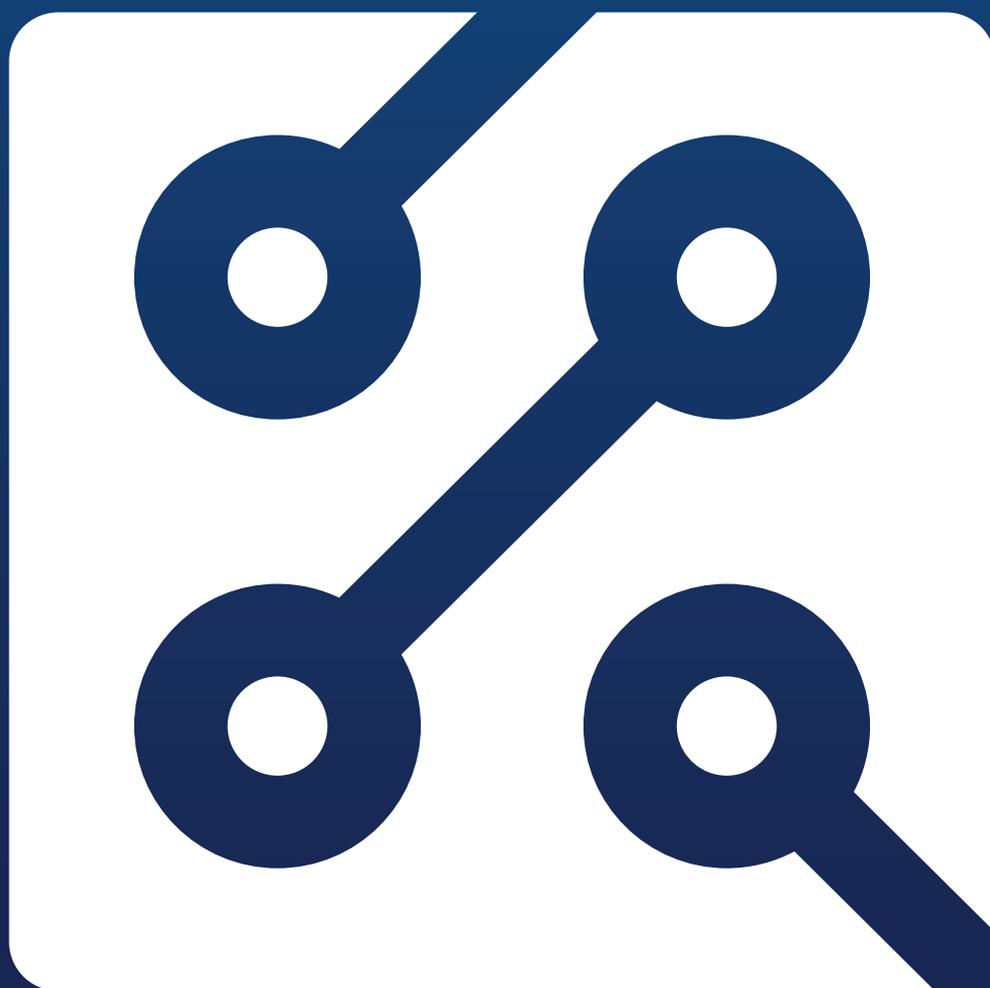


Principles for Environmental Risk Assessment of the Sediment Compartment

Proceedings of the Topical Scientific Workshop
Helsinki, 7-8 May 2013



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Principles for Environmental Risk Assessment of the Sediment Compartment: Proceedings of the Topical Scientific Workshop

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FIGURE 1: CONCEPTUAL OUTLINE FOR METALS

1. Introduction and aims

ECHA's topical scientific workshops facilitate dialogue between academia, regulators, the regulated industry and other stakeholders in order to assess the regulatory impact of the latest scientific developments in a particular area. The aim is that new or improved approaches of practical use in REACH, CLP and the Biocidal Products Regulation will emerge, catalysed by the discussions and emerging common understandings in the workshops.

Following a proposal from a group of experts, ECHA organised the first Topical Scientific Workshop on Risk Assessment for the Sediment Compartment.

The Topical Scientific Workshop on Risk Assessment for the Sediment Compartment was held from 7 to 8 May 2013 at ECHA, bringing together experts in the field of sediment risk assessment to brainstorm and develop updated scientific principles and guidelines for assessing ecological risks of chemical substances for freshwater and marine sediments. Recent developments for particular substance types (such as metals) and a broad understanding of risk assessment methodologies in other regulated products and from schemes outside the EU were part of the discussion.

The primary objective of this workshop was to review the state of the art and to develop updated scientific principles and guidelines for assessing ecological risks of chemical substances for freshwater and marine sediments. The discussion elements included:

- Discussing the current state of the science on sediment toxicology.
- Reviewing current risk assessment frameworks for sediments relying on the extrapolation from the pelagic community, and developing further recommendations on the applicability of these extrapolation approaches.
- Addressing the water-sediment interface and the epi-benthonic community.
- Establishing links among available lines of laboratory and field evidence on ecotoxicity, bioavailability, and ecosystem quality/function, and specifically for freshwater systems.
- Developing general principles applicable to different regulatory schemes, considering the protection goals set forth by current regulatory processes whilst focusing on the regulation of chemicals under REACH and CLP. The broader context is biocides, plant protection products and pharmaceuticals, and broader legal instruments are also relevant, e.g. the Water Framework Directive, the Industrial Emissions Directive, and equivalent regulatory processes in non-EU jurisdictions.

The workshop brought together over 100 experts from around the world to set the scientific principles for assessing risks to the sediment compartment in all regulatory contexts. The two-day workshop included general plenary sessions with case studies and topical breakout group sessions, where the participants discussed specific recommendations on how to use scientific knowledge for regulatory purposes.

1.1 WORKSHOP ORGANISATION

The scientific organisation of the workshop was handled by an international Scientific Committee (SC). The SC members were appointed in their personal capacity but overall represented a broad worldwide coverage of national and international organisations and sectors, including experts with regulatory, business and academic backgrounds.

International Scientific Committee composition

EU and International Institutions

Jose Tarazona, Co-Chair, ECHA
Bram Versonnen, Co-Chair, ECHA
Bernd Gawlick, JRC
Joop de Knecht, OECD

National Regulatory Organisations

Henrik Tyle, Danish EPA
Willie Peijnenburg, RIVM
Robert M. Burgess, US EPA
Mario Carere, ISS

Industry/Business

Hugo Waeterschoot, Eurometaux
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Tiina Multasuo
Francesca Pellizzato
Anne-Mari Karjalainen
Daniele Ape
Laurence Deydier Stéphane
Charmaine Ajao
Derek Knight

The main responsibilities of the SC included the identification of the specific objectives and main topics to be covered and the overall workshop structure; identification of the invited speakers, topics for the background documents, and other workshop participants; revision of the background documents prepared by selected experts; chairing the breakout sessions and the preparation of the workshop conclusions and the workshop proceedings. Following the completion of the workshop the SC were responsible, as associate editors, for providing editorial suggestions to improve the proceedings document.

The contribution of the SC members has been the key and essential element for this workshop's success, and ECHA acknowledges the invaluable contribution provided by the external members.

A structured pre-workshop consultation with the experts identified through an expression of interest was conducted for producing "thought starter" background documents that were prepared by the local organising committee and other experts and finalised by the SC.

In addition, nine case studies, an introduction to the EU regulatory framework for sediment risk assessment and a summary of relevant guidance documents were prepared and distributed to the participants prior to the workshop and are described below.

The workshop covered the following three main topics:

- Problem definition and conceptual model for sediment risk assessment (RA)
 - Protection goals and ecological relevance.
 - Risk characterisation and environmental impact assessment.
- Exposure assessment
 - Environmental fate and transfer of chemicals from water to suspended matter and sediment.
 - Behaviour processes, within sediment distribution, ageing, and bioavailability estimations.
- Effect assessment
 - Effect assessment for epi-benthonic organisms, relevant taxonomic groups and experimental tools.
 - Effect assessment for benthonic organisms, relevant taxonomic groups and experimental tools.

The workshop included key speakers, a presentation of selected case studies, a poster exhibition and discussions in six breakout groups covering the following topics:

Group 1A: Risk assessment: problem definition and conceptual model. Focus: Prospective risk assessment.

Group 1B: Risk assessment: problem definition and conceptual model. Focus: Retrospective risk assessment.

Group 2A: Exposure assessment. Focus: Organic chemicals and pesticides.

Group 2B: Exposure assessment. Focus: Metals.

Group 3A: Effect assessment. Focus: Effect assessment using tests on sediment organisms.

Group 3B: Effect assessment. Focus: Integrated testing strategies, EPM and use information from other taxa.

The present proceedings describe the background documents ('thought-starters' and regulatory introduction) as they were distributed to the participants (sections 2, 3.1, 3.2, 4.1, 4.2, 5.1, 5.2) and the outcome of the workshop (sections 3.3, 3.4, 4.3, 4.4, 5.3, 5.4, 6). Whenever there were different views in the working groups, these are reported in the proceedings. References in the regulatory introduction and thought-starter sections were kept, but are not comprehensive. No referencing was done in the other sections. A literature list is, however, given at the end of the proceedings. Further integration of the thought-starter documents and the outcome and recommendations of the workshop with full references is foreseen in a publication/publications in a scientific journal.

2. Introduction to the EU regulatory framework for sediment risk assessment

This summary of the EU regulatory framework for sediment risk assessments presents examples of the linkage between the scientific developments and regulatory decision making in this field. This summary has been prepared as a background document for facilitating the workshop discussions and does not represent a position of ECHA. Readers are referred to the legal texts and guidance documents produced by the responsible European Institutions.

2.1 INTRODUCTION

Environmental risk assessments (ERA), including sediment assessments, are typical tools for supporting decision making in the regulatory context, and cover all kinds of spatial situations, from local to worldwide assessments, under very different regulatory contexts. Typical extremes for chemical ERAs are the purely predictive and generic assessments conducted for marketing chemicals (e.g. substances under REACH, or pre-marketing authorisations for pesticides, biocides, pharmaceuticals, etc. existing in many jurisdictions) and the retrospective site-specific assessments conducted on contaminated areas as diagnosis tools in the identification of ecological effects and the responsible stressors. In between these two extremes, there are several regulatory processes using risk-based tools or risk assessment elements for prospective and monitoring purposes. These include the processes for setting ecological quality standards/criteria, the emission-permit authorisations, the assessment of risk associated with contaminated sediments and its management, etc.

All these processes have common elements as well as specificities. This workshop was intended to create consensus around the available scientific tools, needs and challenges regarding the risk assessment of the sediment compartment in all these different regulatory processes.

The EU regulatory system can be used as an example for the identification of the different regulatory needs, and therefore the main elements of this system and the current guidelines are summarised in this introduction.

2.2 SEDIMENT RISK ASSESSMENT UNDER REACH

Except when there are exceptions, all substances marketed or imported in the EU above one tonne per year must be registered under REACH. For the registration, the company must gather information according to a set of regulatory requirements and demonstrate safe use. The information requirements are linked to the annual tonnage. Sediment specific requirements are only mandatory above 100 (fate data) and 1 000 tonnes per year (ecotoxicity data), respectively; and can be waived due to justified specific and general adaptations.

The ECHA guidance¹ offers default emission factors and a generic environmental fate scenario based on the previous TGD (Technical Guidance Document for Risk Assessment, see reference to biocides in the next section). It allows a generic predictive assessment based on the tonnage, use and operational conditions, standardised through a set of use descriptors, particularly the Environmental Release Categories (ERCs). ERCs are linked to conservative default release factors to be used as a starting point for a first tier environmental exposure assessment. The physical-chemical and fate properties of the substance are then used to predict the behaviour of the chemical in the Sewage Treatment Plant (STP) (e.g. using the model SimpleTreat 3.10). For the local assessment, the release of treated wastewater is the only sediment exposure route considered relevant. The exposure is quantified as the Predicted Environmental Concentration in sediment (PEC_{sed}). The concentration in freshly deposited sediment is taken as the PEC for sediment, estimated from the PEC in water and experimental or estimated partitioning rates to suspended matter. The guidance offers default values for all relevant parameters, thus a generic local PEC_{sed} can be calculated and considered applicable to all local emissions in Europe, although the default

¹ ECHA Guidance documents on Information Requirement and Chemical Safety Assessment:

Chapter R7. Endpoint specific guidance

Chapter R.10. Characterisation of dose [concentration] - response for environment

Chapter R.16. Environmental exposure estimation

<http://echa.europa.eu/guidance-documents/guidance-on-information-requirements-and-chemical-safety-assessment>

values can be adapted to specific conditions if justified. The local risk for wide-dispersive uses (e.g. from consumers or small, non-industrial companies) is estimated for a default STP serving 10 000 inhabitants. In addition, a regional assessment is conducted for a standard area, a region represented by a typical densely populated EU-area located in Western Europe (i.e. about 20 million inhabitants, distributed in a 200 x 200 km² area). For calculating the regional PEC_{sed}, a multi-media fate-modelling approach is used (e.g. the SimpleBox model). All releases to each environmental compartment for each use, assumed to constitute a constant and continuous flux, are summed and averaged over the year and steady-state concentrations in the environmental compartments are calculated. The regional concentrations are used as background concentrations in the calculation of the local concentrations.

The effect assessment is based on the estimation of the Predicted No Effect Concentration (PNEC_{sed}). In the absence of ecotoxicological data for sediment-dwelling organisms, the PNEC_{sed} may be provisionally calculated using the equilibrium partitioning method (EPM). This method uses the PNEC_{water} for aquatic organisms and the suspended matter/water partitioning coefficient as inputs. If ecotoxicity data on sediment dwelling organisms is available, the PNEC is calculated using the lowest value and an Assessment Factor (AF) related to the amount of information. The default AFs are 100, 50 and 10 for freshwater (for one, two or three long-term No Observed Effect Concentrations (NOECs) from sediment invertebrate species representing different living and feeding conditions) and range between 10 000 and 10 for the marine environment. There are no recommendations for using Species Sensitivity Distributions (SSD) or other higher-tier approaches; thus, registrants should develop and justify the cases for using these methodologies.

In the risk assessment, the PEC_{sed} is compared to the PNEC_{sed} through the Risk Characterisation Ratio (RCR=PEC/PNEC). For substances with a log K_{ow} greater than five (or with a corresponding K_{psed} value), the PEC/PNEC ratio resulting from the EPM is increased by a factor of 10 to take into account possible uptake through ingestion of sediment. This approach is considered as a screening level assessment of the risk to sediment dwelling organisms. If a PEC/PNEC ratio greater than one is derived with this method, then tests – preferably long-term (i.e. chronic) – with benthic organisms using spiked sediment must be conducted for a more realistic risk assessment.

