEC	EU DAR
Fipronil	*Chironomus riparius*		0.08 [a]	28d NOEC	Footprint
Spinetoram	*Chironomus riparius*	Emergence	3.89 [a]	28d NOEC	EU DAR
Thiamethoxam	*Chironomus riparius*	Emergence	4.0 [a]	28d NOEC	Footprint/EU DAR
Acaricide					
Tebufenpyrad (acaricide)	*Chironomus riparius*		25.6 [a]	28d NOEC	Footprint/EFSA review report

[a] Assuming 2.5% organic carbon content in OECD 218 standard sediment.

3.6 Fungicides

Papers reporting experimental semi-chronic sediment toxicity data for fungicides are scarce. For three fungicides only 10d sediment toxicity data could be found with a maximum number of two test species per individual fungicide (Table 12). The two sediment toxicity data available for triphenyltin-acetate indicate that the benthic ephemeropteran *Epheron virgo* (10d EC50 of 4.25 µg/g OC) is a factor of approximately 5 more sensitive that the standard test species *C. riparius* (10d EC50 of 21.07 µg/g OC) (De Haas et al., 2005).

Table 12

Semi-chronic sediment toxicity data for fungicidal substances.

Compound	Species	Effect endpoint	EC50 (µg/g OC) Mean (range)	Toxicity endpoint	References
Penflufen	*C. dilutus*	AFDW	340 [a]	10d NOEC	EU DAR
Pyraclostrobin	*H. azteca*	Mortality	>1921 [b]	10d LC50	Ding et al., 2011
	C. dilutus	Mortality	346	10d LC50	
	C. dilutus	Growth	160	10d NOEC	
Triphenyltin acetate	*Chironomus riparius*		21.07 [c]	10d EC50	De Haas et al. 2005
	Ephoron virgo		4.25 [c]	10d EC50	

[a] Assuming 2.5% organic carbon content in OECD 218 standard sediment.

[b] Range of values given as >4330, >963 and >470 µg/g OC for three sediments.

[c] Assuming 58% organic carbon content of organic matter.

Chronic toxicity data (test duration ≥ 21 d) were found for 22 fungicides (Table 13). These chronic toxicity data, however, predominantly concern values derived from 28d sediment toxicity tests with the freshwater insect *C. riparius*. For not a single fungicide chronic toxicity data for more than one benthic species or for a marine species could be found. This is surprising since many fungicides have biocidal properties that may impact different taxonomic groups of aquatic organisms (Maltby et al., 2009).

It is anticipated that in the near future more sediment toxicity data for fungicides and the oligochaete species *Lumbriculus variegatus* will become available, since a sediment toxicity test with this species currently is a data requirement for PPPs that trigger risks due to sediment exposure and is recommended in the Tier 1 effect assessment procedure for fungicides by EFSA (EFSA, 2013).

For the fungicides cyprodinil, cyproconazole and penthiopyrad both 28d EC50 and 28d NOEC values are available for *C. riparius*. Overall, the 28d NOEC value is not more than a factor of 2 lower than the corresponding 28d EC50 value.

Duft et al. (2003) report an 56d EC50 and 56d EC10 value for the snail Potamopyrgus antipodarum and tributyltin of respectively 0.09 µg/g OC and 0.0002 µg /g OC (Table 13), suggesting that the standard test species *C. riparius* (see Table 12) may not be a representative sensitive taxon for this organotin fungicide.

Table 13
Chronic sediment toxicity data for fungicidal substances.

Compound	Species	Effect endpoint	EC50/NOEC (µg/g OC)		References
			Mean	Toxicity endpoint	
Bixafen	*Chironomus riparius*	Emergence	35.6 [a;b]	28d EC50	EU DAR
Bromuconazole	*Chironomus riparius*		125 [a]	28d NOEC	Footprint/EFSA peer review
Cyprodinil	*Chironomus riparius*	Emergence	6480 [a] 3200 [a]	27d EC50 27d NOEC	EU DAR
Cyproconazole	*Chironomus riparius*	Emergence	3520 [a] 2000 [a]	28d EC50 28d NOEC	EU DAR
Difenoconazole	*Chironomus riparius*		400 [a]	28d NOEC	Footprint/EFSA peer review
Disodium phosphonate	*Chironomus riparius*		2724 [a]	28d NOEC	Footprint
Fenbuconazole	*Chironomus riparius*		320 [a]	28d NOEC	Footprint/EFSA peer review
Fenhexamid	*Chironomus riparius*		2112 [a]	28d NOEC	Footprint
Fenpropidin	*Chironomus riparius*		1600 [a]	28d NOEC	Footprint
Fludioxonil	*Chironomus riparius*	Emergence	1600 [a]	28d NOEC	Footprint
Fluopyram	*Chironomus dilutus*	Emergence	1040 [a]	54d NOEC	EU DAR
Imazalil	*Chironomus riparius*		6616 [a]	28d NOEC	Footprint
Isopyrazam	*Chironomus riparius*	Emergence	2240 [a]	28d NOEC	EU DAR
Penconazole	*Chironomus riparius*		1008 [a]	28d NOEC	Footprint
Penthiopyrad	*Chironomus riparius*	Mortality	2712 [a] 2000 [a]	28d LC50 28d NOEC	EU DAR
Picoxystrobin	*Chironomus riparius*		200 [a]	28d NOEC	Footprint
Propiconazole	*Chironomus riparius*		1000 [a]	28d NOEC	Footprint
Quinoxyfen	*Chironomus riparius*	Emergence	21.92 [a]	28d NOEC	Footprint
Thiabendazole	*Chironomus riparius*		120 [a]	28d NOEC	Footprint
Triadimenol	*Chironomus riparius*		26.68 [a]	28d NOEC	Footprint
Triazoxide	*Chironomus riparius*		400 [a]	28d NOEC	Footprint
Triphenyltin	*Potamopyrgus antipodarum*	Repro	0.09 [c] 0.0002 [c]	56d EC50 56d EC10	Duft et al., 2003

[a] Assuming 2.5% organic carbon content in OECD 218 standard sediment .

[b] Active ingredient.

[c] Production of unshelled embryos; recalculated from TPT-Sn to TPT.

3.7 Herbicides

Table 14 summarizes the semi-chronic (test duration 10-13 d) sediment toxicity data for benthic organisms and herbicides. Table 15 further summarizes the chronic (test duration ≥21 d) sediment toxicity data.

For six herbicides 10-13d L(E)C50 data for benthic organisms (including rooted macrophytes) could be found (Table 14). The test species concerned *H. azteca* (one out of twelve data points), *C. dilutus* (three out of twelve), *C. riparius* (two out of twelve) and the rooted macrophyte *Myriophyllum aquaticum* (five out of twelve data points).

Chronic (28d) toxicity data for *C. riparius* could be found for eleven herbicides (Table 15), while for one herbicide (linuron) 21d toxicity data could be found for the macrophyte *Myriophyllum spicatum* (Table 16).

The toxicity data for *H. azteca* and *Chironomus* species as mentioned in Tables 14 and 15 overall are in the higher range (with the exception of the 28d *C. riparius* NOEC for benfluralin, diflufenican and flumioxazine) when compared with the reported EC50 values for the macrophyte *M. aquaticum* in Table 14, which is not surprising in view of the specific toxic mode-of-action of herbicides. The lowest sediment toxicity value found was for the herbicide metsulfuron-methyl and the aquatic macrophyte *M. aquaticum* (0.021 µg/g OC). The expectation of relatively low toxicity of herbicides to benthic animals is probably the main reason for the very low number of papers found for this class of compounds as well as the fact than most herbicides are relatively water soluble and do not have a strong tendency to partition into sediments.

Table 14
Semi-chronic sediment toxicity data for herbicides and the benthic invertebrates Chironomus dilutus, Chironomus riparius and Hyalella azteca and the rooted macrophyte Myriophyllum aquaticum.

Compound	Species	Effect endpoint	EC50 / LC50 (µg/g OC)		References
			Mean (Range)	Toxicity endpoint	
Atrazin	*C. dilutus*	Mortality	>186	10d LC50	Douglas et al., 1993
Atrazin	*M. aquaticum*	RGR fresh weight Yield fresh weight	28[a] 20.4[a]	10d E_rC50 10d E_yC50	Teodorovic et al., 2012
Atrazin	*M. aquaticum*	Yield fresh weight	116	13d E_yC50	Schreiber et al. 2011
Bentazone	*Ch. riparius*	Mortality Growth	276000 (209000-325000) 10850 (7200-14500)	10d LC50 10d NOEC	Mäenpää et al., 2003
DNOC	*M. aquaticum*	Yield fresh weight	348.4	13d E_yC50	Schreiber et al. 2011
Ioxynil	*C. riparius*	Growth	787	10d NOEC	Mäenpää et al., 2003
Metsulfuron methyl	*M. aquaticum*	Yield fresh weight	0.021	13d E_yC50	Schreiber et al. 2011
Oxyfluorfen	*H. azteca* *C. dilutus* *C. dilutus*	Mortality Mortality Growth	>6140[b] 630 312	10d LC50 10d LC50 10d NOEC	Ding et al., 2011

[a] Assuming 2.5% organic carbon content in OECD 218 standard sediment,

[b] Range of values given as >12300, >3400 and >2720 µg/g OC for three sediments.

The 21d EC50 value for *Myriophyllum spicatum* and the photosynthesis-inhibiting herbicide linuron of 632 µg/g OC (Table 16) is relatively high when compared with the 10-13d EC50 values reported for *Myriophyllum aquaticum* and the photosynthesis inhibitor atrazin (20.4 - 116 µg/g OC) (Table 15). This may be explained by the fact that the test with *Myriophyllum aquaticum* concerned a sediment contact test without overlying water (Teodorovic et al., 2012; Feiler et al., 2013), while the test with *Myriophyllum spicatum* was conducted in a water-sediment test system with a water column above a sediment compartment. In the latter test system Burešová et al. (2013) spiked the sediment with linuron. The authors showed that already after seven days concentrations of linuron in shoot tissues were at high levels that stayed more or less constant thereafter (test with duration of 21d). At day 7 concentrations in the overlying water were still very low, while pore water concentrations were 1000 times higher.This indicates that the linuron in the *Myriphyllum spicatum* shoots primarely originated from the sediment (pore water) compartment. This could also be substantiated by modelling approaches.

From a theoretical point of view, for rooted macrophytes the ecotoxicologically relevant exposure concentration in sediments will be the herbicide concentration in pore (interstitial) water, since plants do not consume particulate organic matter fractions like typical benthic animals. In terms of the effects observed on *M. spicatum* in the test conducted by Burešová et al. (2013), the EC50 value based on pore water concentrations was higher than that based on linuron concentrations in the overlying water, but, as discussed above the EC50 based on pore water concentrations seems to be most realistic.

Table 15

Chronic sediment toxicity data for herbicides and benthic invertebrates.

Compound	Species	Effect endpoint	EC50/NOEC (µg/g OC)		References
			Mean	Toxicity endpoint	
Aclonifen	*Chironomus riparius*	Emergence	4400 [a] 1280 [a]	28d EC50 28d NOEC	EU DAR
Aminopyralid	*Chironomus riparius*		1868 [a]	28d NOEC	Footprint
Benfluralin	*Chironomus riparius*		4.48 [a]	28d NOEC	Footprint
Diflufenican	*Chironomus riparius*		80 [a]	28d NOEC	Footprint
Dimethachlor	*Chironomus riparius*		1000 [a]	28d NOEC	EU DAR
Flumioxazine	*Chironomus riparius*		28.8 [a]	28d NOEC	Footprint
Halosulfuron-methyl	*Chironomus riparius*		200 [a]	28d NOEC	Footprint
Metazachlor	*Chironomus riparius*		317.2 [a]	28d NOEC	Footprint
Penoxsulam	*Chironomus riparius*	Develop. rate & emergence	32400 [a]	28d NOEC	EU DAR /Footprint
Propanil	*Chironomus riparius*	Development rate	640 [a]	28d NOEC	EU DAR
Trifluralin	*Chironomus riparius*	Growth rate	33680 [a] 4800 [a]	30d EC50 30d NOEC	EU DAR

[a] Assuming 2.5% organic carbon content in OECD 218 standard sediment.

Table 16

21d EC50 data (measurement endpoint relative growth rate of wet weight biomass) for the photosynthesis-inhibiting herbicide linuron and the rooted macrophyte Myriophyllum spicatum in water-sediment test systems of which the sediment was spiked with linuron. The toxicity values are expressed in terms of total sediment concentration (µg/kg OC), and concentration in pore water and overlying water (µg/L). Data derived from Burešová et al. (2013).

	Sediment (µg/g OC)	Pore water (µg/L)	Overlying water (µg/L)
21 d E_rC50 (RGR wet weight of *Myriophyllum spicatum*)	632 [a]	1095	22.7

[a] Assuming 2.5% organic carbon content in OECD 218 standard sediment.

In the scientific literature, and in the EU data bases, no sediment toxicity data could be found for the emergent rooted macrophyte *Glyceria maxima*, although this species is mentioned as a potentially suitable test species for herbicides (EFSA, 2013).

Most experience with sediment toxicity testing on macrophytes is developed within the context of retrospective risk assessments to evaluate the potential toxicity of historically polluted sediments. Feiler et al. (2004) developed for this purpose the sediment contact test with *M. aquaticum* (see also ISO, 2010). Biernacki et al. (1997) developed a sediment toxicity test with *Vallisneria americana* based on naturally contaminated sediments. Their research revealed that an index of the leaf-to-root surface area ratio was a reliable predictor of sediment phytotoxicity; the ratio of leaf-to-root mass was also useful but proved less consistent results. Shoots grown in sediments that were relatively less contaminated with organic compounds had lower values of the leaf-to-root surface area ratio, while plants grown in more contaminated sediments had greater values.

Most studies with rooted macrophytes and polluted sediments focussed on the ability of the plants to take up contaminants from sediments. Hinman and Klaine (1992) studied macrophyte uptake from a model sediment (sand) soaked in spiked growth medium. They found lower concentrations in macrophytes exposed via the spiked model sediment than after exposure to a medium with no sediment present. Uptake of hydrophobic chemicals has been studied by modeling and in experiments (Gobas et al., 1991; Roessink et al., 2010; Dhir et al., 2009; Vanier et al., 2001). None of these studies quantified effects on macrophytes of standardized sediment pesticide exposure.

3.8 Relation between NOECs for *Chironomus riparius* derived from 28d sediment-spiked and 28d water-spiked OECD toxicity tests

For thirty-four PPPs (nine insecticides, one acaricide, fifteen fungicides, nine herbicides) 28d NOEC values for both a water-spiked and sediment-spiked *C. riparius* test could be retrieved from EU data bases (including IUPAC Footprint) (Table 17). Overall, the NOEC expressed in terms of concentration per kg dry weight sediment is higher when for the corresponding PPP also the NOEC expressed in concentration per litre overlying water is higher.

In Figure 1 the correlation between the 28d NOECs of the water and sediment spiked *C. riparius* tests is presented (data from Table 17) on basis of linear regression analysis. The fitted line is y = 0.913x – 0.918, in which y is the log NOEC µg/L as derived from the OECD water-spiked *Chironomus riparius* test, x the log NOEC µg/kg dw sediment as derived from the OECD sediment-spiked *Chironomus riparius* test, 0.913 is the slope and -0.918 is the intercept. The coefficients of correlation and determination are 0.776 and 0.603 respectively. These coefficients indicate a fairly good but not perfect correlation between these corresponding NOECs. The interpretation of the correlation in part my be hampered by the fact that the NOECs mentioned in Table 17 usually are expressed in terms of nominal/measured initial concentrations of the PPP in either the overlying water or sediment. Note that during the toxicity test with the same PPP the rate of dissipation and bioavailability may differ between water and sediment compartment, and this difference may be substance dependent.

Table 17

28d NOEC values for Chironomus riparius as derived from the spiked sediment (NOEC µg/kg dw) and spiked water (NOEC µg/L) OECD toxicity tests. Data derived from EU data bases, including IUPAC Footprint.

Name substance	Type of substance	Effect endpoint	Test duration	NOEC (µg/kg dw sed)	NOEC (µg/L)
Buprofezin	Insecticide	emergence	28 d	2720	100
Chlorantranilprole	Insecticide	emergence	28 d	5	2.5
Fipronil	Insecticide		28 d	0.2	0.1
Gamma-cyhalothrin	Insecticide	emergence	28 d	12.6	0.047[#]
Lambda-cyhalothrin	Insecticide		28 d	105	0.16
Lufenuron	Insecticide	emergence	28 d	40	2.0
Spinetoram	Insecticide	emergence	28 d	97.2	0.75
Tau-fluvalinate	Insecticide	emergence	28 d	200	0.24
Thiamethoxam	Insecticide	emergence	28 d	100	10
Tebufenpyrad	Acaricide		28 d	640	190 (110 mm)
Bixafen	Fungicide	emergence	28 d	20000	15.6
Bromuconazole	Fungicide		28 d	3125	250
Cyproconazole	Fungicide	emergence	28 d	50000	5000
Difeconazole	Fungicide		28 d	10000	15
Fenbuconazole	Fungicide		28 d	8000	1730
Fenhexamid	Fungicide		28 d	52800	6200
Fenpropidin	Fungicide		28 d	40000	1000
Fludioxonil	Fungicide	emergence	28 d	40000	200
Imazalil	Fungicide		28 d	165400	181
Penconazole	Fungicide		28 d	25200	2000
Picoxystrobin	Fungicide		28 d	5000	62500
Propiconazole	Fungicide		28 d	25000	8000
Quinoxyfen	Fungicide	emergence	28 d	548	128
Thiabendazole	Fungicide		28 d	3000	2000
Triadimenol	Fungicide		28 d	667	100
Aclonifen	Herbicide	emergence	28 d	32000	472[$]
Aminopyralid	Herbicide		28 d	46700	130000
Benfluralin	Herbicide		28 d	112	231
Diflufenican	Herbicide		28 d	2000	100
Dimethachlor	Herbicide	emergence	28 d	25000	4000
Halosulfuron-methyl	Herbicide		28 d	5000	10000
Penoxsulam	Herbicide	Dev & emer	28 d	810000	61000
Propanil	Herbicide	Developm.	28 d	16000	1900
Trifluralin	Herbicide	Growth rate	30 d	120000	250

[#] developmental rate; [$] 21 days.