2.3 VERTICAL PRE-MARKETING LEGISLATIONS: PLANT PROTECTION PRODUCTS

The guidance for biocidal products is also based on the TGD² and the provisions are similar to those presented for REACH, but take into account the different pathways for environmental release associated with the variety of use patterns for biocides. However, a different approach is used for pesticides under the Plant Protection Products (PPP) legislation.

The current practice for pesticides is based on the Guidance Document (GD) on aquatic risk assessment (Sanco/3268/2001 rev.4 (final) 17 October 2002) but is under revision. According to the current guidance on aquatic ecotoxicity, the assessment of risk to sediment organisms is triggered by the results of a water/sediment dissipation study conducted with the radiolabelled substance. Sediment assessment is required for active substances which appear with more than 10% of applied radioactivity (AR) in the sediment. *Chironomus* sp. (*Insecta, Diptera, Chironomidae, Chironominae*) is the required freshwater test organism to assess potential effects on sediment-dwelling organisms. To prevent unnecessary testing with substances of low toxicity to invertebrates, the water-only NOEC in the chronic Daphnia test (or in a comparable study with insects when this group of organisms is more sensitive) must be <0.1 mg/l for testing with sediment-dwelling organisms to be warranted. For persistent substances (see EU-Guidance-Document 9188/VI/97),

² EU-TGD Part 2

http://ihcp.jrc.ec.europa.eu/our_activities/public-health/risk_assessment_of_Biocides/doc/tgd/tgdpart2_2ed.pdf

it may be justified to require a life-cycle test on chironomids to generate data on reproduction effects. It is well-established that for non-polar organic compounds of $\log K_{ow}$ up to 5 that in such a system at equilibrium, adequate predictions of toxicity in sediment can be made from the concentration in the water phase³.

The exposure to active substances is evaluated using 10 FOCUS (Forum for Co-ordination of pesticide fate models and their Use) surface water (SW) scenarios⁴. Each of these scenarios should apply to the 90th percentile of the exposure concentration in a large region. At the time of the development of the FOCUS SW scenarios, comprehensive databases for checking this assumption were not available, so it is not currently clear if the FOCUS scenarios are good predictions of this 90th percentile. EFSA (the European Food Safety Authority) has developed a consistent methodology for scenario derivation that could be applied to improve the exposure assessment⁵.

The FOCUS calculation partitions the substance between water and sediment and assumes that equilibrium exists (i.e. worst-case because dilution would be expected in nature). The concentration in the water phase will reflect the 'bioavailable' concentration in the sediment. Consequently, using the appropriate water phase concentration, *Daphnia* toxicity data and the standard triggers for aquatic invertebrates as established in the uniform principles (e.g. Commission Regulation (EU) No 546/2011), it is possible to determine whether there is potential for sediment toxicity.

The risk characterisation is performed through the toxicity/exposure ratios (TERs). If the toxicity/exposure ratios (TERs) (based on the maximum exposure concentration from the FOCUS SW modelling) for *Daphnia* are less than 100 or 10 for acute or chronic endpoints, respectively, the sediment triggers are met and testing of sediment dwelling organisms should be required. For insecticides, where it is possible that *Daphnia* are not a representative test organism (e.g. neonicotinoids), acute toxicity data for *Chironomus riparius* can also be used to trigger long-term sediment studies. If the TER resulting from the maximum PEC at Step 2 and the *C. riparius* 48 h LC50 is less than 100, then long-term sediment testing is required, if the sediment exposure triggers are met. Although data requirements specify *Chironomus* sp. as the test organism, and survival and development (including emergence of adults) as endpoints, no further guidance is included on the type of study to be conducted (e.g. the "spiked-sediment" toxicity test (OECD 218) or the "spiked water" toxicity test (OECD 219)).

There has been some debate about under which circumstances the "spiked water" or "spiked sediment" method is most appropriate. Data generated using either method should be judged on its own merits, although the spiked water test may be seen as providing a more realistic exposure scenario for most pesticide applications. However, data from spiked sediment studies can be particularly useful for addressing risks from exposure to contaminated sediment, particularly if there is an accumulation of the compound in the sediment over time (e.g. from multiple applications and/or through different exposure routes). For sediment toxicity tests, the concentrations in the pore water, the overlying water, and the sediment should be measured. There are some reservations with respect to the OECD 219 which includes the fact that analytical measurements in sediment are not routinely conducted. It is arguable that such analyses are not necessary if suitable data on the partitioning of the substance from a water-sediment study are available. Therefore, reasoned cases that include the estimation of likely levels in sediment, using data from the water-sediment study, may also be acceptable. In such situations, the notifier should demonstrate that the conditions in the water-sediment study are comparable to those in the "spiked water" test. The estimation

³ Di Toro, D. M., Zarba, C. S., Hansen, D. J., Berry, W. J., Swartz, R. C., Cowan, C. E., Pavlou, S. P., Allen, H. E., Thomas, N. A. and Paquin, P. R. 1991. Technical basis for establishing sediment quality criteria for nonionic organic chemicals using equilibrium partitioning. *Environmental Toxicology and Chemistry*. 10:1541-1583.

⁴ <http://viso.ei.jrc.it/focus/sw/index.html>

⁵ <http://www.efsa.europa.eu/en/efsajournal/doc/2562.pdf>

of levels should include consideration of metabolites present in the sediment where this is relevant for the risk assessment. Additional analytical measurements in a study may sometimes be valuable to decide on the validity of a test and may help to avoid additional testing with living organisms. NOEC values from “spiked water” studies that are expressed as initial concentrations in the water phase should be compared to initial PECs for the water column, and those from “spiked sediment” tests should be compared to PECs in sediment. Since both studies are long-term tests, the appropriate trigger for further evaluation is 10. If the trigger is not passed, a range of higher-tier studies are possible to further refine the risk assessment. Toxicity to sediment-dwelling invertebrates may also be addressed in a suitably designed microcosm or mesocosm study.

In addition to the above guidance, the following practice regarding sediment risk assessment has become a standard practice in the assessment of the risk of pesticides by Member States and EFSA: modelling exposure with FOCUS SW provides both exposure data for water and sediment. If an active substance is very lipophilic and used repeatedly, exposure may build up in the sediment (i.e. predicted by the FOCUS SW tool). If only a spiked-water test with *Chironomus* is provided, the derived endpoint from the water phase is transformed to an equivalent concentration in the sediment and vice versa.

The Aquatic GD for the risk assessment of pesticides is currently under revision. As a first step, a revision of the guidance for pelagic organisms at ‘edge-of-field’ is due in the middle of 2013. A revision of the sediment effect assessment for pesticides is expected to be initiated by EFSA in Autumn 2013 [note that after the workshop, the updated pelagic aquatic guidance has been published⁶, the sediment part is still under revision]. In the draft new aquatic ‘edge-of-field’ GD, the following guidance is given on sediment/soil dwellers in relation to sediment risk assessment: “This GD has its focus on a tiered risk assessment procedure for aquatic organisms living in the water column in edge-of-field surface waters”. Nevertheless, a preliminary (Tier 1) risk assessment procedure for sediment-dwelling organisms based on the 28-d water-spiked water-sediment test with *Chironomus riparius* or *Lumbriculus* spp. is also incorporated, since this concerns a data requirement under the PPP regulation. A later Scientific Opinion of the EFSA Panel on Plant Protection Products and their Residues (PPR) in the series mentioned above will deal in detail with the effect assessment for sediment-dwelling organisms by paying attention to a wider array of sediment-dwelling species. For standard toxicity tests with aquatic organisms, the EC10 is recommended as a substitute for the NOEC. When accumulation of an active substance in aquatic sediments is indicated or predicted by environmental fate studies, the impact on a sediment-dwelling organism shall be assessed. The chronic risk to *Chironomus riparius* (OECD 218, 219) or *Lumbriculus* spp (OECD 225) shall be determined. An appropriate alternative test species may be used where a recognised guideline is available. The active substance should be applied to either the water or the sediment phase of a water/sediment system and the test should take into account the major routes of exposure. The key endpoint from the study should be presented in terms of mg substance/kg dry sediment and mg substance/L water. The PPR Panel recommends a preference for conducting a water-spiked study. Sediment-spiked studies could be part of higher tier testing. This GD focuses on exposure via the water phase. A scientific opinion addressing the effect assessment for sediment organisms in detail will be developed by the PPR Panel in the near future.

The existing GD and the draft revised GD so far only include exposure via water and do not include exposure by food. This route may be important for sediment browsers – especially for organic compounds partitioning to the sediment surface. New tools are needed to consider effects and exposure.

2.4 ENVIRONMENTAL CONTROL AND MONITORING: THE WATER FRAMEWORK DIRECTIVE (WFD)

⁶ <http://www.efsa.europa.eu/en/efsajournal/doc/3290.pdf>

The WFD establishes management by river basin – the natural geographical and hydrological unit – as the best model for a single system of water management. For each river basin district – some of which will traverse national frontiers – a “river basin management plan” should be established and updated every six years. The WFD aims to achieve the good ecological and chemical status for all waters by 2015. There are a number of objectives in respect of which the quality of water is protected. The key ones at the European level are general protection of the aquatic ecology, specific protection of unique and valuable habitats, protection of drinking water resources, and protection of bathing (swimming) water. These protection goals are similar to those considered in other jurisdictions, for example under the Clean Water Act in the USA. All these objectives must be integrated for each river basin. It is clear that the last three – special habitats, drinking water areas and bathing water – apply only to specific bodies of water (i.e. those supporting special wetlands; those identified for drinking water abstraction; those generally used as bathing areas). In contrast, ecological protection should apply to all waters: the environment should be protected to a high level in its entirety.

The sediment assessment is part of the “Surface water” protection, which includes three levels – ecological protection, chemical protection and the protection of specific uses.

The classification of the surface water bodies is based on the ecological and the chemical status.

Good ecological status is defined in terms of the quality of the biological community, the hydrological characteristics and the chemical characteristics (included specific pollutants relevant at national or river basin level). Due to ecological variability, no absolute standards for biological quality can be set that apply across the entire Community, thus the controls are specified as allowing only a slight departure from the biological community which would be expected in conditions of minimal anthropogenic impact, as determined by relevant reference sites. A set of procedures for identifying the ecological status of a water body have been developed. The ecological status is defined through a set of ecoregions and ecotypes, comparing the situation in the water body with those of relevant reference sites. Inter-calibration exercises have been conducted to ensure a common understanding regarding the application of the general principles. The ecological status is based on the direct assessment of the biological community, which includes macrophytes and phytobenthos as well as benthic invertebrate fauna for rivers and lakes, and macroalgae, angiosperms and benthic invertebrate fauna for coastal and transitional waters.

The chemical status protection is defined in terms of compliance with all the environmental quality standards (EQS) established for the chemical substances of the European list of priority (currently 45 + 8). The EQS are concentrations derived in water column, sediment and biota that should protect human health and the environment. The Directive 2008/105/EC and the new Directive 2013/39/EC, published in compliance with Article 16 of the WFD, gives a useful role to sediment: Member States have the possibility to derive environmental quality standards for the priority substances in sediment compartment for specific water bodies. Furthermore, the analysis of sediments for specific priority substances is useful for the analysis of the trend.

A large set of guidance documents⁷ have been developed in the context of the common implementation strategy of the WFD. Guidance No. 25 – Chemical Monitoring of Sediment and Biota and Guidance No. 27 – Deriving Environmental Quality Standards are the most relevant for the sediment compartment.

Guidance No. 25 describes the conditions for monitoring chemicals in sediments, including sampling design, passive sampling methods, analytical methods, etc. In addition, the guidance provides indications for the use

⁷ https://circabc.europa.eu/faces/jsp/extension/wai/navigation/container.jsp?FormPrincipal_idcl=FormPrincipal:libraryContentList:page&page=1&FormPrincipal_SUBMIT=1&org.apache.myfaces.trinidad.faces.STATE=DUMMY

of ecotoxicity methods in a Triad approach, combining the three assessment methods: chemical, bioassay, and ecology. Specific references are made to toxicity identification evaluation (TIE) and effect-directed analysis (EDA), which combine biological and chemical analysis with physicochemical manipulation and fractionation techniques⁸.

Guidance No. 27 describes the derivation of the environmental quality standards. These values are compared with the measured concentrations for determining the chemical status of the water body in relation to the priority pollutants. A $\log K_{oc}$ or $\log K_{ow}$ of ≥ 3 is used as a trigger value for the assessment of sediment effects for organic chemicals. Some substances can occur in sediments even though they do not meet these criteria so, in addition, evidence of high toxicity to aquatic organisms or sediment-dwelling organisms or evidence of accumulation in sediments from monitoring, would also trigger derivation of a sediment EQS. The methodology is also based on the TGD but has been updated with additional guidance, including that developed for pesticides. The quality standards for the sediment are derived using the EPM or the AF method as described for REACH, and there are additional recommendations for using mesocosm studies and higher tier methods. Furthermore, the EQS Guidance includes guidance on derivation of a maximum allowable concentration (MAC-EQS) besides the derivation of an annual average concentration (AA-EQS) (the latter of which is equivalent with the PNEC_{sed} – derivation in REACH). It should be noted that the sediment EQS can only be used for the first tier assessment; if the measured concentrations exceed the sediment EQS, and the sediment EQS is not scientifically robust for taking the final decision, site-specific assessments of the benthic community, including the use of bioassays, are conducted for assessing the chemical and ecological status.

2.5 OTHER RELEVANT EUROPEAN LEGISLATION

In addition to those described in the previous sections, there are many other pieces of European legislation which may benefit from the update of sediment risk assessment protocols. These include the International Plant Protection Convention (IPPC) and Industrial Emissions Directives, which establishes the principles for setting emission permits, the Environmental Liability Directive, the Seveso Directives on major accidents, the Waste Directive, etc. Indirectly and in certain cases, sediment assessments may be relevant for the Habitats Directive which establishes basic principles for the protection of areas of high ecological value. No specific guidance for sediment risk assessment has been developed.

2.6 MANAGEMENT OF CONTAMINATED SEDIMENTS

There is no specific EU legislation regarding the handling of contaminated sediments but the WFD and other general regulations offer some basic principles⁹. In addition to the Community legislations, most site-specific assessments are conducted under national law. This is the case for the assessment of contaminated sediment for remediation or dredging purposes.