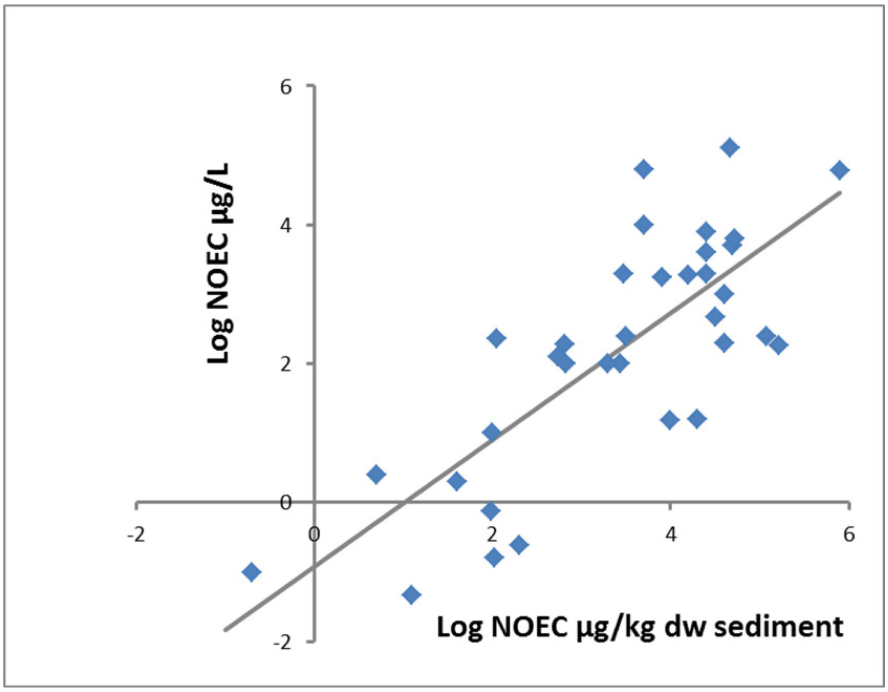

Figure 1 *Relationship between log NOEC (µg/L) of the water spiked OECD test and log NOEC (µg/kg dw sediment) of the sediment spiked OECD test for different PPPs (see Table 17) and the insect Chironomus riparius.*

3.9 Influence of hydrophobicity of insecticides on acute toxicity to Hyalella azteca and Chironomus species

Since *H. azteca* and *C. dilutus* are arthropods and have nervous systems, these species are expected to be especially sensitive to insecticidal compounds, rather than to non-insecticidal compounds. The relationship between the acute toxicity and the hydrophobicity of the insecticide, as expressed by the logarithm of the octanol-water partition coefficient (K_{ow}), was investigated in more detail. This was done to explore the potential value of QSAR approaches on basis of log K_{ow} to predict sediment toxicities in case of missing data. Values for (log) K_{ow} were taken from Tomlin (2003), as were molecular weights which were used to transform lethal concentrations in µg/g OC into µmoles/g OC. For species where more than a single toxicity value was available, the geometric mean was used as an average toxicity value. For the organochlorine pesticides and the acetyl-cholinesterase inhibitor mexacarbate no log K_{ow} was available in Tomlin, whereas the value for the pyrethroid bifenthrin was given as >6 and this compound was therefore also excluded. Data is given in Table 18.

In view of the very limited number of toxicity data available, all insecticidal compounds were treated primarily as belonging to a single data set. However, within the insecticidal compounds there may be large differences in the mode of action, and for this reason the second stage of the analysis distinguishes between pyrethroids and non-pyrethroid insecticides.

Figure 2 shows a plot of log (1/LC50) for *Hyalella azteca* vs. log K_{ow} for all insecticides in Table 18, i.e. the pyrethroids and non-pyrethroid insecticides for which K_{ow} was available in Tomlin (2003). Figures 3 and 4 give similar plots for the toxicity data of *C. dilutus* and *C. riparius*, spanning slightly different ranges of K_{ow} values because of the variation in compounds for which LC50 data for the different species were available.

Table 18

Hydrophobicity and sediment toxicity of insecticidal compounds.

Compound	Log K_{ow}	Log (1/LC50)[a]		
		H. azteca	*C. dilutus*	*C. riparius*
Cyfluthrin	5.95	2.43	-	-
Cypermethrin	6.6	3.06	2.58	-
Deltamethrin	4.6	2.81	2.92	-
Esfenvalerate	6.22	2.50	-	-
Fenpropathrin	6.0	2.34	1.59	-
L-cyhalothrin	6.9	3.01	2.21	-
Permethrin	6.1	1.46	1.20	-
Tefluthrin	6.4	2.16	-	-
Abamectin	4.4	1.64	3.69	-
Carbaryl	1.85	-	-	1.14
Carbofuran	1.52	-	2.93	2.71
Chlorpyrifos	4.7	1.91	1.69	-
Diazinon	3.3	1.30	-	-
Dichlorvos	1.9	-	-	2.60
Ethion	4.28	-	-	1.47
Fipronil	4	2.03	-	3.53
Malathion	2.75	-	-	3.18
Methylparathion	3	-	3.31	-
Mevinphos	0.127	-	-	2.41
Parathion	3.83	-	2.08	-
Propargite	5.7	-0.22	-0.44	-
Propoxur	1.56	-	-	1.76

[a] LC50 in µmoles/g OC.

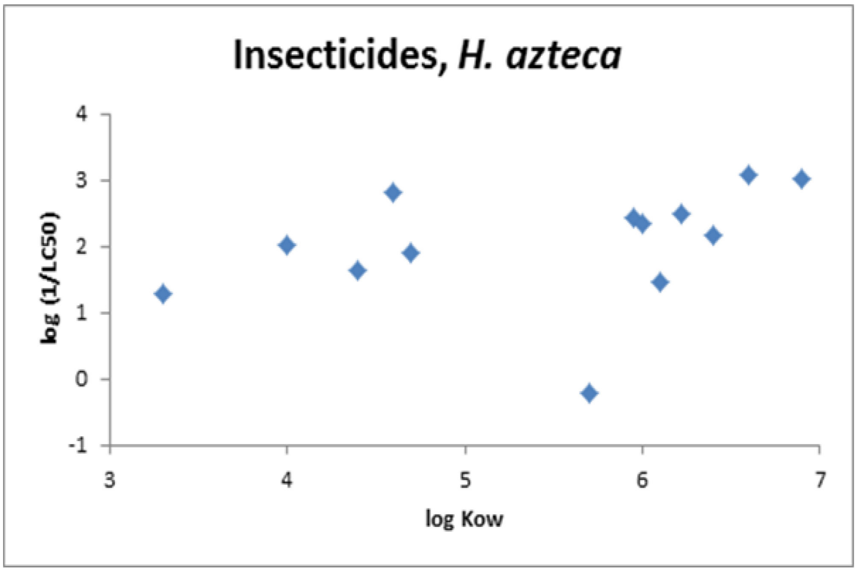

Figure 2 *Acute toxicity (1/LC50) of insecticides in Table 17 to Hyalella azteca as a function of their octanol-water partition coefficient (LC50 in µmoles/g OC).*

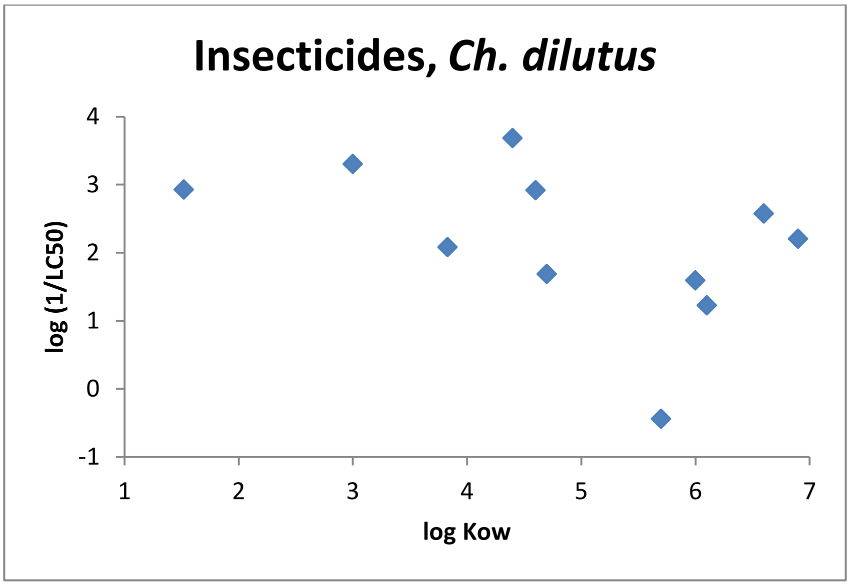

Figure 3 *Acute toxicity (1/LC50) of insecticides in Table 17 to Chironomus dilutus as a function of their octanol-water partition coefficient (LC50 in µmoles/g OC).*

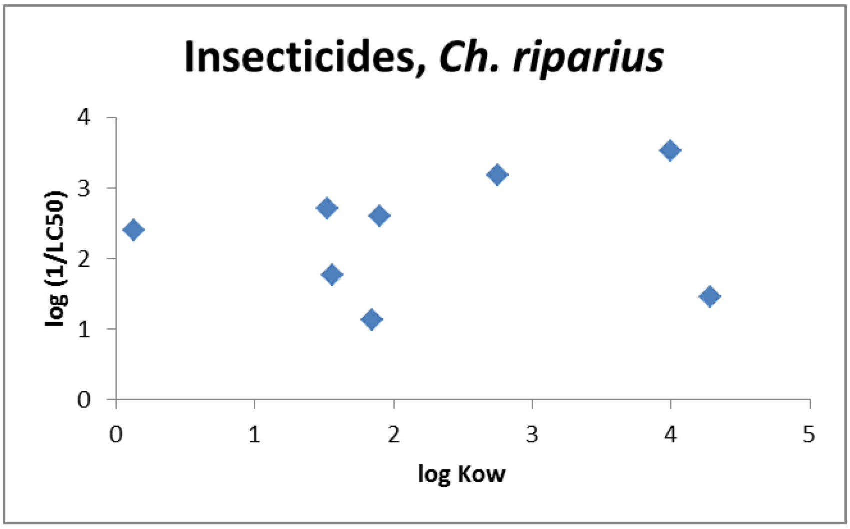

Figure 4 *Acute toxicity (1/LC50) of insecticides in Table 7 to Chironomus riparius as a function of their octanol-water partition coefficient (LC50 in µmoles/g OC).*

Assuming a linear relationship between log (1/LC50) and log K_{ow}, a coefficient of determination, equal to the fraction of variance in log (1/LC50) explained by the variation in log K_{ow}, can be calculated for the three sets of toxicity data. The results of this calculation are given in Table 19, where the toxicity data for propargite were excluded because this compound is much less toxic than other compounds of similar hydrophobicity. However, even when excluding propargite the relationship between toxicity and hydrophobicity remains very weak, which is also obvious from Figures 2 - 4.

Table 19

Coefficient of correlation and coefficient of determination for the linear relationship between log (1/LC50) and log K_{ow} for Hyalella azteca, Chironomus dilutus and Chironomus riparius, including all compounds into a single linear relationship.

Species	Coefficient of correlation	Coefficient of determination	Number of data points
Hyalella azteca	0.335	0.11	13
Chironomus dilutus	-0.460	0.21	11
Chironomus riparius	0.138	0.02	8

When separate correlations are calculated for pyrethroid and non-pyrethroid insecticides, the relationships do not improve substantially (Table 20). Within the group of pyrethroids which presumably act through a similar mode of action, the coefficients of determination are very low and non-significant.

Table 20

Coefficient of determination for toxicity versus log K_{ow}, distinguishing between species and pyrethroid and non-pyrethroid insecticides (values in parenthesis give the number of data points on which the correlation was based).

Species	Coefficient of determination	
	Pyrethroids	Non-pyrethroids
Hyalella azteca	0.01 (8)	0.41 (5)
Chironomus dilutus	0.12 (5)	0.42 (6)
Chironomus riparius	- (0)	0.02 (8)

Hence, it appears that for the compounds under consideration the hydrophobicity is not related in a simple fashion to the 10d LC50 of *H. azteca*, *C. dilutus* and *C. riparius*. This seems to suggest that QSAR methods that primarily use log K_{ow} information to predict sediment toxicity may not be the way forward. However, the validity of this conclusion is severely hampered by the limited size of the data set involved.

4 PPP effect assessment for sediment-dwelling organisms

4.1 Trigger for sediment effect assessment

In edge-of-field situations, and considering the emission routes drift, surface run-off and drainage addressed by the exposure assessment of PPPs, sediments will typically be contaminated through migration of the active substance from the overlying aqueous phase into the sediment, i.e. the substance will first pass through the aqueous phase before settling in the sediment.

In the former Guidance Document on Aquatic Ecotoxicology under Directive 91/414/EEC (SANCO, 2002), and its recent update (EFSA, 2013), sediment toxicity tests with benthic organisms are required if in the water-sediment fate study >10% of the applied radioactivity of the parent compound is present in the sediment at or after day 14, and the chronic toxicity value (EC10 or NOEC) derived from the 21d *Daphnia* test (or another comparable chronic toxicity tests with a relevant crustacean or insect) is <0.1 mg/L. Moreover, according to SANCO (2002) compounds applied more than once, with a potential for accumulation of residues in the sediment should be given consideration for sediment testing as well.

This reflects that gradual build up or accumulation of PPPs in the sediment phase will only occur for hydrophobic and slowly degrading chemicals, or after repeated applications, and only for this category of PPPs exposure through the sediment may pose a higher threat than the initial, aqueous, exposure immediately following entry into the water.

Due to their nature especially strongly hydrophobic and slowly degrading chemicals will result in long-term exposure. For such chemicals chronic instead of acute endpoints from longer lasting tests, are more plausible predictors of toxicity under field conditions. If chronic toxicity is the endpoint to be tested, ideally the exposure concentration in the sediment of the test system that is used to express the effects should be a (time weighted) average concentration in the course of the toxicity test. Furthermore in chronic risk assessments it is common practice that the effect estimate concerns a chronic measurement endpoint (e.g. growth, reproduction, emergence time) expressed in terms of EC10 or NOEC values.

4.2 Choice of Tier 1 benthic test species

As previously stated, the vast majority of papers summarised in this document dealt with toxicity data for *H. azteca*, *C. dilutus* and *C. riparius*. However, various other species have also been used in sediment toxicity experiments (species are specified in Tables 1 - 16). *Hyalella azteca* appears to be the most often used species for sediment toxicity testing in North America, which is not surprising in view of its abundance in lakes and rivers of North America (Barba and Sánchez, 2007). Since the species is not indigenous in Europe, it is not often used in European sediment toxicity testing, where the preferential species seems to be *Chironomus riparius*. In the near future more data for *Lumbriculus variegatus* may become available in Europe, since this oligochaete worm was selected as a standard test species for PPP registration (see e.g. EFSA, 2013).

The choice of what species should be considered ‘standard’ for toxicity testing is governed by many factors, such as the availability of internationally accepted test protocols and the sensitivity of the standard test species relative to other species (which is, of course, dependent on the substance tested) and the representativeness of the test species for the environmental compartment/habitat under evaluation. For each species proposed/selected there will usually be arguments pro and contra. The use of *H. azteca* has e.g. been questioned by Wang et al. (2004), who observe that this species derives little nutrition from sediments and should be considered epibenthic, primarily responding to contaminants in the overlying water column, a point also made by Palmquist et al. (2011), who observe that *H. azteca* may be an overly conservative model for community or ecosystem-level impact assessments. Doig and Liber (2010) have investigated the dependence of the degree of burrowing of *H. azteca* on various environmental factors like sand content of the sediment, the size of the animals, and various other factors, which seems to indicate that strict standardization of test protocols using this species is a prerequisite for successful use of such tests in sediment toxicity assessment. However, such objections have also been raised against the use of *Chironomus riparius* by e.g. De Haas et al. (2002) who concluded that this species is not a suitable test organisms for assessing sediment toxicity since its response is heavily influenced by the nutritional value of the sediments under consideration. This criticism may be less important in prospective risk assessment procedures that are largely based on standardized sediment toxicity tests, including a standardised sediment composition (e.g. OECD tests).