⁸ Carere M, Dulio V, Hanke G, Polesello S. "Guidance for sediment and biota monitoring under the common implementation strategy for the water framework directive". TRAC. "Trends in analytical chemistry". Volume 36. June 2012. Pages 15-24).

⁹ See for example: http://www.sednet.org/download/Sednet_booklet_final.pdf

3. Risk assessment in sediments

3.1 “THOUGHT STARTER” BACKGROUND DOCUMENT ON RISK ASSESSMENT

Apart from editorial changes, the text below is copy of the original thought-starters sent out to the workshop participants.

3.1.1 Problem formulation and protection level in sediment risk assessment

Ecosystem risk assessments should be thought of in a holistic way within the context of overall freshwater, marine, or estuarine environmental assessments. This means that ecosystem risk assessment should not be seen as a series of complementary but separate risk assessments for pelagic organisms and for the sediment compartment. The protection of benthic communities or populations (rather than individuals) should be considered as an element of aquatic risk assessment in general.

The sediment assessment should focus on those cases when the benthic community is expected to trigger the overall assessment. In fact, many guidance documents include thresholds for triggering the sediment assessment (e.g. based on the binding potential of the chemical). If waterborne exposure is expected to be the most significant exposure route, the assessment of the pelagic community may be sufficiently protective to also protect the benthic community. Further, the chemical properties may suggest the potential relevance of other routes triggering the sediment assessment. An option for such chemicals is to include organisms with additional exposure routes (contact with or feeding on sediments). The sediment risk assessment should be based on species representative for different trophic levels, feeding strategies, and habitats. As many benthic organisms are exposed to and affected by overlying waters, this exposure compartment must be considered (includes interface, overlying waters and suspended materials). In addition, it is important to consider the organism life-history and ecology that can modify exposure. For example, some organisms build tubes and hence, although they live in the sediments, they are not exposed to the sediments or pore water exclusively but also to the overlying water as they bioirrigate their burrows. Others live on top of, not in the sediments. Ecology is critically important to understanding exposure and too often overlooked.

As for any risk assessment, the level of protection is a management matter, not a scientific one, as protection of ecosystem functions can be achieved through different sets of management decisions. Which one to choose depends upon the economics, human health and ecological concerns, and the aesthetical value of the ecosystem. Nevertheless, protection goals need to be defined. These can include, for example, the protection of ecosystem services, wildlife, and ecological receptors that serve as the base of the food chain and are important to matter and energy flow through the aquatic freshwater and marine environments.

A physiological and ecological relevance scale that considers four response levels:

1. homeostasis (=healthy system),
2. compensation (=apparently healthy system but under pressure),
3. disturbance (=system structure and/or functionality no longer within the homeostatic range), and
4. failure (=system is deteriorating and services collapsing).

It is possible to set the protection level based on an abundance drop, reduction of number of species, and/

or decline in the number of functional groups. These will give different thresholds, from which risk managers can use all of them for risk assessment purposes and provide a range of predictions indicating different levels of stress to the ecosystem. The current risk assessment scheme is somewhat arbitrary in the way that it chooses to assess the risk to sediment organisms. The sediment compartment first needs to be examined using an approach such as the ecosystem services approach to define what we are aiming to protect on a species, population, and ecosystem level as well as on what spatial and temporal scale.

It may be possible to consider the protection of ecosystem services, rather than specific organisms, although the traditional ecotoxicity testing approaches are unlikely to be able to provide this information. A healthy sediment system should be capable to support a pelagic ecosystem through benthic-pelagic coupling and sustain functions such as organic matter breakdown and sediment reworking. Its background geochemical properties, levels of biodiversity, and nutrient assimilation capacity should all be comparable to those of regional reference sites. The risk assessment should focus on how chemical substances might compromise these key properties and processes. It is noted that general guidance on how to protect ecosystem services is not that detailed and more general than guidance on how to derive PNEC_{sediment} or EQS_{sediment} values.

3.1.2 Selection of relevant taxonomic groups and ecological functions

Most sediment risk assessments focus on benthic invertebrates. Rooted aquatic plants are currently poorly covered. Microorganisms are also barely considered. OECD Test Guidelines are limited to two invertebrate groups, and this may be a main constraint in some regulatory contexts. Regarding the invertebrate community, and especially infaunal species, it is important to realise that different functional groups are represented: detritivores, filter-feeders and predators. Each represents different energy pathways and different trophic levels in aquatic food webs, and hence may express different responses to chemical exposures. In addition, there are many pelagic organisms feeding on sediment and deposited materials.

Most sediments contain complex micro-environments that can vary in space and time. For example, anaerobic zones may start as little as 2 mm below the surface layer. Aerobic niches created by burrowing organisms (e.g. sediment reworking) will complicate the chemical dynamics and exposure. Anaerobic degradation has been identified as a key primary degradation route for some chemicals, and although the assessment of relevant degradation products is part of the legal requirements in many jurisdictions, in practice this is not really covered in most risk assessments.

The functions provided by infaunal sediment communities include nutrient cycling, sediment stability, support for the pelagic food chain, and maintenance of habitat for pelagic organisms. Carbon and nitrogen cycling are clearly relevant. Recovery of nutrients and removal or breakdown of excess nutrients and compounds should also be considered, as should any function relevant for reducing the impact of eutrophication on dissolved oxygen levels. Functions generally relevant and expected to be indirectly impacted by chemicals include the grazing potential and availability of providing habitat for resident and transient populations; these functions are only covered in higher tier assessments. Regarding contaminated sediments and the link between sediment quality and ecosystem functions, SedNet offers relevant information¹⁰.

Sediment assessments are conducted on freshwater, transitional (e.g. estuarine and coastal lagoons) and marine systems. In broad terms, all systems share similar functions and taxonomic groups, but also differences are observed, e.g. insects in freshwater systems versus echinoderms in marine systems. In estuarine environments, species can be distributed through a very wide salinity range. Overall, there is

¹⁰ See: <http://www.sednet.org/download/J-Brils.pdf> and http://www.sednet.org/download/Sednet_booklet_final.pdf

greater diversity of species presented in marine waters, but this should be put in the context that oceans represent over 70% of the Earth surface and about 97% of the Earth waters, while freshwater systems represent less than 1%; thus, the complexity of a particular aquatic ecosystem depends on a myriad of factors, not just on its allocation as freshwater, transitional (estuarine) or marine.

At a screening level, the same ecological receptors may be viewed as relevant to the different environments (i.e. marine, estuarine, freshwater), although separation of the different environments may be worthwhile where adequate data are available to assess each separately. Data availability may be a major consideration, as there are likely to be relatively few substances with sufficient data to carry out independent assessments for the different systems. However, data collected in one compartment may inform another. The relevance of knowledge on the mechanisms of action and key drivers in one system (e.g. freshwater) for the other systems can be considered, for example, to identify particularly sensitive groups or functions. Overall, the possibility for combinations and/or extrapolation among the different systems may be assessed using the following considerations:

1. sediments perform similar functions in each environment;
2. whether or not there are important and predictable differences in sensitivities among representative benthic groups from each system;
3. major taxonomic differences exist among environments; and
4. differences in the geochemical features of the sediment processes that influence bioavailability/exposure to the various types of sediment organisms.

Regarding consideration 1, the same general ecological receptors and functions noted above are suitable for all three environment types, thus the discussion is more at the “ecotype” level (e.g. rooted aquatic macrophytes are particularly important in some ecosystems, including some estuaries and coastal lagoons, but also some coastal and riverine areas, ponds and shallow lakes).

Regarding considerations 2 and 3, for chemicals with generic narcotic-type modes of action, based on thermodynamic or critical body burden theory there should not be major differences regarding toxicity at equilibrium. Nevertheless, due to species specific feeding strategies, habitat or exposures there could be differences prior to the equilibrium being reached. For chemicals with specific mechanisms of action (e.g. neurotoxins), from several papers it seems that the sensitivity distributions of taxonomically similar freshwater and marine species to organic pesticides do not differ significantly¹¹. For chemicals with insecticidal activity, a particularly relevant issue is the relative sensitivity of aquatic insects, including sediment dwellers such as chironomids, versus other arthropods, such as crustaceans; but also marine non-crustacean arthropods, such as horseshoe crabs and sea spiders. An equivalent assessment is needed for other biologically active chemicals.

Finally, for consideration 4, two complementary factors should be considered. Firstly, those related to chemical interactions and the influence of salinity, pH, redox reactions, and other general conditions on the chemical speciation, dissociation, etc. that may affect bioavailability. Secondly, the biological adaptations that may affect uptake and elimination but also other toxicokinetic and toxicodynamic elements. The estuarine environments are especially challenging because across the salinity gradient there is a transition from a freshwater to a marine species dominated biological diversity. This gradient is characterised by

¹¹ See EFSA Literature review on the sensitivity and exposure of marine and estuarine organisms to pesticides in comparison to corresponding fresh water species <http://www.efsa.europa.eu/en/supporting/pub/357e.htm>

species with a freshwater background that have developed adaptations and/or tolerances to the saltwater environment and vice versa. This may result in differences in sensitivity between freshwater and saltwater representatives of the same taxonomic groups. The capacity of organisms to adapt to a salinity gradient can also be very different resulting in certain species being more sensitive when closer to their limit of tolerance within the gradient.

3.1.3 Risk characterisation tools and metrics

Once the necessary information has been gathered, risks can be assessed from:

1. a chemical perspective (e.g. frequency or probability to exceed regulatory thresholds);
2. an ecotoxicological perspective (e.g. deviation of an ecotox response in comparison to a reference sediment); and
3. an ecological perspective (e.g. deviation of an ecological state in comparison to a reference site).

To aggregate these lines of evidence, MultiCriteria Decision Analysis (MCDA) is available. On the other hand, if sufficient data are available, probabilistic tools may be used.

For lower tier screening type assessments, there are no primary conceptual differences regarding risk characterisation tools between predictive and prospective assessments. However, the departure points may differ as the exposure and effect tools may be significantly different. At this lower-tier level, there should not be substantial differences, other than scale and any associated factors, such as interconnections and global change contributions, between local and regional assessments. For highly hydrophobic industrial substances, local ERA will be driven by suspended solids released particularly from Waste Water Treatment Plants (WWTPs).

Depending on the area of release, there could be near complete movement of suspended solids (SS) to the sediment compartment (e.g. in a lake system) or almost complete transport to a distant zone (e.g. fast flowing river). In estuaries the deposition/resuspension of sediment is very high. Current methods taking into account adsorption at equilibrium at local sites are therefore not always meaningful but at least cover worst case scenarios. Local exposure will be from a point source whereas regional exposure will be more diffuse. The processes driving the exposure and distribution of the substances in these two situations will differ, in particular, when degradation and distribution processes are taken into account; these processes are more relevant in the regional scale. For chemicals with direct (e.g. pesticides, fertilisers) or indirect (e.g. through soil applications of WWTP sludge) releases in the terrestrial compartment, run-off, drainage and soil erosion may be relevant pathways at the river basin level. In some regional scale assessments, the concentration of the substance is assumed to be constant without changes over time but these assessments should take into account how chemicals are transported. One element for discussion is the need to consider specific ecotypes accounting for different sediment transport properties (e.g. the rhithron (upper part with high slope and fast and turbulent flow) and potamon (downstream part, warmer, slower and finer in substrate) zones of rivers, shallow and deep lakes, delta-type and fjord estuaries) for generic risk assessments. Regional-level monitoring often helps to identify and/or prioritise areas of concern that might need a more specific and directed study to inform environmental management decisions.

For higher tier confirmatory assessments, the risk characterisation tools are driven by the methods used to present the exposure and effect assessments. There are also significant differences between generic and site-specific assessments. Sediment quality standards should be used as initial screens and for permitting purposes (e.g. discharges). Local-scale assessments, which can be used for remedial decision making, require

a much more close examination of physical, chemical, and biological elements of the aquatic system. It might be expected that more is known of local biodiversity and ecosystem service provisions in conservation/resource supply areas (e.g. fisheries) than at the regional level, whereas in other areas, proxy measures may be required to establish 'at-risk' receptor classes. Regional assessments should focus on large-scale processes which include diffuse and widely dispersive sources (e.g. near and far-field emissions and transport of materials), and should set broad 'regional norms' for key ecosystem properties, where sufficient knowledge is available. A combination of tools is essential in these cases as they each measure different things and have associated strengths/limitations. Key tools include habitat characterisation, indigenous biotic metrics, toxicity/bioassays (laboratory and *in situ*), chemistry (including bioavailable fractions) of each sediment compartment. Whole sediment toxicity tests with field collected sediments or with spiked sediments can be used to develop generic or site specific sediment quality guidelines (SQGs). These SQGs can be generated using concentrations of contaminants in either whole sediment or in pore water. Normalising the water or sediment concentrations to factors influencing bioavailability and toxicity is also needed. The potential for sediment transport may lead to significant differences between local and regional exposures. In some cases, substances which partition to sediments may only result in relatively localised contamination, meaning that only the local exposure scenarios are of real ecological relevance.

One of the main challenges in sediment assessments is the heterogeneity in sediments (e.g. organic carbon; particle size etc.) and associated biota. Local assessments can account for these differences, especially as they affect bioavailability, and can focus on the specific organisms that are present in that location. Regional risk assessments have to account for the range in variability that is present, and develop a risk estimate that is sufficiently protective of vulnerable areas without being overly protective of other locations. This can best be accomplished using a spatially-explicit approach that essentially captures the heterogeneity of the region, with sub-assessments for local conditions. If only a single approach is used, then some consideration needs to be given for using it as a starting point, so that local assessments can deviate from the regional risk value (i.e. either be at greater or lesser risk). The concept of ecoregions should be extended to sediments such that regional assessments make ecological (not political) sense. This would include, at a minimum, consideration of sediment characteristics (i.e. as above – organic carbon, grain size); depth of water; temperature (i.e. cold-water versus warm-water systems); and should account for the different water bodies (e.g. lakes, streams/rivers). Freshwater, estuarine, and saltwater would be treated separately and not be included in one regional assessment. In a regional risk assessment, the overall risk assessment, including the different point and diffuse emissions, should be included in order to evaluate if protection goals are achieved. It may be difficult to apply the ecological recovery option in a regional risk assessment, and the ecological threshold level seems more appropriate for cumulative exposure as it covers all relevant sources and chemicals.