For retrospective and site specific risk assessments experts advocate the simultaneous use of a range of species when assessing the toxicity of a given natural sediment or a specific substance, resulting in 'test batteries' of several of the more commonly used species in toxicity testing in parallel (see e.g. Ducrot et al., 2005; Feiler et al., 2013), including less commonly used species like bacteria (Rönnpagel et al., 1995; Heise and Ahlf, 2005), nematodes (Kammenga et al., 1996; Traunspurger et al., 1997) or macrophytes (Feiler et al., 2004), or alternatively including more differentiated schemes of testing including a variety of systems differing in trophic levels and/or complexity (see e.g. Beketov et al., 2013). Such a battery of test species and test systems is also important to calibrate/validate the different effect assessment tiers in prospective risk assessment of sediment exposure (Diepens et al., 2013) including that of plant protection products.

Based on the available sediment toxicity data for different test species and PPPs, the benthic insects *Chironomus riparius* and/or *Chironomus dilutus* seem to be suitable and representative standard test species in prospective risk assessments to evaluate effects of sediment exposure to insecticides in edge-of field freshwater ecosystems (Table 3, 9 and 10), although for pyrethroids and several organophosphorous insecticides the crustacean *Hyalella azteca* (Table 6) may be more suitable. This observation is in accordance with available toxicity data for insecticides and aquatic organisms predominantly dwelling in the water column, in that arthropods (insects and crustaceans) can be considered as the most sensitive taxonomic group (see e.g. Maltby et al. 2005). Selecting *Chironomus riparius (*or another OECD chironomid such as *C. acutus*) and a benthic crustacean indigenous for Europe (or *Hyalella azteca*) as the set of Tier 1 standard test species for sediment effect assessment of insecticides therefore seems to be a logical choice. The insect *Chironomus riparius* already is selected in Europe as standard test species in sediment risk assessment, although data for other OECD *Chironomus* species may be used as well. Sediment toxicity data for *Hyalella azteca* may be readily available when mining the data bases for the registration of insecticides in North America. Another option might be to always select *Chironomus* as Tier 1 standard test species in the effect assessment for sediment-dwelling organisms and insecticides, and to request a toxicity value for a representative benthic crustacean only if the toxicity data for the type of insecticide under evaluation and typical water column arthropods indicate that crustaceans overall are more sensitive than insects (e.g. chronic toxicity value of *Daphnia* is more than a factor of 10 lower than that of *Chironomus* in water-only tests).

Based on the available sediment toxicity data for fungicides (Tables 12 and 13) it is difficult to identify the most relevant Tier 1 test species, since the number of taxa that were used in sediment toxicity tests is limited to only a few. Furthermore, the available information for triphenyltin seems to indicate that not necessarily arthropods comprise the most sensitive benthic organisms. In addition, from species sensitivity distributions for fungicides constructed with toxicity data of more typical water column aquatic organisms (Maltby et al., 2009) it appears that representatives of a wider array of different taxonomic groups may be sensitive to fungicides. If risks of sediment exposure are triggered, the benthic insect *C. riparius* and the benthic oligochaete *Lumbriculus variegatus* are the Tier 1 test species in Europe. For this reason an option might be to use one of the following combinations as Tier 1 standard test species to assess effects of sediment exposure to fungicides: (1) the insect *Chironomus riparius* (or *C. dilutus*) and the oligochaet worm *Lumbriculus variegatus* if the toxicity data for typical water column organisms due not indicate herbicidal properties, (2) either *Chironomus riparius* or *Lumbriculus variegatus* (the latter if e.g. the terrestrial worm and Tier 1 test species *Eisenia* is relatively sensitive) and a rooted macrophyte (e.g. *Myriophyllum* or *Glyceria*) if the toxicity data for typical water column organisms indicate herbicidal properties of the fungicide. The final selection of the two Tier 1 test species should be informed and motivated by the available information on sensitivity of water (column) organisms for the same fungicide and related substances with a similar toxic mode-of-action (read across).

On basis of the available sediment toxicity data for herbicides (Tables 15 - 16) it seems logical to select a rooted macrophyte as Tier 1 test species (e.g. *Myriophyllum*) if risks of sediment exposure to herbicides is triggered. The sediment contact test with *Myriophyllum aquaticum* (Feiler et al., 2004; ISO, 2010) seems to be a good candidate Tier 1 test in case the herbicide primarily affects dicots, at least under the condition that a standard OECD sediment is used that is spiked with the herbicide. If the herbicide primarily affects monocots *Glyceria maxima* may be a more appropriate test species, although no data could be found in the literature to underpin this. However, the data presented in Table 15 seem to suggest that also *C. riparius* may be a relatively sensitive benthic test organism for some herbicides (e.g. benfluralin and flumioxazine). Unfortunately no sediment toxicity data for herbicides and *Lumbriculus variegatus* are available. A reasonable option for the effect assessment of herbicides for benthic organisms is to select as Tier 1 standard test species a rooted macrophyte (e.g. *Myriophyllum*) and either the insect *Chironomus riparius* or the oligochaet worm *Lumbriculus variegatus*. The final selection of the two Tier 1 test species should be informed and motivated by the available information on sensitivity of water (column) and soil organisms for the same herbicide and related substances with a similar toxic mode-of-action (read across). Another option might be to always select a rooted macrophyte (e.g. *Myriophyllum*) as Tier 1 standard test species in the effect assessment for sediment-dwelling organisms and herbicides, and to request a toxicity value for *Chironomus* or *Lumbriculus* only if the toxicity data for the type of herbicide under evaluation indicate that typical water column invertebrates may be sensitive as well (e.g. 21d EC10/NOEC of *Daphnia* differs less than factor of 10 from that of the most sensitive primary producer).

4.3 What is the ecotoxicologically relevant concentration?

OECD Guideline 218, the sediment-water *Chironomid* test using spiked sediment, specifies that as a minimum the concentrations in overlying water, pore water and sediment should be measured (OECD, 2004a). Effect concentrations should be expressed as concentrations in sediment, based on dry weight, at the beginning of the test. Similarly, the sediment-water *Chironomid* life-cycle test using spiked water or spiked sediment (OECD Guideline 233), specifies the same minimum set of measurements in overlying water, pore water and sediment (OECD, 2010). Although effect concentrations should be expressed as a concentration in the sediment at the start of the test, Guideline 233 does not explicitly specify on what basis the L(E)Cx and NOEC values should be expressed.

OECD Guideline 225 (*Lumbriculus* toxicity test using spiked sediment) specifies that the concentration in sediment and overlying water should be verified through measurement, although the Guideline also outlines a method for isolation and subsequent measurement of the chemical in pore water. Effect concentration should be expressed in mg/kg sediment on dry weight basis (OECD, 2007).

The U.S. EPA OPPTS 850.1735 Guideline (whole sediment acute toxicity invertebrates, freshwater) states that 'Concentrations of spiked chemicals may be measured in sediment, interstitial water and overlying water ...', but does not specify on what basis effect concentrations should be expressed, other than 'In some cases it may be desirable to normalize sediment concentrations to factors other than dry weight, such as organic carbon for non-ionic organic compounds or acid volatile sulfides for certain metals.' (US EPA, 1996).

The European Food Safety Authority (EFSA) has recently published a Scientific Opinion on the assessment of exposure of organisms to substances in soils (EFSA, 2010a). They advocate that the 'Ecologically Relevant Concentration', i.e. the concentration which is considered relevant for assessing effects, should be reported both in concentration units of mass of pesticide per mass of dry soil, and in parallel as a concentration in pore water (EFSA, 2009; EFSA, 2010a). If the rationale behind the advocated use of both measures of exposure (insufficient scientific knowledge on the importance of various routes of uptake) would also hold for sediment, which seems likely, then this would strongly suggest that toxicity data generated for sediment organisms should also be reported both on the basis of pore water concentrations and on the basis of sediment mass (or OC mass in sediment). This is obviously not yet in line with OECD and EPA guidelines, where the most common suggestion is to report effect concentrations on the basis of sediment mass only.

The use of pore water concentrations as the basis for calculation of effect concentrations, however, may introduce some new uncertainties. Sappington (2013) points out that caution should be taken when using calculated instead of measured pore water concentrations, since slight differences in quality of organic carbon may result in large differences between assumed and truly occurring partitioning in sediments. Xu et al. (2007) also stress that, although organic carbon normalized concentrations expressed on the basis of sediment weight and pore water concentrations reduce variability due to sediment type, but not to aging, it is the free concentration in pore water that is essentially independent of sediment conditions, and this free concentration would therefore be preferred as the basis for calculation of effect concentrations. However, analytical error in measured pore water concentrations tends to increase with chemical hydrophobicity, resulting in increased uncertainty (Sappington, 2013) and expressing risk on the basis of sediment concentrations only may avoid complications resulting from analytical uncertainty in measured pore water concentrations.

4.4 Possible chronic effect assessment procedure for sediment-dwelling organisms

As stated above, hydrophobic and slowly degrading PPPs in particular will result in long-term sediment exposure. Risks due to short-term exposure of sediment organisms most likely will be covered by the risk assessment schemes for typical water column organisms, since (1) peak concentrations of these hydrophobic PPPs in the water column may be relatively high and trigger acute risks to pelagic and epi-benthic water organisms, and (2) most typical sediment-dwelling species are taxonomically related to typical water column species. Consequently, risk assessment schemes for PPPs and sediment-dwelling organisms should focus on chronic effects due to long-term exposure in the sediment compartment.

Most of the studies encountered in the literature review report acute and semi-chronic toxicity values in terms of L(E)C50, based on measurement endpoints like mortality, inhibition of growth or reproduction etc. For chronic risk assessment of sediment organisms, it seems advisable to report results of long-term exposure studies in terms of ECx, for example EC10, or NOEC (according to EFSA (2013) ECx values are preferred).

From the literature review it appears that the results of semi-chronic 10 d L(E)C50 values seem not to deviate more than a factor of 5 from corresponding NOEC values from chronic tests (duration ≥28 d). Examples for this are the toxicity values reported for *Hyalella* and *Chironomus dilutus/riparius* and the compounds DDD (Tables 2 and 4), lambda cyhalothrin (Tables 5 and 7), abamectine, lufenuron, teflubenzuron and fipronil (Tables 10 and 11). An exception on this rule of thumb is the observation that the 56 d EC50 for *Chironomus dilutus* and permethrin is a factor of 29 lower than the reported 10d LC50 (Tables 4 and 5).

In the Sections below a possible tiered effect assessment approach for PPPs and sediment toxicity data is explored by evaluating the PPPs for which sediment toxicity data are available for at least five different benthic taxa.

Since a chronic risk assessment seems to be the most appropriate way forward for sediment-dwelling organisms subject to PPP exposure, and the majority of data available are acute or semi-chronic in nature, we used the following extrapolation procedure to estimate toxicity values that can be used in the chronic effect assessment:

1. 28d NOEC values are used as such.
2. 28d EC50 values are extrapolated to chronic EC10/NOEC values by applying an AF of 3.
3. 10-12d L(E)C50 values are extrapolated to chronic EC10/NOEC values by applying an AF of 5.
4. 1-4d L(E)c50 values are extrapolated to chronic EC10/NOEC values by applying an AF of 10.

Note that this procedure is adopted here only to obtain a large enough data set to enable exploring the scope of possible higher-tier approaches. It is by no means the intention to propose these extrapolation procedures in the regulatory effect assessment. By using the extrapolation procedure described above, for four substances only (the insecticides endosulfan, cypermethrin, permethrin and chlorpyrifos) a chronic toxicity data set could be obtained that comprised at least five different test species. A Tier 1 effect assessment on basis of at least two standard test species of benthic organisms (see proposal in Section 4.2), the Geometric mean approach (see e.g. EFSA, 2013) and the Species Sensitivity Distribution (SSD) approach was explored. For the SSD approach the computer program ETX 2.0 was used (Van Vlaardingen et al., 2004).

As explained above, to get insight in the sensitive taxonomic groups of benthic organisms that are of potential importance for the sediment effect assessment, in first instance the available information on toxicity data and species sensitivity distributions available for typical water organisms (and soil organisms) can be explored. It is reasonable to assume that for PPPs with a specific toxic mode-of-action the potential sensitive taxonomic groups will be the same for water, soil and sediment organisms. For insecticides the potential sensitive taxonomic group is Arthropoda (including crustaceans and insects) (e.g. Maltby et al., 2005).

Endosulfan

The (estimated) chronic toxicity data for different benthic taxa and the organochlorine insecticide endosulfan are reported in Table 21. Note that all these toxicity data were estimated by applying an AF of 5 to the reported L(E)C50 values (for background data see Table 3).

The geometric mean estimated chronic NOEC/EC10 values for the two corresponding benthic crustaceans and insects are 70.1 µg/g OC and 17.3 µg/g OC, respectively. For one Polychaete species an estimated NOEC/EC10 is available (17 µg/g OC for *Nereis virens*). This information suggests that in sediments not only arthropods may be sensitive. Nevertheless, the sediment toxicity value for the insect *C. dilutus* (freshwater) and the polychaete *N. virens* (marine) are quite similar.

Table 21

Comparison of (estimated) chronic sediment toxicity data for endosulfan between the amphipods Hyalella azteca and Leptocheirus plumulosus, the insects Chironomus dilutus and Jappa kutera and the polychaete Nereis virens.

	Estimated chronic EC10/NOEC values (µg/g OC)				
	H. azteca	***L. plumulosus***	***C. dilutus***	***J. kutera***	***N. virens***
	170.6	28.8	4.6	64.8	3.4
Geomean	70.1 (Crustacea)		17.3 (Insecta)		3.4 (Polychaeta)

The Species Sensitivity Distribution approach (SSD) was applied to the five estimated chronic toxicity data (four arthropods and one polychaete) available for endosulfan (see Figure 5). The Anderson-Darling test for normality was accepted at all levels, indicating a proper fit of the curve.

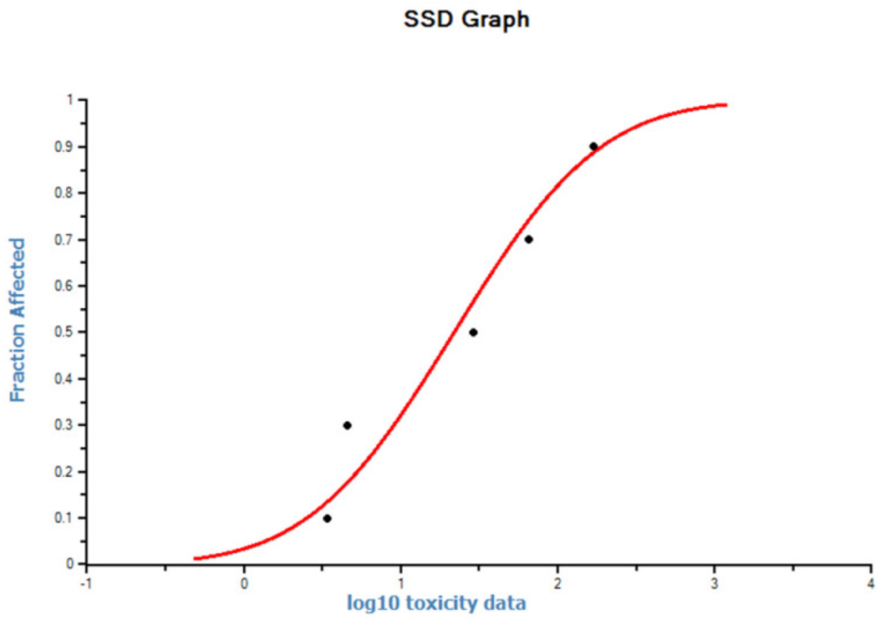

Figure 5 *Species Sensitivity Distribution curve on basis of the five estimated chronic sediment toxicity data for endosulfan reported in Table 21.*

The median Hazardous Concentration to 5% of the species (HC5) on basis of estimated chronic toxicity data for endosulfan is 1.09 µg/g OC. The corresponding lower limit HC5 (LL HC5), however, is as low as 0.02 µg/g OC, reflecting the low number of toxicity data used to construct the curve as well as the relatively high variability in sensitivity between different arthropod taxa.

Assuming that (1) *C. dilutus* is a representative and sensitive Tier 1 benthic species for endosulfan in edge-of-field surface waters, (2) toxicity data for all benthic invertebrates (including freshwater and saltwater species) can be used in the Tier 2 assessment, and (3) by following a more or less similar effect assessment approach as used to derive RACs for water organisms (EFSA, 2013), the chronic effect assessment procedure for endosulfan and sediment-dwelling organisms may be as follows:

Tier 1 $\mathbf{RAC_{sed;ch}}$ = chronic toxicity value of *C. dilutus*/AF = 4.6/10 = 0.46 µg/g OC.
Tier 2A Geom-$\mathbf{RAC_{sed;ch}}$ = Geomean chronic toxicity for insects/AF = 17.3/10 = 1.73 µg/g OC or chronic toxicity value for *N. virens*/AF = 3.4/10 = 0.34 µg/g OC.
Tier 2B SSD-$\mathbf{RAC_{sed;ch}}$ = median HC5 benthic invertebrates/AF = 1.09/3 = 0.36 µg/g OC (Note that EFSA (2013) proposes an AF of 3 in chronic effect assessments for aquatic invertebrates).

An appropriate micro-/mesocosm experiment on the ecological impact of endosulfan, and focusing on sediment exposure, could not be found. The results of the different tiers do not deviate much for endosulfan.

Cypermethrin

The (estimated) chronic toxicity data for different benthic taxa and the pyrethroid insecticide cypermethrin are reported in Table 22. Note that all these toxicity data were estimated by applying an AF of 5 to the reported 10-12 d L(E)C50 values (for background data see Table 3).