3.1.4 Screening identification and extrapolation tools

Some regulatory approaches include screening methods to trigger the sediment assessment or to conduct assessments when no ecotoxicological information is available. The Equilibrium Partitioning Method (EPM) is used for REACH and biocides in Europe. Equilibrium partitioning and solubility-based approaches are very useful (for organic substances), as they use physical-chemical properties to determine what is possible in terms of exposure. The K_{ow} also provides an indication of the potential for bioaccumulation. The K_{oc} is very useful for understanding the role that organic carbon plays in the sequestration of the chemical in sediments whereas water solubility limits the amount of chemical available to the biota. Taken together, these metrics can qualitatively and quantitatively describe the amount of chemical that will be available in the sediment to which the biota may be exposed. They can be used to categorise and screen chemicals, and then be applied to make adjustments for site-specific differences. These methods are all useful but all have limitations. Particular limitations include site-specific differences in key bioavailability controls.

The EPM method appears to be better for the sediment compartment than for soil. It provides a valuable screening approach for use in the absence of information on sediment effects, although the predictions provided are uncertain. Relative to uncertainty, the EPM approach provides a good estimate of whether a specific chemical, or class of chemicals (e.g. PAHs), is likely to have any effect. However, most chemicals in sediments are present in mixtures and the EPM is currently not capable of estimating the adverse effects of all of the combined effects of all of the chemicals in the mixture. The EPM based on just organic chemicals partitioning into sediment organic carbon (K_{oc}) tend to over-predict exposures and therefore is over-predictive. When the EPM model includes sediment organic carbon and black carbon (K_{bc}), it tends to under-predict exposures and therefore is under-protective. This probably occurs because we do not have good methods for determining the types of black carbon that are in sediment and we have limited K_{bc} for individual types of black carbons (e.g. coal fly ash, diesel soot, char). The EPM model has the advantage of being simple and easily applicable in the absence of measured data in prospective assessments, it can also be used in retrospective assessments based on sediment concentrations of contaminants ($\mu\text{g/g}$ dry) and the organic carbon concentration in sediments (g OC/g dry). It should therefore be used as a first tier, which can be applied to see if the risk is predicted to be very high or very low. An approach used under the US EPA Superfund and applicable here is to link the need for further information with the outcome of the risk characterisation considering the uncertainty. For example, if the RCR is close to 1 (i.e. between 0.5 and 1), requirements for further studies or more exposure information will automatically be triggered. Nevertheless, the extra factor of 10 applied to the RCR for substances with $\log K_{ow} > 5$ and equivalently highly adsorptive substances is not validated; for substances with a high K_{oc} , tests with spiked sediments should be a data requirement. Certain surfactants (notably cationics, but not only) are very poorly estimated by these methods and an alternative approach should be sought for evaluating such materials.

More guidance on the applicability of the EPM would be useful. This should include a critical review/discussion on the use of the EPM. For instance, the following questions should be addressed:

1. How does the EPM, presuming that the method is based on the assumption that the pore water concentration and the concentration in the pelagic are equivalent, reflect reality?;
2. How should the information be used when the assumption is that the contaminants are at equilibrium between the interstitial waters, sediments and organisms but not with the overlying water? Taking into consideration that sediments can act as sinks (and sources) of substances, in many cases equilibrium between overlying pelagic water masses/water column and the pore water is not achieved, and the concentrations in pore water are expected to be higher;
3. How to address ionisable substances? How to take into account the effect of pH and salts (K, Mg, Na, SO_4 , Cl) on the properties, especially $\log K_{ow}$ values?;
4. How to apply the AVS-SEM method (acid volatile sulphides – simultaneously extracted metals) for predicting bioavailability of metals?

In many situations, the sediment is a dynamic system that is affected by currents causing turbulence, and benthic organisms also cause the mixing/turbulence of sedimentary material resulting in the potential for an exchange of gasses. The AVS also varies seasonally around the year. The upper sediment level is typically expected to be aerobic, which may limit the use of the AVS-SEM approach for estimating the bioavailability of certain metals; however, based on experience, if AVS-SEM > 0 the concept can be used because the aerobic phase is highly influenced/dependent of the metal binding capacity of the nearby anaerobic phase (with a pool of free AVS which can bind (precipitate) metals). As the Ni case study used in this workshop shows, we can also begin to consider empirically-based bioavailability models, which are based on EPM concepts but consider the dynamics of sediment phases and the species-specific interactions between organism and sediment-associated contaminants.

Another issue that needs exploration is bound residues, both for metals and organic substances. It is not clear today whether unextractable bound residues should really be considered as a concern to the sediment compartment as they will not be bioavailable; however, the uncertainty lies in the degree to which an otherwise unavailable chemical may (with time) become available due to (for example) diagenetic processes.

The physico-chemical properties of contaminants can also be used to identify if the substance can absorb or adsorb to sediment. If not, a more detailed assessment is not useful. If yes, the assessment can be either quantitative or qualitative. Guidance documents should also be improved by proposing methodologies according to one of the three following scales: ecosystem, effluent or substance.

For screening and EPM lower tier assessment based on equilibrium conditions, the same processes and values are used for estimating the PEC_{sed} and PNEC_{screening}, the result is that the same risk quotients (PEC/PNEC ratios) are obtained for water and for sediments in some cases (e.g. $\log K_{ow}$ between 3 and 5 under REACH), the added value of this approach is therefore questionable.

3.1.5 Risk characterisation for impact assessment and informing decision making

In the regulatory context, the risk assessment is conducted as one of the elements for decision making. The specific conditions for using the risk characterisation outcome in the decision making process depend on each regulatory process. Ecoregion variability in physicochemical and biological characteristics will cause the risks, and the expected impacts on the sediment community and the associated pelagic community, to vary dramatically. A key element for regulatory risk assessments should be a weight-of-evidence (WoE) approach that is based on independent lines of evidence that include laboratory and/or field toxicity data, mechanistic information that supports these data, incorporation of refinements such as bioavailability modelling, and good monitoring information that demonstrates widespread exposure of the contaminant in question to benthic, infaunal communities. Elements that are recommended for consideration when using the outcome of the sediment risk assessment in a regulatory context are:

1. concentration-effects relationships (i.e. toxicity data) that include site-specific data when specific locations or contaminated sites are in question;
2. food-chain bioaccumulation and consumption risks to humans and/or ecological receptors;
3. bioavailability of sediment contaminants;
4. sources of contaminants to the sediments;
5. system dynamics of the sediment environment (e.g. sediment stability, transport, contaminant flux) and how that may affect exposures;
6. what the realistic future uses and ecological conditions of the water body are expected to be given the environmental setting (e.g. pristine, industrialised, urban, abandoned industrial, agricultural, many other types);
7. How to incorporate ecosystem services into the assessment.

The use of distributions of data (rather than data from a single point) in the risk assessment will offer the regulator more information for comparison in a cost-benefit approach of the control or remedial clean up measure.

Taking into consideration that sediments can act as sinks (and sources) of substances, it is particularly important to distinguish between preventive assessments, aiming to avoid sediment pollution, and corrective assessments, aiming to mitigate the effects of contaminated sediments. This distinction directly affects decisions about the choice of available tools, e.g. sediment toxicity tests conducted with spiked sediments to assess the toxicity and bioavailability of contaminants in sediment in the case of preventive risk assessments versus those conducted with field-collected sediments to assess the site-specific aspects of sediment contamination (e.g. measuring directly the effects of potentially toxic concentrations) in the case of retrospective/corrective risk assessments. Monitoring programmes with risk-based sediment quality standards represent the intermediate category.

In the regulatory context, it is important to know if sediment is going to be a relevant compartment for each specific use. If risk is identified for a use, mitigation measures should be established. The use of toxicity data for setting generic sediment safety standards, or for discharge permitting, necessarily means being protective but not predictive. This will result in over-protection of most areas in order to be protective of the more sensitive ecosystems. This is one reason to have different standards and approaches for freshwater, estuarine, and saltwater systems (i.e. to reduce the underlying variability and therefore reduce the amount of over-protection). It is also helpful to develop risk-based standards that are equations, rather than single numbers, so they can be easily adapted to site-specific conditions that affect bioavailability and/or chemical fate. It should be assumed that initial hazard and risk assessments will be more conservative (cautious) than higher tier and field assessments, with the caveat that there may, at times, be exceptions to this rule due to emergent properties of environmental interactions that are not predicted from laboratory studies.

The starting element for these sediment risk assessments should be a risk quotient (e.g. PEC/PNEC ratio or TER) based on sediment tests. Results from risk assessments based on EPM should only be used as screening tools; however, no regulatory consequences, other than requesting further information and testing, should be derived from EPM-based assessment. The PNEC based on sediment test results can be used to derive quality standards. The protection of populations and ecological functions should be used as the protection goal. Broader ecological values such as biodiversity, species richness, endemism, etc. and ecosystem services are not directly addressed and should be difficult to address until much more high performance population models are available. Adaptation of the SPEAR assessment tool to make a link between the sediment and the organisms might be considered. Putting more emphasis on mesocosm and field data (i.e. benthic species monitoring) adds ecological relevance to the assessment. For decision making, many elements beyond those covered by a generic risk assessment need to be considered. The risk assessment should inform issues such as contaminant load and toxicity evolution, residence times, extent of water-mixing, and on the expected consequences for related activities such as fisheries, aquaculture or bathing. In addition, local permitting authorities need to consult national legislation (e.g. on dredging limit values). It is highly essential to develop site-specific sediment quality guidelines (EQSs) for more accurate and robust risk assessment, while it is equally important to validate the EQS through field validation studies. This will provide a check and balance for the risk assessment process.

Sediments may be a key compartment for PBT/vPvB (persistent, bioaccumulative and toxic/very persistent and very bioaccumulative) substances, and it would be useful to give more specifications on the applicability of the criteria for sediment. The OECD TG 308 is the test method mostly used, but there are other elements that require further guidance (e.g. for K_{ow} , how to clarify temperature, how to address bound residues). Certain substances of potential concern (not fitting PBT/vPvB criteria but with certain elements of these) and expected to be highly present and persistent in sediments and potentially bioavailable could be highlighted for monitoring (e.g. under the WFD).

Broader ecological values such as biodiversity, species richness, endemism etc. can be addressed at this point and considered in the integrated assessment of sediment quality (e.g. by comparing appropriate metrics to a “reference condition”, meaning that no one set is applicable, and must be hydrologic type/

ecoregion type dependent following the AQEM/STAR approach developed for the EU; AQEM/STAR is a pan-European macro-invertebrate ecological database and taxa inventory¹²). The consideration of issues such as biodiversity and species richness ideally needs to be considered alongside tools which are able to describe these factors under unstressed conditions. This is due to the fact that different environments and habitats may support different levels of diversity and species richness under unimpacted conditions. Tools such as RIVPACS (River Invertebrate Prediction and Classification System¹³) are able to provide indications of benthic macroinvertebrate communities under reference conditions, although many of the assessments performed so far suggest that these communities respond predominantly to exposures via the overlying water.

Sediment quality triads and diversity indices (e.g. based on dominance or information approaches), should also be considered. Ecological metrics focusing on biodiversity, species richness, endemism, etc. (or improvements to them) could be included in the long-term ecological goals for the recovery of a contaminated sediment ecosystem. However, these types of ecological measurements are not often useful as leading lines of evidence to inform decision making because it is difficult to adequately link them to contamination levels due to the confounding influence of numerous other environmental factors and stressors that affect populations and communities of organisms. However, these ecological measurements can be used to complement or augment a clean-up decision that is itself based upon dose-response data, especially in cases where a risk range is determined from the risk assessment. In some cases, these “confounding factors” can either attenuate or exacerbate the effects of chemicals.

An important area for future research is to understand how co-occurring stressors interact so that decision-making in risk assessments might be better informed. A risk assessment for managing/recovering contaminated sediments should not only be defined according to the compliance of a threshold, but also by taking into account the local features (e.g. such as biodiversity, endemism, species richness) by local surveys, or by including qualitative parameters. The evolution of the ecological compartments can also be a key factor to be compared with the initial studies.

Expressing uncertainty is a key element for any assessment and should be addressed and explained differently in each case. The overall uncertainty should be reflected in a weight of evidence approach with qualitative tools, as, unfortunately, no suitable/informative numerical tools are available; ranging from low to high with indications of what the key components driving uncertainty are and hence providing the basis for moving forward and addressing them.

The risk assessor should also add their own professional opinion about the certainty of the assessment in a qualitative discussion. There are however statistically based methods covering some assessments or processes (e.g. for full probabilistic risk assessments, for comparing reference versus test site conditions, for developing species sensitivity distributions, for covering parametric uncertainty based on probability density functions for parameters in the case of modelling and generic scenarios etc.). There are also many tools and approaches available to perform higher-level uncertainty analysis such as Monte Carlo analysis, interval analysis, Bayesian methods, second-order Monte Carlo, probability bounds analysis, and many others. These should be considered when weighing options for risk management. EFSA’s Scientific Committee approach on describing uncertainties in RA can partly be applied to risk assessment for the sediment compartment. Whenever possible, uncertainty and variability should be addressed independently. If this is not possible and both aspects are combined, it is important to indicate at least which elements have been considered and how both aspects have been combined.

¹² <http://www.aqem.de>

¹³ <http://www.ceh.ac.uk/products/software/rivpacs.html>

3.2 ELEMENTS FOR DISCUSSION

The following questions were used to initiate the working group discussions:

1. The standard RA structure includes complementary risk assessments for pelagic organisms and for the sediment compartment: Which elements/receptors should be covered by the sediment compartment? How should the water/sediment interface and the exposure via suspended matter be included in the sediment RA?
2. Which taxonomic groups and ecosystem functions should be considered as key ecological receptors¹⁴ in sediment RA?
3. Are the same ecological receptors suitable for freshwater, estuarine and marine sediment compartments?
4. Which level of protection is required for the different ecological values¹⁵ in the sediment compartment? How should this level of protection be defined and quantified?
5. Which qualitative, deterministic and probabilistic tools can be used for the characterisation of sediment compartment risks?
6. What are the main conceptual and methodological differences for conducting local and regional assessments of the sediment compartment?
7. Are the approaches described in the current guidance documents on sediment assessment useful and sufficient? Are current tiered protocols and screening methods, particularly the EPM¹⁶ and prioritisation/exclusion criteria¹⁷ suitable and validated? Which are the main elements requiring improvement or scientific update?
8. Which key elements should be considered when using the outcome of the sediment risk assessment in a regulatory context? Which issues are particularly relevant for specific processes such as generic sediment safety assessments for marketing/authorisation/restriction¹⁸; setting environmental quality standards/criteria; or local permits authorisations)?
9. How can biodiversity, species richness, endemism, and other ecological concerns be included and considered in the risk characterisation for the sediment compartment?
10. Are there available ways for expressing the overall uncertainty of the risk assessment performed in the sediment compartment?

3.3 OUTCOME OF THE WORKING GROUP DISCUSSIONS

¹⁴ Ecological receptors refer to species, taxonomic groups, trophic levels and ecological functions that could be adversely affected by the stressor and for which exposure and risk should be assessed

¹⁵ Ecological values refer to the services provided by a healthy sediment community

¹⁶ Equilibrium Partitioning Method estimating the risk to sediment by comparing the predicted pore water concentration with the predicted no effect concentration for pelagic organisms

¹⁷ e.g. criteria for conducting or not a sediment assessment based on solubility, K_{ow} and K_{oc} thresholds

¹⁸ e.g. those related to REACH, or pesticides, biocides, pharmaceuticals regulations

The following sections reflect the discussions from the working groups. Whenever there were different views in the working groups, these are reported.

3.3.1 Problem formulation and protection level in sediment risk assessment

The participants recognised that the three generic problem formulations as identified in the 'thought starter' and summarised hereunder could be used for guiding the discussions. It was, however, decided not to focus on the details of these particular applications of RA approaches but rather on the generic scientific issues and/or problems underlying the sediment RAs in general.

The three generic problem formulations used by the working group participants were:

1. Predictive risk assessments for marketing of chemicals, such as REACH or the authorisation of pesticides, biocides, etc.
2. Setting quality standards and criteria for sediment, to be compared with measured values (chemical and/or biological) from monitoring programmes covering potentially contaminated sediments, such as in the WFD or similar legislations.
3. Assessments for supporting risk management of contaminated sediments, including the evolution of the sediment status and the potential risks for other compartments due to management decisions.

Participants were of the opinion that current RA approaches for the aquatic environment, i.e. using complementary or sometimes completely separate assessments for the pelagic and benthic/sediment compartment, may be simple and practical but do not reflect ecological reality. The available science should be used and new science should be developed to allow accounting for the interaction between the pelagic and benthic compartment. It was suggested that one way to initially address this issue is to assess the relative sensitivity of pelagic versus benthic organisms/communities. As such, it can then be evaluated if protection of one compartment also protects the other. However, it was stressed that, next to the assessment of intrinsic sensitivity differences, differences in contaminant bioavailability and persistence and differences in organism exposure routes also need to be evaluated to ensure that the risks to relevant communities/ compartments are considered. It was recognised that more research on these issues is needed as e.g. the distinction between the water column and sediment organisms is not always clear.

The working group then discussed the issue of how the ecology and habitats of benthic and epi-benthic organisms should be considered in sediment RAs. It was concluded that more ecological (e.g. organism's micro-habitat, life-history, life-cycle,...) and physiological aspects of sediment-dwelling organisms should be included in the selection of test species used in RAs. It was also recognised that the number and types of species presently used in (standard) test protocols may be insufficient to reflect all of the ecological/ physiological aspects (and possibly the sensitivity) of benthic communities. As in most current RAs, benthic invertebrates are the most frequently used test organisms. The working group recognises the need to evaluate other taxa such as plants (rooted and non-rooted), fish and biofilm/periphyton species, microbial functions. It is also recommended that a set of relevance criteria be developed to judge the acceptability of data from existing and new species, endpoints and methodologies.

3.3.2 Selection of relevant taxonomic groups and ecological functions

As indicated above, participants were of the opinion that the selection of currently available toxicity test protocols and (standard) species (mostly invertebrates) used in the sediment RAs is too limited to cover

the ecological and physiological complexity of benthic communities. The working group recognised that this is an important knowledge gap in current approaches. It was recommended that a major research effort should be conducted to select and develop test protocols with epi-/benthic test species/communities which – combined – reflect the ecological structure and function of benthic communities needed to protect this environmental compartment.

Environmental protection values (PNEC, EQS...) for the pelagic and terrestrial environment are – for data-rich substances – frequently derived using the Species Sensitivity Distribution (SSD) approach. This approach has, however, only rarely been applied to the sediment compartment. Due to the lack of guidance (regulatory aspect) on the number and type of data to be used in a sediment SSD and the lack of toxicity data and test protocols for a sufficient number of distinct species reflecting benthic community complexity (scientific aspect), most participants felt that the uncertainty associated with the use of the SSD approach is still high. The major research effort referred to in the previous paragraph may address some of these concerns. Participants were of the opinion that in principle the SSD approach can/should also be used for sediment RAs but that the current applicability of SSDs might be limited to very extensively studied substances only. If used, the justification provided to use an SSD should be evaluated on a case-by-case basis.

In the context of the SSD, it was discussed which type of toxicity data should be used for the distribution construction: single toxicity test results or the geometric means of all available toxicity data for a certain taxon? A concern was expressed that through the use of geometric means across a certain taxon (e.g. invertebrates) sensitive species are possibly combined with insensitive species thus resulting in SSD data points which 'exhibit' an overall average sensitivity. The group felt that the use of geo-means across taxa eliminates the diversity of the toxicity data populating the SSD, i.e. it eliminates possible toxicity values, which may be important from an ecological point of view. This approach was therefore not supported. Within a regulatory context most often geometric means are only taken within the same species (for similar endpoints and test duration) and not across taxa. Multiple values for the same endpoint with the same species should be investigated on a case-by-case basis, looking for reasons for differences between the results. Typically the most sensitive of assumed ecological relevant endpoints like survival, growth, development and/or reproduction is being used per species. For equivalent data on the same end-point, the test duration and conditions per species, the geometric mean should be used as the input value for the calculation. If this is not possible, perhaps because valid results are considered to be too variable, then grouping and combining the values, e.g. by pH ranges, and using reduced numbers of values should be considered. The effects that these different treatments have on the derived value (and on the resulting risk characterisation) should be investigated and discussed. For sediment data, an obvious way of normalising the data would be to use OC for organic compounds, and AVS for metals. Finally, the group discussed if NOEC from species which were tested but did not exhibit a response should be included in an SSD. It was felt that if the regulatory context prescribes the use of a full SSD approach to e.g. derive a HC5, as is the case in the EU, then maybe NOECs from these species/tests should also be used. However, besides the fact that some people felt that NOECs are in no case scientifically justified, the inclusion of unbounded NOEC values could introduce a great deal of uncertainty and might therefore, not be used directly for establishment of the SSD curve. For some, the preference is to use EC10s, or the lowest effect concentrations that can be accurately determined from a concentration-effect model.

A number of working group members also expressed their concern about the size of AF currently commonly used in the RAs in general, and in sediment RAs in particular. They state that as many of the species used in regulatory tests are rather insensitive to contaminants, the application of currently used AFs might/will lead to environmental protection values that may not be protective for all types of sediments. The group recognises that the science supporting the size of AFs is rather limited. The major research effort referred to above may also contribute to revising the size of AFs for sediments thus providing a more science-based decision making.

Further discussions addressed the use of the newly developed SPEAR approach to sediment RAs. This field-oriented approach uses existing ecological/physiological knowledge of certain traits to evaluate the effects of contaminants at the population/community level. Alternative similar models are being developed. It was concluded that these approaches may certainly be useful for retrospective RAs as a screening approach and may also be helpful in the development of new prospective RAs as it supports the selection of (alternative/new) test species based on traits useful for a specific chemical, and it can support the post-hoc evaluation of the ecological relevance of a screening RA. Further validation is, however, needed if it is to be employed beyond the current use and preferentially these methods are used as one of many lines of evidence in a sediment assessment framework.

The working group finally briefly discussed if the data collected in one environment (e.g. freshwater) may inform RAs performed for another environment (e.g. marine/estuarine), or in other words, are the same ecological receptors suitable for freshwater, estuarine and marine sediment compartments. In general, participants felt that read-across to different environments may provide some information when data for one particular environment is absent. However, it was stressed that this should only be done if differences between these environments – such as presence of phyla/taxa, water composition affecting contaminant behavior and effects, and others – can be accounted for in a scientifically meaningful way (i.e. based on data).

3.3.3 Risk characterisation tools and metrics

The working group addressed the question if – for screening and lower tier assessments – the sediment risk characterisations should be performed independently from the pelagic characterisation, or if it should preferably be integrated into a single aquatic assessment. It was felt that conceptually and based on many scientific considerations, the pelagic and benthic assessment should be assessed in an integrated manner, i.e. as one system, accounting for all possible exposure and effect interactions. However, the group did suggest to keep the final risk characterisations for the pelagic and sediment compartment separate as this will allow risk managers to take more direct actions.

The group further discussed the question of whether local and regional risk estimations based on equilibrium partitioning (EqP) are (always) over-protective or sometimes under-protective. No definitive answer was agreed upon. In general, the group agreed that EqP approaches can be a useful screening tool in initial phases of sediment assessments, but they may not assess all major contaminant exposure routes (e.g. dietary consumption). In many applications of EqP, a potentially high contaminant exposure via the dissolved phase may indicate an elevated risk for that contaminant. However, for organisms that are known to be exposed to sediment contaminants primarily via their diet, indication by EqP of a low risk should trigger further consideration of dietary exposure. It was also acknowledged that some organisms that are the target of the protection measures may perturb their sedimentary environment resulting in non-equilibrium conditions. Nevertheless, it was suggested that for generic local and regional RAs, equilibrium conditions can be assumed and that these screening assessments may/should be supplemented with probabilistic approaches for the exposure and effects assessments (double probability curves). More research on the applicability of EqP is needed.

3.3.4 Screening identification and extrapolation tools

The group did not discuss the use of screening methods (e.g. EPM) to trigger sediment assessments or to conduct assessments when no ecotoxicological information is available. In-depth discussions and some recommendations are presented in section 4.

The working group addressed the following question: “Are ecological taxa and functions particularly relevant

for the sediment assessment but of much lower relevance for the pelagic community (e.g. gastropods or sediment microbial functions)?” It was concluded that certain taxa are indeed more relevant for a sediment RA compared to those in an RA for the pelagic community. Indeed, as indicated in 6.3.2, both epibenthic and infauna should be used in the toxicity testing phase and care should be taken that various types of behaviour and lifestyles are covered in the selected test battery. It was suggested that current test protocols need to be improved to account for these factors (including feeding mode and contaminated food). It was recognised that there is currently little scientific information available on the effect of contaminants on microbial functions or on the interaction between microbes, macrofauna and contaminants in sediments. The working group recommends that research be performed to evaluate the importance of including these types of assays and endpoints in sediment RA approaches.

3.3.5 Risk characterisation for impact assessment and informing decision making

The working group focused on the following questions and issues:

- Should the focus of the sediment assessment be part of a full aquatic systems assessment, the structure of the sediment community, or both?
- Is it feasible and desirable to move into “ecosystem services” approaches for addressing the impact of chemicals in the sediment compartment?

The types of ecosystem services of the sediment compartment were discussed and it was concluded that as many substances may affect the whole aquatic system through the benthic compartment, sediment ecosystem services (e.g. oxygen production, providing food) may be useful (additional) assessment criteria. It was, however, recognised that more research needs to be performed to establish robust relationships between regulatory protection goals and ecosystem service performance.

- Is a qualitative assessment of the uncertainty in the weight of evidence approach sufficient? What is the role of expert judgement in the uncertainty assessment for sediment?

The working group concluded that in a deterministic RA, as is currently done in the majority of regulatory RAs, biological (and other) variability and uncertainty are largely neglected. Probabilistic approaches, however, do allow a quantitative assessment of some types of the uncertainty and sensitivity analysis associated with aspects of the RA should be undertaken to allow for a more objective evaluation of the outcome of the assessment. This type of analysis also allows an informed and quantitative dialogue between the risk assessor and risk manager.

3.4 RECOMMENDATIONS

3.4.1 For regulation

- Current regulatory RA approaches for the aquatic environment predominantly consist of separate assessments of the impact of contaminant on the pelagic and on the benthic/sediment compartment. Although this general approach may be simple and practical, it does not reflect ecological reality. New regulatory approaches (different tiers of complexity) should be developed – based on the available and new science – which reflect the interaction of the pelagic and benthic compartments.
- The number of presently available (standard) sediment test protocols and the number of species covered

are not sufficient to reflect all of the ecological/physiological aspects (and possibly the sensitivity) of benthic communities. Additional taxa need to be investigated for their sensitivity and a number of these can then be used in regulatory exercises. These could:

1. include taxa such as plants (rooted and non-rooted), fish, insects, molluscs, and biofilm/periphyton species and possibly microbial functions etc.; and
 2. account for more ecological (e.g. organism's micro-habitat, life-history, life-cycle...) and physiological aspects of sediment-dwelling organisms.
- Although the Species Sensitivity Distribution approach has only rarely been applied to derive environmental reference values for the sediment compartment, this approach can be used for sediment RAs with a proper justification. However, because of the lack of guidance (regulatory aspect) on the number and type of data to be used in the SSD, including the use of unbounded NOECs, and the lack of toxicity data and test protocols for a sufficient number of distinct species reflecting the complexity of the benthic community (scientific aspect), considerable fundamental and applied research is needed before the SSD approach can become a standard procedure in regulatory exercises.
 - Review of the relevance and the science underlying the size of the assessment factors (AFs) used in current sediment RA approaches. Possible revision of these AFs.
 - In-depth evaluation of how field-oriented approaches that use existing ecological/physiological knowledge of certain traits to evaluate the effects of contaminants at the population/community level can be used in regulatory retrospective and prospective RAs.
 - Data collected in one environment (e.g. freshwater) may inform RAs performed for another environment (e.g. marine/estuarine). Read-across environments can provide some information when data for one particular environmental compartment is absent provided that differences between these environments – such as the presence of phyla/taxa, water composition affecting contaminant behaviour and effects, and others – can be accounted for in a scientifically meaningful way.
 - Many substances affect, through the benthic compartment, ecosystem services of the whole aquatic system. The use of sediment ecosystem services may provide useful (additional) assessment criteria in RAs. More research is needed to establish robust relationships between regulatory protection goals and ecosystem service performance.

3.4.2 For scientific research

- An extensive and focused research programme needs to be developed to address fundamental issues related to the integration of the pelagic and benthic compartment into one aquatic risk assessment. Issues for research needs that were identified include:
 1. assessment of the relative sensitivity of pelagic versus benthic organisms/communities;
 2. differences in contaminant bioavailability and persistence; and
 3. organism exposure routes.
- A major, coordinated research effort should be conducted to select and develop test protocols with (epi-)benthic test species/communities which – combined – reflect the ecological structure and function

of benthic communities, which is necessary to protect this environmental compartment (cf. above: second bullet).