Table 22

Comparison of (estimated) chronic sediment toxicity data for the pyrethroid insecticide cypermethrin between the amphipods Hyalella azteca, Eohautorius estuarius, Ampelica abdita and Corophium volutator, and the insect Chironomus dilutus (for background data see Table 5).

	Estimated chronic EC10/NOEC values (µg/g OC)				
	H. azteca	***E. estuarius***	***A. abdita***	***C. volutator***	***C. dilutus***
	0.07	0.28	12.0	0.06	0.21
Geomean	0.34 (Crustacea)				0.21 (Insecta)

The geometric mean chronic toxicity for cypermethrin on basis of estimated chronic EC10/NOEC values for the four benthic crustaceans is 0.34 µg/g OC, a value higher than the estimated chronic EC10/NOEC for the benthic insect *C. dilutus* (0.21 µg/g OC). The Species Sensitivity Distribution approach (SSD) was applied to the five estimated chronic toxicity data (all arthropods) available for cypermethrin (see Figure 6). The Anderson-Darling test for normality was accepted at levels of 0.05 and lower and rejected at 0.1, illustrating that the SSD curve did not fit the toxicity data very well. The median Hazardous Concentration to 5% of the species (HC5) on basis of estimated chronic toxicity data for cypermethrin and presented in Figure 6 is 0.007 µg/g OC. The corresponding lower limit HC5 (LL HC5), however, is 0.00004 µg/g OC.

Following the same procedure as described above for endosulfan chronic effect assessment, and selecting *H. azteca* and *Chironomus* as Tier 1 test species, the procedure for cypermethrin may be as follows:

Tier 1 $RAC_{sed;ch}$ = estimated chronic EC10/NOEC of *H. azteca*/AF = 0.07/10 = 0.007 µg/g OC.

Tier 2A Geom-$RAC_{sed;ch}$ = estimated chronic EC10/NOEC for *C. dilutus*/AF = 0.21/10 = 0.021 µg/g OC. (Note that the geomean value of 0.34 µg/g OC for benthic crustaceans is higher than that for *C. dilutus*= 0.31 µg/g OC).

Tier 2B SSD-$RAC_{sed;ch}$ = median HC5 benthic arthropods/AF = 0.007/3 = 0.002 µg/g OC.

The Tier 2B RAC appears to be lower than the Tier 1 and Tier 2A RACs. This probably can be explained by the phenomenon of the high variability in available toxicity data fror crustaceans. In particular the high value for the marine crustacean *Ampelica abdita* forces the lower tail of the SSD curve to the left relative to the toxicity values of the most most sensitive arthropod species. Excluding the toxicity value of *Ampelica abdita* in the SSD curve results in the SSD curve presented in Figure 7. The median Hazardous Concentration to 5% of the species (HC5) on basis of estimated chronic toxicity data for cypermethrin and presented in Figure 7 is substantially higher (viz., 0.027 µg/g OC) than the one derived from Figure 6. This is also the case for the corresponding lower limit HC5 (0.0013 µg/g OC). Note that the Anderson-Darling test for normality was accepted at all levels, indicating a proper fit of the curve. Using the HC5 of the curve presented in Figure 7 and applying an AF of 3 results in a **Tier 2B SSD-$RAC_{sed;ch}$** of 0.009 µg/g OC (a value slightly higher than the Tier 1 $RAC_{sed;ch}$).

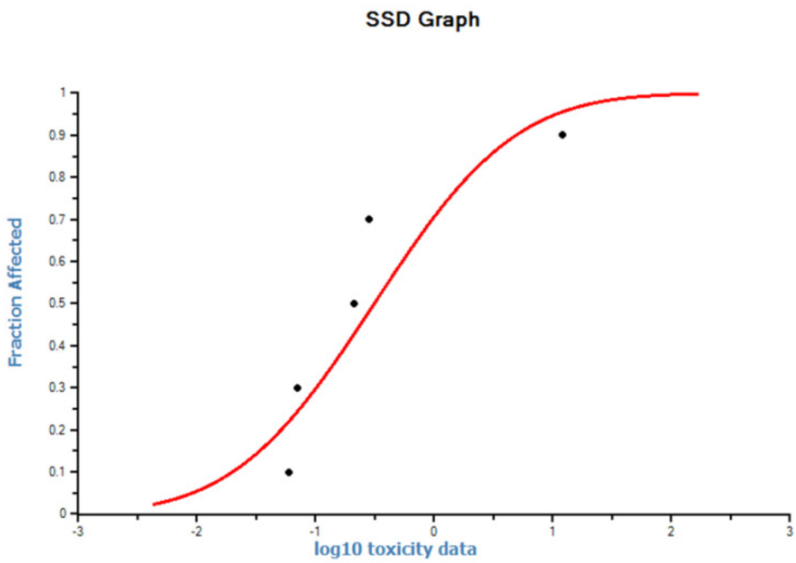

Figure 6 *Species Sensitivity Distribution curve on basis of the five acute sediment toxicity data for cypermethrin reported in Table 22.*

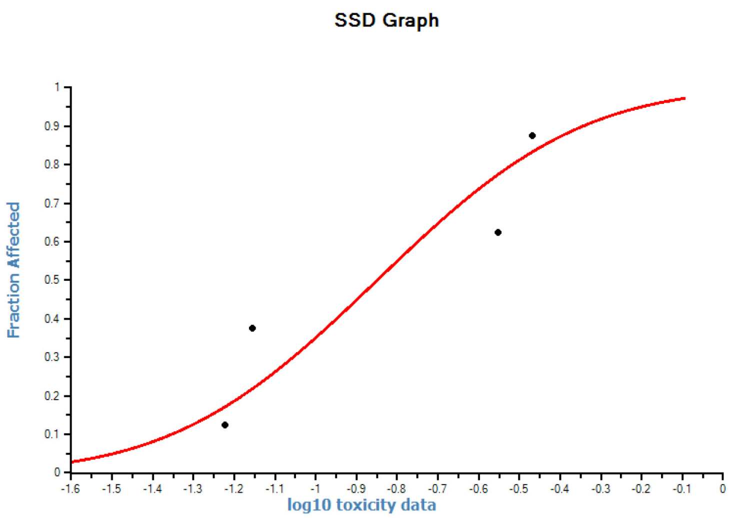

Figure 7 *Species Sensitivity Distribution curve on basis of the four acute sediment toxicity data for cypermethrin reported in Table 22 and excluding the toxicity value of Ampelica abdita.*

Permethrin
The (estimated) chronic toxicity data for different benthic taxa and the pyrethroid insecticide permethrin are reported in Table 23. Note that most of these toxicity data were estimated by applying an AF of 5 to the reported 10-12d L(E)C50 values (for background data see Table 5), except the value for *C. dilutus* wich was derived by applying and AF of 3 to the 56d EC50 reported in Table 7.

Table 23
Comparison of (estimated) chronic sediment toxicity data for the pyrethroid insecticide permethrin between the amphipods Hyalella azteca, Eohautorius estuarius and Ampelica abdita, and the insects Chironomus dilutus and Chironomus riparius.

	Estimated chronic EC10/NOEC values (µg/g OC)				
	H. azteca	*E. estuarius*	*A. abdita*	*C. dilutus*	*C. riparius*
	2.74	3.60	228.6	0.28	4.38
Geomean	13.10 (Crustacea)			1.11 (Insecta)	

The geometric mean estimated chronic EC10/NOEC for the three benthic crustaceans is 13.10 µg/g OC, while that is 1.11 µg/g OC for the two benthic insects. The Species Sensitivity Distribution approach (SSD) was applied to the five chronic toxicity data (all arthropods) estimated for Permethrin (see Figure 8). The Anderson-Darling test for normality was accepted at all levels. The median Hazardous Concentration to 5% of the species (HC5) on basis of estimated chronic toxicity data for permethrin and presented in Figure 8 is 0.066 µg/g OC. The corresponding lower limit HC5 (LL HC5) is 0.0002 µg/g OC.