- Development of solid science to allow the use of the SSD approach for sediment RAs with confidence. This should include how to deal with lab-to-field comparisons.
- In-depth evaluation of how new field-oriented approaches (such as SPEAR and other similar models), which use existing ecological/physiological knowledge of certain traits to evaluate the effects of contaminants, can inform retrospective and prospective RAs.
- In general, coordinated fundamental and applied research needs to be performed to support all of the regulatory recommendations given above.

4. Exposure assessment in sediments

4.1 “THOUGHT STARTER” BACKGROUND DOCUMENT ON EXPOSURE ASSESSMENT

Apart from editorial changes, the text below is copy of the original thought-starters sent out to the workshop participants.

4.1.1 Contaminant release and key environmental fate processes

The key processes to be considered depend on the type of assessment, and in general differ between local and regional assessments. On a local scale, two main situations are currently considered. For industrial chemicals the PEC is estimated for those substances originating from a point source emission, the STP outflow, therefore the most important processes will be those of dilution and distribution of the substance in the water body away from the outflow. Any models created need to realistically model these processes within the water body.

Pesticides can enter a water body by spray drift, drainage, surface runoff and atmospheric deposition. The most important processes determining their environmental fate once they are in the water column are advection and dispersion, sorption and desorption processes. Parts of the pesticide may also volatilise and/or degrade before entering the sediment compartment, which may result in negligible accumulation within this compartment. These environmental processes also regulate the movement of other chemicals directly released into soil, such as veterinary pharmaceuticals. Drainage and runoff may also be relevant for industrial chemicals released into the terrestrial environment, e.g. through the application of STP sludge as fertiliser or soil amendment. For regional assessments, a low level, diffuse concentration is being considered and thus partitioning between water/sediment and degradation/dissipation will be most important.

Once the chemical has reached the water body, sorption and desorption processes and those related to the dissipation (including degradation) are the most important for understanding determinants of the environmental fate. It should be noted that the assessment of sediment contamination is only relevant for chemicals that prefer to be in that compartment. Sorption and desorption direction goes from matrices/ compartments with higher chemical activities (concentration is generally a poor representative) to the ones with lower chemical activities, and their rates to reach equilibrium are strongly affected by the hydrodynamics in a system. These processes often significantly influence whether (for labile compounds) degradation occurs and to what extent. At the sediment-water interface and in the sediment layer advection,

dispersion and diffusion are the important processes, but precipitation and dissolution of solids must also be considered. Such mechanisms can also take place in deeper layers due to biological perturbation of sediments.

Precipitation and dissolution of solids may be a highly relevant transfer mechanisms for ionic substances and metal compounds. For example, oxic environments can become sub-oxic or anoxic. This will cause re-dissolution of Fe and Mn oxyhydroxides. This in turn causes release of metals (and P), prior to precipitation of metal sulphides in such anoxic environments. These processes of precipitation and dissolution are particularly important and dynamic near the sediment-water interface and they influence the distribution and bioavailability of metals in sediments.

Thus, the main mechanisms which define the environmental fate processes are partitioning between water and suspended particulate matter (SPM), and gravitational settling of SPM to the bottom. From a scientific point of view, SPM is an operationally-defined compartment, where the interface between what is 'suspended' and unconsolidated sediments is not always clear (e.g. where a sediment may be considered as suspended when water represents >90% of the volume). The characterisation of SPM is also operational, because it depends on the kind of instrument (centrifuge, filtering, ultrafiltration) used to separate the aqueous and solid phases. It is also site-specific because it depends on the physical and chemical characteristics of SPM. Many studies have concentrated on partitioning modelling under equilibrium conditions, but few took into account the dynamic hydrological processes. A more comprehensive and detailed modelling of the settling processes is needed to form the basis for understanding the actual distribution of contaminants on a regional scale, and maybe on a local scale as well, in order to achieve an adequate time and site/region specific assessment. On the site scale, the rate of consolidation of deposited SPM and the subsequent transition towards equilibrium (EqP concept) and perturbation from equilibrium (e.g. due to bioturbation, resuspension) need to be considered.

Sorption (and desorption when the bound concentrations exceed equilibrium concentrations or when equilibrium concentrations change) may be assessed and quantified using equilibrium partition coefficients; although in the real environment other processes such as ageing add complexity to the estimation. However, many systems are very dynamic and careful consideration of chemical equilibrium assumptions may be necessary. Consequently, the issues that need to be addressed here are: (i) how generally applicable are generic laboratory derived partition coefficients, and (ii) whether environmental conditions allow equilibrium to be achieved (e.g. how frequently resuspension occurs, or bioturbation processes that introduce oxygen to depth and influence redox gradients). Algorithms are needed to predict coefficients from basic variables for water and sediment.

For non-ionic neutral organic chemicals partitioning in sediments is generally related to organic carbon, which is considered to be the main sorbing phase, i.e. K_{doc} , K_{poc} . Problems with this approach have been noted (e.g. when other binding phases such as black carbon are present; when sorption/desorption kinetics are slow relative to environmental transport processes). The Freundlich equation is the most commonly used equation to quantify sorption.

In the case of metals and other ionisable compounds, K_d is generally believed to be appropriate for predicting fate, although it must be recognised that distribution coefficients integrate the binding of metals with multiple solid phases, meaning that K_d s can vary several orders of magnitude among different sediments. Notably, K_d estimations may not accurately estimate partitioning in anaerobic sediments because of the presence of sulphides, which have extremely high affinities for some cationic metals. Metal partitioning relationships are often greatly improved by more detailed description of the chemical speciation to appropriately describe metal complexation with dissolved inorganic ligands (e.g. Cl^- , SO_4^{2-} , etc.), and non-linear binding to dissolved and particulate organic matter as to AVS, Fe and Mn oxide phases, or clays in very silty sediments. Competitive interactions of major ions (e.g. Ca^{2+} , Mg^{2+}) and other metals for the inorganic

and organic binding sites also play a critical role. The use of the TICKET-Unit World Model has been proposed for metals¹⁹.

Discrete particle settling, coagulation processes and the settling of flocs need to be considered in defining an overall settling rate. The settling rates are ultimately a function of the characteristics of suspended matter (e.g. particle size distributions, surface charge) and the receiving water environment (e.g. turbulence, velocity of water current, water chemistry). The assumption that the only critical source of contaminants to the sediment compartment is through adsorption to suspended matter, followed by sedimentation is a vast over-simplification of reality, and neglects key processes such as sediment transport. Sediment transport plays a major role in the introduction, spatial distribution, and longevity of contamination in areas of high hydrodynamic energy. Deposition and re-suspension of sediment relate to hydrodynamic differences that may exist between different types of environment (e.g. marine, estuarine, riverine and lacustrine). Sediment transport processes may also depend on the season or on the biological activity; for example, in riverine environments, resuspension of sediments occurs predominantly in a specific season (flood events in spring and periods prone to heavy rainfall). These processes can be very relevant for site/region specific assessments. Sediment resuspension events may be frequent or infrequent, and will influence the cycling of many contaminants and potentially naturally occurring stressors, such as ammonia that will influence sediment communities and function. It should be noted that some regulatory processes (e.g. marketing authorisations) require generic approaches and models covering widely dispersed users and emissions.

Once the sediment is settled, the sediment processes (initially diagenesis) that influence bioavailability need to be considered (including the chemical changes and processes that may change exposure pathways for certain organisms). For the contaminants, transformation and degradation processes (e.g. hydrolysis, photolysis, biodegradation), as well as dissipation processes such as volatilisation that affect the overall fate of the chemical within the water body need to be described.

The contaminant-specific physical-chemical parameters, essential for a proper exposure assessment in the sediment compartment, are those describing the processes mentioned above. They all depend on the fate related properties of the substance. For organic chemicals, the parameters such as solubility, pKa, Henry's Law constant, vapour pressure and the partitioning coefficients are the most relevant environmental fate parameters. For non-ionic organic chemicals, the parameter that is most important is partitioning which can be initially described by the K_{ow} or K_{oc} (with consideration of black carbon). For detailed assessments, the most important parameter is the activity of the chemical, which controls its partitioning. For routine determinations of exposure, the freely dissolved concentrations (C_{free}), a function of the chemical's activity, can be used to predict toxicity. In recent years, C_{free} has been measured with equilibrium sampling techniques (i.e. passive sampling devices), which often give more accurate data compared to traditional EqP calculations with its generic K_d values. For ionic substances or substances capable of being ionised that may also react with charged binding sites (i.e. clays, various ligand forming species; Mg, Ca, OH, CO_3 etc.), the essential parameters that need to be described are the ionic strength, type of charge (negative/positive), and the pH dependent K_{oc} , K_{ow} and water solubility.

Regarding sediment characteristics, a major player for organic chemicals is the sedimentary organic carbon (OC) content that can be further divided between amorphous, soft or new and condensed, old or black carbon. This division of types of sedimentary organic matter is especially relevant for non-ionic organics. The monitoring of parameters such as grain/particle size, surface area, organic carbon content, organic nitrogen content, iron, manganese, calcium and aluminium should be measured routinely. An understanding of the nature of binding or association of a contaminant with the sediment is critical.

¹⁹ <http://www.unitworldmodel.net>

For metals, the most critical physico-chemical parameters defining their fate in the environment are the charge/covalence, speciation and bioavailability parameters further depending on environmental characteristics such as pH, redox conditions, organic carbon, AVS, Fe/Mn oxides, and sediment particle size should be considered. Schemes based on such parameters are more problematic or less appropriate for organic substances which partition into organic matter.

4.1.2 Available exposure models/scenarios and metrics for sediment exposure assessment

4.1.2.1 Prospective risk assessment

The equilibrium partitioning theory has been mostly used to predict the exposure of benthic organisms to non-ionic hydrophobic contaminants. In the regulatory context, stepwise risk assessment approaches are frequently used, starting with very simple and cautious assumptions and models. If no potential risk is identified even for the worst-case conditions, a conclusion of low concern is sufficient for the regulatory decision. Additional data and refinements to more realistic conditions are only needed, if a concern is concluded using the simplistic approaches. A tiered assessment process, including triggers for further assessment, is often included in the regulatory guidance.

For prospective risk assessment there are exposure scenarios available e.g. for the EU biocides and REACH processes, but they are extremely simplistic in practice. For example, emission is usually assumed to be from point (solution) sources and the contaminant is assumed to partition/adsorb instantaneously and homogeneously throughout the sediment layer. Emerging data indicate that the contaminant associates with the sediment less strongly than aged or pre-existent contaminants. Consequently, assessments of risk posed by contaminants spiked into sediments can be considered conservative in comparison to the same contaminants in many polluted sediments at field locations. No realistic considerations of the fate processes are included. The EqP approach used for biocides/REACH is limited because it:

- only calculates the PEC in suspended sediment,
- is not volume limited and
- is compared with ecotoxicology data from laboratory test conditions that are likely to differ from field exposure conditions (e.g. water only exposures for pelagic organisms or the chemical spiked directly to the sediment if sediment toxicity data are available) to that assumed in the model.

Most existing models do not consider other major sources of contamination to the sediment compartment, such as sediment transport from other contaminated locations. Also lacking in the models used is the exposure to particulates that may either be contaminants themselves or may serve as sources of contaminants even being bioavailable themselves. Some representative examples are the antifouling paint particles and tire particulates, that may represent sparingly soluble sources of contaminants (e.g. Cu, Zn), but may transform to more bioavailable and potentially toxic forms with time. The emission of the chemical bound to suspended particles may also be a relevant process. For example, EUSES assume an emission to water of 15% for a non biodegradable chemical with a $\text{Log } K_{ow}$ of 6 and Henry constant no higher than $1 \text{ Pa}\cdot\text{m}^3\cdot\text{mol}^{-1}$; in many cases this value will exceed the solubility limit and most of the emission is expected to occur as particle bound substance.

Regarding the active ingredients of pesticides, for which both knowledge on the use profile and data availability is generally much higher than for industrial chemicals at the European level, the exposure scenarios are built differently. The active substances are evaluated using some of the 10 FOCUS surface

water scenarios²⁰. Each of these scenarios should apply to the 90th percentile of exposure concentration in a large region. At the time of development of the FOCUS Surface Water scenarios, comprehensive databases for checking this assumption were not available, so it is not yet clear how well the FOCUS scenarios represent the 90th percentile found in aquatic systems. EFSA (European Food Safety Authority) describes a consistent methodology for scenario derivation that could be applied to improve the exposure assessment²¹.

On a national level, Member States use exposure scenarios as well; for example, the Netherlands use a specific scenario because Dutch surface water is relatively vulnerable. Actual fate data is used (i.e. sediment/water study) and exposure values assume a homogeneous distribution through the upper five centimetres. Next, a comparison of the other ecotoxicology data to the exposure data through this upper layer is performed. This approach seems to equalise better with contaminant behaviour in a pond system. However, there are questions on how this approach could be applied to continuous releases and whether it is truly representative of the majority of aquatic systems.

For regional/continental estimations, multimedia models (e.g. MacKay Fugacity Models such as Level III EpiSuite) offer information on the expected relevance of the sediment compartment in the overall distribution of the chemical among the different environmental compartments.

Regarding metals, although environmental fate models have been developed for predicting metal concentrations in various environmental compartments, including sediments, as a function of metal loadings from natural and anthropogenic sources; the prediction of sediment metal concentrations is still problematic. In particular, although the existing models may be conceptually appealing, it is very difficult to validate them against field data. Perhaps, this shortcoming is not a major problem for risk assessment *per se*; at least for the data-rich metals (since their ambient concentrations are reasonably well known); but it does constitute a major obstacle for the risk assessment of data-poor metals and for their risk management (e.g. for deciding whether reducing a particular metal input will in fact result in a meaningful decrease in the ambient metal concentration).

Once metals have reached the benthic sediment compartment, there are three recognised possible exposure routes:

1. the sediment porewater (for benthic organisms that burrow in the sediment);
2. The water overlying the sediment water interface (for epibenthic organisms; for benthic organisms that burrow in the sediment and create burrows that connect with the overlying water, and through which the overlying water circulates); and
3. the solid sediment (for sediment-ingesting organisms). The behaviour of the organism will govern which exposure route is most important, and the dominant exposure route may change for different life stages or due to different activities of an individual life stage.

The biotic ligand model (BLM) has been used to predict the toxicity of metals as a function of water chemistry, but to date the application of the BLM to the sediment compartment is extremely limited. Such models are available for some metals, but they have not been widely developed and validated using sediment toxicity data. These EqP-based models predict only the dissolved exposure route and do not even discretely consider dietary exposure, which may be important because many benthic organisms ingest considerable quantities of sediments, in which bacteria, algae, smaller organisms and organic matter are found. The

²⁰ <http://viso.ei.jrc.it/focus/sw/index.html>

²¹ <http://www.efsa.europa.eu/en/efsajournal/doc/2562.pdf>

metrics for model-based equilibrium partitioning is not an issue as based on the parameters and default assumptions, the model results can be expressed in different ways.

There are also bioaccumulation and trophic transfer models and simplified calculations, e.g. based on Biota-Sediment Accumulation Factor (BSAF), for estimating the expected exposure for fish and other organisms feeding on sediment dwelling organisms, but the transfer models mostly focus on non-ionisable organic substances.

4.1.2.2 Retrospective risk assessments

In the case of retrospective risk assessments, analytical measurement is usually the starting point for the exposure assessment. Direct sediment analysis can be complemented with or replaced by other tools, such as passive sampling devices that aim to absorb available concentrations of organic chemicals in a manner similar to, or at least mimicking of, the way absorption occurs by biota. For non-polar organic chemicals, a very promising approach is to do equilibrium sampling into a polymer. The concentration in the polymer can then be multiplied by the lipid to polymer partition ratios in order to obtain an accurate prediction for equilibrium partitioning concentrations in lipids. Passive sampling devices are generally better developed for organic contaminants, but samplers for metals are also available and can target labile or (readily released) fractions.

The metrics for defining and presenting the exposure levels are essential in retrospective risk assessments. Different sinks may require different metrics. Assuming a variety of organisms will be exposed by different routes, it is expected that one single metric will not be sufficient. Currently, the total dry weight (typically dry weight concentrations in settled matter or concentrations in the water column as an indication) and pore water concentrations are used as indicators. Pore water concentrations and total sediment concentrations (or both) will be needed, depending on whether uptake is mainly through body surface (contact) or diet. There is a need to evaluate the state of the science regarding the relative importance of dissolved (pore water) versus dietborne exposure as they pertain to the manifestation of toxic effects, as toxicity is currently the predominant basis of risk assessment (unless food chain effects are evaluated). When both should be quantified, it should be considered that addressing dietborne exposure is not simple. How should dietborne exposure be quantified?

It is probably a good general target to use the same metrics as far as possible. However, if there are good reasons to use different/several metrics, for example, because of differences in organism habitat use and/or life history characteristics or behaviour of the substances, then this use of different metrics should be applied. For example, the concentrations in suspended matter may be very useful for considering transport or exposure to certain species (e.g. filter feeders such as oysters) that live near but not in sediments. Normalising concentrations of organic chemicals to a fixed OC content reduces the variability but does not correct for differences on the nature of the OC.

When dealing with bioaccessibility/bioavailability, it appears that the best metric, for the moment, is the freely dissolved pore water concentration, both for metals and organic chemicals. Note, however, that when using pore water concentrations to quantify sediment exposure, the assumption may reflect the conditions for uptake through the dermis and gills, while for ingested sediment, the physico-chemical conditions in the digestive system may affect the exposure. Therefore, the geochemical environment of the digestive system must be characterised in order to begin modelling speciation and activity. However, as indicated above, different organisms may experience bioavailability in different ways.

Passive sampling devices based on organic polymers can be used to determine freely dissolved pore water concentrations of organic compounds. As good relationships with body burden concentrations have been observed; there is a tendency to assume that all uptake is through the free dissolved phase, but this is not necessarily the case. The good relationships are found because the freely dissolved concentrations directly

reflect the chemical activity in the system. Uptake by a passive sampling device can also be transferred to a lipid basis (e.g. $\mu\text{g/g}$ polymer); an excellent parameter for assessing exposure. The result is basically given as the lipid based concentration as if the organism was in equilibrium with the sediment. This approach can be used as an (complementary) exposure metric in laboratory bioassays for reducing interlaboratory variability.

It is generally recognised that total metal concentrations are often poor predictors of metal bioavailability and the risk posed by metals. For metals, the best metric for bioavailability appears to be the freely dissolved pore water concentration. For the assessment of metal bioavailability, the technique of diffusive gradient in thin films (DGT) is becoming increasingly used as a useful in situ passive sampling device for providing information of metal bioavailability, at the sediment-water interface and in deeper sediments. Costello et al. (2012) showed that DGTs are useful in tracking the flux of Ni from sediments and among different binding phases, but DGT-measured Ni poorly predicted the invertebrate response to metal. The biodynamic model proposed by Rainbow and Luoma (2005) is a good starting point for assessing the dietborne exposure to metals.

For metals, the bioavailable fraction is a function of sediment AVS in anoxic sediments, with OC and Fe/Mn becoming increasingly more important in oxic/sub-oxic sediments. These factors and other sorptive phases like organic carbon and Fe/Mn oxides explain the majority of variability in toxicity to infaunal benthic organisms, among sediments with different chemistries. Freely dissolved concentrations can be calculated from pore water concentrations if the partitioning coefficient K_{DOC} and the Dissolved Organic Carbon (DOC) concentration are known or can be determined directly by measurements (e.g. using passive sampling devices). Chemical activity can be determined using speciation models, and this requires quantitative characterisation of pore water geochemistry. It is very important to note that pore water geochemistry will vary substantially from that of the overlying water, e.g. higher DOC, different pH, higher hardness etc. At the sediment water interface, fluxes of metals (e.g. DGT) can be a particularly useful measure of potential metal exposure.

Based on the discussions on bioaccessibility/bioavailability above, there is good reasoning behind the use of the pore water concentration as the main metric to assess exposure; however, this is not often performed in ecotoxicological studies and may be difficult to perform due to specific testing conditions (e.g. the use of artificial sediment) and the lack of operational definitions and harmonised methods. Particularly for many metals, accurate pore water measurements can be difficult as the separation of pore water from sediments often results in experimental artefacts, and pore water metal concentrations often displace large gradients in the top one centimetre of sediments due to the redox gradient changing the dominant metal-binding phases (e.g. from Fe/Mn-oxides, that are then reduced and dissolved releasing metals, and then metal sulphide formations).

The important consideration in the choice of metric is that the conceptual model used in the exposure estimation is identical to that used in the ecotoxicological testing. Therefore, it is assumed that if the PEC is determined in suspended matter (representative of the upper few millimetres of sediment), then exposure in the ecotoxicology study should be performed with an equivalent material or, if not, it should be considered whether the effect measure could be normalised relative to the exposure measure. Alternatively to the latter, it should be considered how cautious the approach should be if different metrics for effects and exposure are being used. The metrics chosen may differ depending on the test species because, for some species, pore water is most likely to be the dominating exposure route, whereas for other species dietary contribution (sediment ingestion) or exposure from filtering overlying water may be equal or more significant routes. At present, under biocides/REACH, detailed guidance is only provided for the first tier, which is simplistic and precautionary in most cases, but not applicable to certain substances/conditions. The mismatch between the exposure used in the ecotoxicology studies (uniform distribution through the sediment) and the assumptions used for the calculation of PECs (suspended matter, upper millimetres), need to be solved when alternative or higher-tier methods are required.

4.1.3 Accounting for contaminant bioavailability and degradation/dissipation in sediment exposure assessment

Research during the last decades has led to several concepts of bioavailability and to many more methods to estimate bioavailability. One reason for disagreement is the confusion of two fundamentally different parameters, accessible quantity and chemical activity.

The accessible quantity describes a mass of contaminants, which can become available to, for example, biodegradation and accumulation. It can be determined with mild extraction schemes or depletive sampling techniques. The chemical activity, on the other hand, quantifies the potential for spontaneous physicochemical processes, such as diffusion, sorption, and partitioning. For instance, the chemical activity of a sediment contaminant determines its equilibrium partitioning concentration in sediment-dwelling organisms, and differences in chemical activity determine the direction and extent of transport between environmental compartments. Chemical activity can be measured (estimated) with equilibrium sampling devices and, theoretically, is closely linked to fugacity and the freely dissolved concentration. However, measurement or modelling techniques are not well developed for estimating chemical activity related to dietary exposure, which may be important for some chemicals. The terms “bioaccessibility” and “bioavailability” as defined in human health toxicology can have relevance here if dietborne exposure is discussed (true bioavailability as a measure of the fraction of exposed substance that is ultimately absorbed in the blood or equivalent stream); nevertheless, there is not an equivalent level of information on toxicokinetics in sediment organisms.

Therefore, there is also a need to differentiate bioavailability from bioaccessibility. Bioavailability can be defined as the fraction of contaminants that are available for uptake by an organism of interest, and therefore is organism specific. The time scale is also relevant, e.g. in relation to food ingestion. Bioaccessibility is how much of a contaminant is accessible but not necessarily how much is assimilated into the organism. Although bioavailability assessments would be more preferable, the only real possibility for measuring bioavailability is by exposing relevant species to sediment (laboratory and/or field) and obtaining the tissue residues and toxicokinetic estimations – or if bioavailability is defined as a parameter related to toxicity to measure the chronic toxicity of the organisms. In the case of tissue concentrations, the bioavailable fraction may often not be correctly estimated as a considerable portion of bioavailable fraction may have already been ‘processed’ by the organism, and only the fraction that remains present as internally bioavailable forms is important (e.g. metals that have been accumulated slowly and stored as granules etc. are often considered as biologically inactive). Bioaccessibility can be measured using other techniques. The BCR extraction approach²² (Community Bureau of Reference method, see also <http://irmm.jrc.ec.europa.eu/>) could be used for some chemicals to try and link solid-state speciation with bioaccessibility. What is really needed, is a unified scheme to evaluate bioaccessibility using more representative biological fluids in validated and standardised new extraction methods (representing the effect of e.g. dietary tract, enzymes, proteins and surfactants).

A method that tries to incorporate (mechanistically) an important basic phenomenon of the system, and which can also be cost efficient, is the estimation of freely dissolved pore water concentration. This can be performed either through models (EqP and BCF) or with chemical analysis for organic substances, but is more challenging for metals. The equilibrium between water/sediment/suspended matter is not an easy endpoint to address and the bioavailability of the substance is dependent on the equilibrium between the different matrices. Many scientific papers confirm the view that with non-ionic organic substances, freely dissolved concentrations in pore water are a good estimate for a pool that will attain steady state with biota

²² Ure, A.M., Quevauviller, Ph., Muntau, H., Griepink, B., 1992. B. EUR report. CEC Brussels, 14763, 1992:85

through bioconcentration. This, of course, is modified by the organism's potential ingestion of the sediment and its gastrointestinal processes, biotransformation, as well as the duration of exposure. Passive sampling devices²³ (PSDs) are very promising tools for the detection of freely dissolved concentrations of organics. Solid phase microextraction (SPME) is one application but it has limited sampler volumes. A larger volume sampling method is offered by coated vials and polyoxymethylene (POM) or polyethylene (PE) film. Some legacy contaminants can be sampled with passive sampling devices but new emerging substances need experiments. However, in addition to detecting environmental concentrations of active substance fraction, passive sampling device concentrations can be converted to lipid based biota concentrations allowing direct effect assessment relying on empirical data from tissue residue approach (or CBR, critical body burdens).

Passive sampling is an excellent tool to measure the bioaccessible fraction of sediments or SPM as well as the chemical activity (or the freely dissolved concentration), allowing bioavailability estimations. Passive sampling devices are also a good tool for giving information on the potential for bioconcentration. This has been well demonstrated for legacy organics but their application for assessing exposure of emerging substances needs additional research. Though, it is also important to recognise that passive sampling devices do not reflect biomagnification or metabolism. Not all passive sampling devices are similarly suitable for measuring the bioaccessible fraction, the chemical activity/freely dissolved concentration or for estimating potential bioconcentration. PSDs based on partitioning of the chemical into a sampler consisting of one phase should probably be preferred. The questions for which PSDs are suitable and mature enough require clarification. Of high importance is the standardisation of passive sampling devices relative to the contaminants and the configurations used; e.g. the various polymers (or the varieties of one polymer) utilised show different partition coefficients for a given substance. Calibration procedures also require standardisation.

The costs for PSDs, including preparation, extraction and clean-up of the PSDs, vary significantly between the different types of PSDs. Recommendations for introducing PSDs in sediment exposure assessment should take the costs into account. One shortcoming of traditional exposure assessment lies in sampling strategies that are discontinuous in time. Sampling is conducted at certain time intervals. Concerning sediments, this is not a problem if the surrounding conditions are more or less constant (i.e. concentration in water and depositing material). Usually, sediments are integrative over time and changes in contaminant concentrations are slow. However, concentrations in water can alter quickly as a result of disturbances. For water sampling, passive sampling devices that accumulate contaminants and provide time-weighted average exposure concentrations, rather than equilibrium concentrations for one point in time, can therefore be advantageous and constitute a more realistic exposure to biota. Note that passive sampling devices can assess porewater concentrations, which are linked to aqueous exposure, but cannot directly account for the uptake flux through particle ingestion.

In the regulatory context, if a PEC is calculated based on the assumption of 100% bioavailability, and the ratio between this PEC and the PNEC indicates no risk, i.e. PEC/PNEC ratio <1, this finding basically means there may not be a need to account for bioavailability any further. However, if the PEC/PNEC ratio is >1, then the exposure assessment (e.g. release rate) of the substance should be refined and/or the bioavailability should be estimated based on physico-chemical data of the substance, monitoring data (if available) and properties of the environment. Bioavailability may depend on environmental conditions such as the content of organic matter in the sediment. Therefore, for a given compound, it can be appropriate to derive PECs specifically for different environmental conditions (such as sediment types). PECs can be calculated for different time periods after the beginning of the exposure, to account for the change in bioavailability over time. Modelling is acceptable for some situations; however, not all chemicals exhibit partitioning behaviour

²³ http://c.ymcdn.com/sites/www.setac.org/resource/resmgr/publications_and_resources/executivesummarypassivesampl.pdf
http://www.normanetwork.net/index_php.php?module=public/workshops/ispra_2012_pdf&menu2=public/workshops/workshops

according to the currently available theoretical models. For example, ionic organic compounds can exhibit complex partitioning that needs to be better understood before their behaviour can be successfully modelled. A bioavailability assessment, approximated through the pore water concentration modelled using the Freundlich equilibrium equation, is incorporated in most European pesticide fate models. To account for non-equilibrium sorption and ageing, rate-limited processes may be included as well if available.