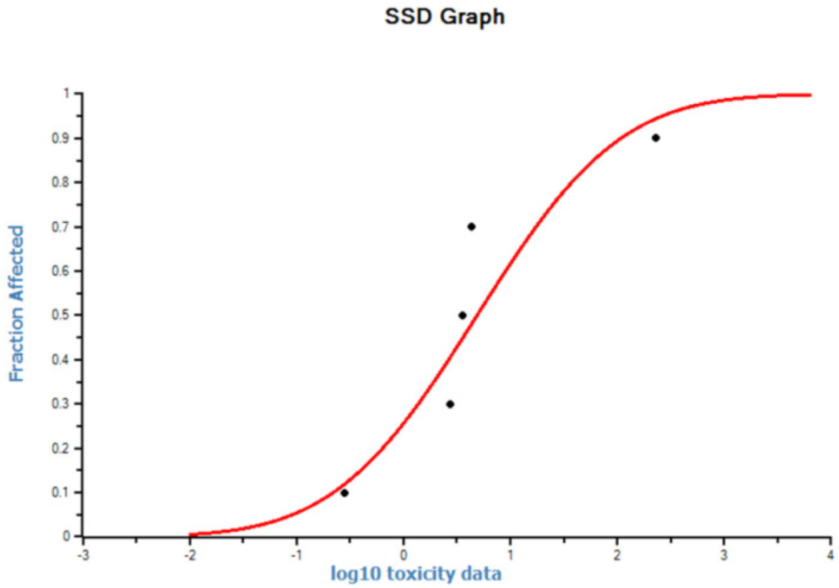

Figure 8b *Species Sensitivity Distribution curve on basis of the five chronic sediment toxicity data for permethrin reported in Table 23.*

A chronic effect assessment procedure for permethrin may be as follows:

Tier 1 RAC$_{sed;ch}$ = chronic value of *C. dilutus*/AF = 0.28/10 = 0.028 µg/g OC.

Tier 2A Geom-RAC$_{sed;ch}$ = Geomean 10d LC50 for benthic insects /AF = 1.11/10 = 0.111 µg/g OC (Note that the geomean value of 13.1 µg/g OC for benthic crustaceans is higher than that for insects).

Tier 2B SSD-RAC$_{sed;ch}$ = median HC5 benthic arthropods/AF = 0.066/3 = 0.022 µg/g OC.

Again the Tier 2B RAC does not deviate much from the Tier 1 RAC, which may be caused by the relatively low number of toxicity data available to construct the SSD curve. An appropriate micro-/mesocosm experiment on the ecological impact of permethrin, and focusing on sediment exposure, could not be found.

Chlorpyrifos

The (estimated) chronic toxicity data for different benthic taxa and the organophosphorus insecticide chlorpyrifos are reported in Table 24. Note that most of these toxicity data were estimated by applying an AF of 5 to the reported 10-12 d L(E)C50 values (for background data see Table 9), except the value for *A. tenuiremis* wich was derived by applying and AF of 10 to the 4d LC50 of 1.74 µg/g OC.

Table 24
Comparison of (estimated) chronic sediment toxicity data for the organophosphorus insecticide chlorpyrifos between the amphipods Hyalella azteca, Eohautorius estuarius and Ampelica abdita, the copepod Amphiascus tenuiremis and the insect Chironomus dilutus.

	Estimated chronic EC10/NOEC values (µg/g OC)				
	H. azteca	***E. estuarius***	***A. abdita***	***A. tenuiremis***	***C. dilutus***
	0.56	2.64	3.18	0.174	1.44
Geomean	0.95				1.44 (Insecta)

The geometric mean estimated chronic EC10/NOEC for the four corresponding benthic crustaceans is 0.95 µg/g OC (only one chronic value for a benthic insect is available = 1.44 µg/g OC). The median Hazardous Concentration to 5% of the species (HC5) on basis of toxicity data presented in Table 24 and the SSD curve presented in Figure 9 is 0.121 µg/g OC. The corresponding lower limit HC5 (LL HC5) is 0.007 µg/g OC.

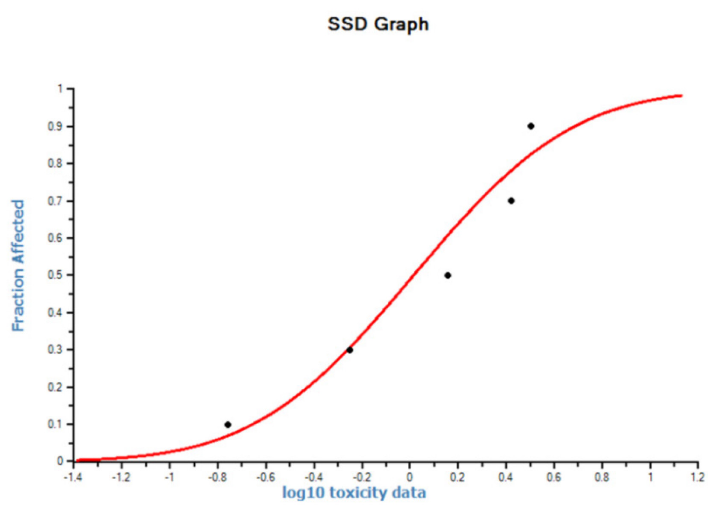

Figure 9 *Species Sensitivity Distribution curve on basis of the five acute sediment toxicity data for chlorpyrifos reported in Table 9.*

Applying the procedure decribed above, a chronic effect assessment procedure for chlorpyrifos may be as follows:

Tier 1 RAC$_{\text{sed;ac}}$ = chronic toxicity value of *H. azteca*/AF = 0.56/10 = 0.056 µg/g OC.
Tier 2A Geom-RAC$_{\text{sed;ac}}$ = Geomean 10d LC50 for crustaceans/AF = 0.95/10 = 0.095 µg/g OC.
Tier 2B SSD-RAC$_{\text{sed;ac}}$ = median HC5 benthic arthropods/AF = 0.121/3 = 0.040 µg/g OC.

The results of the different tiers do not deviate much for chlorpyrifos. An appropriate micro-/mesocosm experiment on the ecological impact of chlorpyrifos, and focusing on sediment exposure, could not be found.

Since for the fungicides and herbicides mentioned in Tables 12 to 16 toxicity data for only a few test species are available, the proposal for the tiered effect assessment procedure cannot be evaluated for these substances.

5 Concluding remarks

This review report illustrates our limited knowledge on potential ecotoxicological effects of sediment exposure to plant protection products, although these products may accumulate in the sediments of edge-of-field surface waters, particularly when they are hydrophobic and persistent. Based on the available data in this review report, building blocks can be extracted to construct possible lower tier effect assessments on basis of standard and additional test species of sediment-dwelling organisms. Before starting an effect assessment procedure for typical sediment-dwelling organisms, and to avoid unnecessary testing as much as possible, it is of utmost importance to explore in the dossier (of the product under evaluation) the toxicity data available for typical water column species and soil invertebrates. This information may guide the final selection of the benthic species that have to be tested.

In the EFSA Aquatic Guidance Document (EFSA, 2013) it is described that lower tiers need to be calibrated/validated by higher tiers. For the effect assessment scheme that assesses risks of sediment exposure to benthic organisms this largely is a research activity to date. In particular for herbicides and fungicides that accumulate in the sediment compartment more laboratory toxicity information is required to get insight in species sensitivity distributions and the potential sensitive taxonomic or functional groups. Furthermore, a potential useful surrogate reference tier to calibrate lower tiers may be tailor-made micro-/mesocosm tests in which the long-term response of benthic populations is expressed in terms of sediment exposure concentrations. For the time being, until enough higher-tier information for sediment organisms becomes available to calibrate the lower tiers, the size of the assessment factors used to derive $RAC_{sed;ch}$ values may be guided by the current practice of the effect assessment schemes for typical water organisms (e.g. EFSA, 2013). Note that the taxonomic groups of typical benthic and typical water column organisms do not deviate substantially.

In this report no attention is paid to possible effects of sediment exposure of PPPs on the performance of the microbial community in the sediment and its upper debris/litter layer. This does not mean that this may not be of importance. EFSA (2010b) identified microbes as one of the key drivers in the risk assessment of PPPs and it was advised to select functional groups as ecological enity and processes as attribute in the specific protection goal for microbes. In the EFSA Aquatic Guidance Document (EFSA, 2013), however, a risk assessment procedure for aquatic microbes is not developed since in regulatory documents Tier-1 data requirements for aquatic microbes are not defined. It was concluded that it needs to be discussed with risk managers whether the potential risks of PPP exposure to aquatic microbes (bacteria, fungi) need to be addressed, and, if so, which tier 1 data requirement should be adopted. This conclusion also applies to the sediment risk assessment scheme to be developed for PPPs.

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improve the
quality of life

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Alterra Wageningen UR is the research institute for our green living environment. We offer a combination of practical and scientific research in a multitude of disciplines related to the green world around us and the sustainable use of our living environment, such as flora and fauna, soil, water, the environment, geo-information and remote sensing, landscape and spatial planning, man and society.

The mission of Wageningen UR (University & Research centre) is ‘To explore the potential of nature to improve the quality of life’. Within Wageningen UR, nine specialised research institutes of the DLO Foundation have joined forces with Wageningen University to help answer the most important questions in the domain of healthy food and living environment. With approximately 30 locations, 6,000 members of staff and 9,000 students, Wageningen UR is one of the leading organisations in its domain worldwide. The integral approach to problems and the cooperation between the various disciplines are at the heart of the unique Wageningen Approach.