For metals, *in situ* techniques such as DGT have increasingly been used to provide information on labile metal concentrations (but like all techniques the limitations still require further examination). Furthermore, the bioavailability of some metals (Ag, Cd, Cu, Cr, Ni, Pb, Zn) can be modelled with SEM-AVS approach but further development is required before suitable BLMs for sediments will be available. The SEM-AVS approach for characterising the bioavailable fraction of metals in the sediment includes consideration of AVS and SEM concentrations sulphide, and organic matter content. AVS in the sediment reacts with dissolved metals to form an insoluble metal sulphide. AVS and SEM are operationally defined terms and refer to the sulphide and metal fractions that are released upon a cold, weak acid extraction. The metal sulphide form is considered non-bioavailable to benthic organisms via the dissolved route.

The amount of AVS in sediments, which is determined by the anaerobicity and the availability of sulphur (including that which comes from decay of proteins of dead biota) in the sediment, serves as a critical parameter in determining metal bioavailability and toxicity in sediments. Metals, in essence, will exist in the form of their respective metal sulphide if the AVS is present in excess of the reactive forms of the sediment metals (SEM) (and the AVS is accessible to the metals in question), and as long as anaerobic conditions persist. On the other hand, if the total concentration of the metals is greater than the concentration of the AVS, then potentially, some fraction of the metals may occur in the pore water, and then other complexation processes in the pore water (which will vary by metal) becomes the relevant process (e.g. binding to dissolved organic carbon). Other solid phases (organic carbon, Fe/Mn oxides, clays) also bind metals, so the probability of risk under situations where SEM > AVS will vary according to these parameters. One limitation of the SEM-AVS approach is that it is not a predictive tool. The Ni case study will offer an illustration on how a predictive bioavailability model can be incorporated into a sediment risk assessment framework. Briefly, bioavailability models are developed for representative benthic organisms. These are then used to normalise sediment toxicity databases. Normalised ecotoxicity data are further used to populate a species sensitivity distribution, which can then yield site/region-specific PNEC values. A key consideration in any bioavailability-based approach is the need to collect data on the distributions of factors that affect contaminant bioavailability. For metal compounds, these should, when possible, include parameters like AVS, and organic carbon, Fe and Mn oxides and particle size.

In conclusion, the term bioavailability is defined in many different ways. The following is an attempt at a definition and delineation of bioavailability and related terms. The total concentration of a chemical in a sediment can be divided into an irreversibly bound pool (i.e. non-extractable, bound residues), reversibly bound, and freely dissolved pool. The reversibly bound and the freely dissolved pool constitute the (bio-) accessible pool. Accessibility is operationally defined. The accessible pool defines the fraction of the total concentration that can undergo degradation, be mobilised or taken up by organisms. However, it is a poor measure for the actual diffusion, partitioning or uptake process, which is rather driven by the freely dissolved concentration or the chemical activity. The chemical activity, as well as the freely dissolved concentration, can be measured by passive sampling devices. Bioavailability is linked to (bio-)accessibility and to the freely dissolved concentration (or the chemical activity). Bioavailability also includes the uptake of a chemical by the organisms. Hence, bioavailability is not only driven by the characteristics of the sediment, but also dependent on the organism.

4.1.3.1 Degradation/dissipation

Degradation or dissipation half-life should be estimated and these estimated half-life can be used in PEC calculation. It is important to evaluate how realistic the half-lives derived from laboratory experiments

are in the field conditions. Actual degradation (rates) may be difficult to predict, as it depends on site-specific conditions (i.e. temp, pH, redox, bacterial community). When the dissipation half-life is used in PEC calculations, the fate of the substance should be known (e.g. binding to organic matter) and it should be considered whether the substance is transformed permanently or adsorbed (and whether it can be desorbed). Transformation products should also be considered as far as possible. For example, if there are intermediate or persistent/recalcitrant transformation products that can be of concern, they should be considered in the risk assessment. Some chemicals can exhibit a very fast half-life in water and tissue and a much slower half-life in sediment, which can also be highly variable depending on the redox state.

Many contaminants can last for years in sediment and may become bioavailable when the sediment is disturbed or bioturbated. Degradability should be incorporated as it is a major factor. However, the standard methodology available e.g. OECD test guidelines and even “simulation” degradation guidelines such as the OECD TG 308, do not, in most cases, simulate the true environmental conditions in particular in relation to microbial species diversity and redox conditions over longer time frames. Furthermore, tests are often conducted so that environmental realistic low concentrations of the test substance are not employed (e.g. because of constraints in relation to analytical feasibility). In addition, the temperature employed in the test is frequently room temperature (about 20°C), which is higher than that prevailing in the environment. Finally, even though TG 308 includes a part for determination of degradation pathways (identification or characterisation of degradation products), this part of the test maybe omitted. When only one or a few degradation half-lives (typically of the parent compound and/or main metabolite(s) are being obtained with TG 308 it is not known how well test data represent the environmental variability impacting real environmental sediment degradation rates.

Similar limitations as those described here for TG 308 may also concern other “simulation” test guidelines such as TG 307 (soil), 309 (surface water), 314 (five different TGs concerning degradation in waste water). In conclusion, even “simulation” degradation test guidelines still provide highly uncertain and/or limited results, which require normative decisions to be made in relation to their use in a regulatory context.

Some organisms have the ability to detect and avoid contaminated sediments, and as a consequence, healthy benthic communities may exist in sediments that have ‘avoidable’ areas (of varying size) that contain elevated concentrations of bioavailable contaminants. The consequences of short to long-term avoidance of contaminated sediments needs to be better understood for the dissipation and degradability estimations.

For metals: degradability is not an issue but speciation, ageing, burial below the depths that are explored/inhabited by benthic organisms and other relevant processes should be considered if feasible. Long-term distribution processes occurring in sediments are not accounted for in short-term laboratory toxicity tests. The contaminant avoidance discussed in the paragraph above has been shown to occur in metal contaminated sediments. Sediments with high metal concentrations may be avoided by larger bioturbating organisms and this will reduce the frequency that oxygen mixes with deeper sediments then consequently results in higher AVS concentrations and lower dissolved metal concentrations. While the dissolved metal exposure is now lower (due to metal-binding to AVS), many organisms may also avoid sediments with high sulfide (AVS) concentrations. For those that don’t avoid sulphide, they may create oxidised niches (e.g. as exist around all burrows) and metals may be more bioavailable near the organism. This clearly underscores the need to consider exposure variability.

Regarding monitoring programmes, degradation processes are less relevant for sediments because of the long residence times in sediments; the compounds that are degradable will have “disappeared” from the matrix. When including bioavailability measurements, degradation is automatically accounted for however. Measurements can be repeated in time to provide information on rates. It is essential that measurements minimally disturb the system to ensure that the bioavailability measured in the samples represents the bioavailability under real conditions.

The formation of metabolites should be considered. Metabolites should be assessed for their toxicity, their bioaccumulation potential, and their persistency. For metals such as mercury, the formation of organometallic compounds is relevant.

4.1.4 Exposure assessment variability, uncertainty and prioritisation

Any exposure assessment will face a considerable number of challenges as both contaminant concentrations and parameters that influence bioavailability (e.g. AVS, POC forms) exhibit considerable temporal and spatial variability. Additional aspects like seasonal and tidal fluctuations in hydrology which influence sedimentation, remobilisation of contaminants, and sediment resuspension also need to be taken into account.

It is a well-known fact that there can be a huge difference in sediment concentrations, within a very fine temporal and spatial grid. This has previously been reflected in the scientific literature, especially concerning legacy chemicals. In practical terms, the spatial and temporal scales should be designed according to the risk assessment objectives, and should be coherent with the effect assessment, ensuring the optimal resolution of the spatial and temporal coverage of the risk characterisation output.

For regulatory purposes, the goal should be to address realistic worst-case scenarios, sufficient for decision making. Exposure scenarios/models should take into account the factors that affect the temporal and spatial variability in release, transport, ageing or any other factors that affect the exposure concentrations. The frequency, spatial distribution and type of emissions (continuous/not continuous) should be documented. In general, it can be useful to obtain several PEC values (e.g. based on maximum and average emissions, or for different sites or areas), for risk assessment. Uncertainty related to each parameter used for calculation should be estimated and documented as far as possible. If the reasons for temporal variability are known, the timing of the assessment can be placed correctly (e.g. during the high exposure). One approach would be to concentrate on season/time when the most vulnerable receptors are under exposure (e.g. fish eggs versus adult fish). The concentrations of AVS clearly vary seasonally with the lowest concentrations typically measured in the spring season. Hence, assessments should be performed under realistic worst-case conditions prevailing in spring. Some indicator of overall uncertainty for PEC could also be useful. Quantitative uncertainty analyses using tools such as Monte Carlo simulations could provide significant insights.

Spatial variability calls for proper sampling plans that consider source location, relation to vulnerable/valuable areas, gradients, sample number in relation to precision and cost efficiency. Risk assessors need to consider first the ecological relevance and then the statistical significance versus the practical significance and the possibility for stratified, composite or even adaptive sampling (instead of systematic). Much of the variability presently measured for organic chemicals in sediments is related to differences in composition of the sediment sampled in time or place but does not reflect the variability of the exposure level. Unless the system is very dynamic and close to pollution sources, the exposure level in terms of chemical activity of organic chemicals (through passive sampling) will not vary a lot.

For pesticides, the current exposure models can simulate the time dependence of the exposure concentration in sediment (i.e. dissolved and total). Spatial variability could be assessed using a spatially-distributed modelling approach. Although there have been some initiatives for performing such a spatial analysis²⁴, there is no commonly agreed methodology for available pesticides. In general, uncertainty of the exposure concentration leads to a shift towards higher exposure concentrations. Uncertainty could be dealt with using a Monte Carlo approach, but simpler procedures are often proposed that use a higher spatial

²⁴ e.g. www.eu-footprint.org

percentile in the exposure assessment²⁵.

Several sampling paradigms have been proposed to derive data representative of large areas of contamination (particularly where the contamination may not be uniform). Several approaches have been proposed using applications of Geographic Information System (GIS) to derive weighted estimates and median values and to sub-divide large contamination areas into smaller geographic units. In many cases (especially many non-polar organic chemicals), tissue concentrations can be very important for exposure estimation because they integrate ambient concentrations over time and space. In other cases, a large number of samples taken according to a statistically robust sampling design are required for sediment or porewater to adequately characterise temporal and spatial variability. It is essential to rationalise sampling in terms of good experimental/monitoring design during the problem formulation stage, unfortunately this is too often overlooked.

The most robust alternative is using probabilistic approaches but, if this is not feasible, peak versus average exposure estimations should be presented, and a time-weighted approach could be considered as the third option. For pesticide RA, we would usually calculate both and decide, depending on available toxicity data, which PEC is the appropriate one for the RA. Usually for pesticides, peak concentrations are of high relevance due to the pulsed exposures, however, considering accumulation in the sediment, TWA-concentrations might become more important. In any case, the concentrations in sediments do not vary with time as drastically as in the water column. Thus, threshold values should be built up to protect the benthic environment from chronic effects. It might also be a good practice to define site specific receptors with the most vulnerable time windows when special attention could be paid, e.g. with lower threshold values.

Priority is subject to the scope of the particular investigation being conducted and also depends on the chemical. Historical pollution of classically used chemicals may pose a risk for higher trophic levels through long-term steady exposure even with decreasing levels in sediment. Emerging contaminants are less monitored and less regulated and can vary in the quantities discharged and may be less persistent. Therefore, they should be monitored more frequently until a better understanding of their behaviour and fate in both water and sediment is achieved.

Maximum (or worst-case) PECs can be used as a first check and if these do not indicate an unacceptable risk, then there is not necessarily a need to refine the PEC any further (for regulatory purposes). If the worst-case scenario shows possible risks, we have to investigate at a more precise level. If the aim is to protect the benthic community, it is necessary to consider the life cycle of the organisms. There are some periods of the organism's life cycle (e.g. early life stages, inter-molt period) which are more sensitive to contaminants. In these cases, the priority is to measure peak concentrations. Higher tier risk assessments should strive to replicate reality to the extent practical. That dictates preferences in risk assessment to characterise "reasonable conditions" and "reasonable worst-case conditions" and to consider exposure scenarios that are plausible. In the case of monitoring programmes, maximum values may be reflecting outliers and errors and will discourage sampling; in contrast the more data, the higher the value. For chronic, long-term assessments, averaging seems reasonable. Considering the "recovering capacity" of ecosystems, this pragmatic approach can be considered as acceptable. However, peak-exposures may also need to be considered because of their acute ecological relevance (e.g. 90th percentile). For remediation purposes, one should aim for realistic concentrations, as worst case estimates might lead to unnecessary remediations on one hand, and averaged concentrations might miss hotspots that should be prioritised for remediation on the other hand. Such a realistic assessment would be best obtained by performing space-resolved bioavailability measurements in sediments, e.g. using passive sampling devices when appropriate. Based on such measurements, hotspots might be identified (maximum concentrations) that could selectively be remediated and locations that do not

²⁵ e.g. <http://www.efsa.europa.eu/en/efsajournal/doc/2562.pdf>

need remediation.

4.1.5 Use of monitoring and field data and the role of site-specific emissions and assessments

Monitoring and field exposure data are valuable tools for retrospective risk assessment and sediment quality assessments. It helps to identify the general status of a specific concrete environment and characterise possible threats. Monitoring and field data can also be invaluable in determining the realism of a risk assessment, provided that the field data include measures of biological effects that can be plausibly linked to exposure to a particular contaminant. This has proven difficult in the past, as the link between exposure and effect is difficult to establish in field situations where mixtures of contaminants are normally present and many non-contaminant factors can modify exposure and confound interpretation of impacts. In this context, recent work in the toxicogenomic field shows some promise that we will be able to identify particular transcriptomic “signatures” that can be linked to a particular contaminant and are also linked to ecologically relevant outcomes/effects.

It is more difficult to use monitoring data for prospective risk assessment in which you have to authorise or deny the environmental release or use of a certain chemical. The source of the chemical that you are tracing can vary enormously and can even be a metabolite of other contaminants. The empirical approaches that involve laboratory and semi-field studies are much more reliable tools in risk assessment, but may not address some processes occurring in the environment. Nevertheless, field data are invaluable in terms of validating models, approaches, and conclusions that are derived from laboratory observation.

When dealing with a site specific risk assessment the situation varies. In this case, it would be very valuable to assess the general quality of the receiving environment, the species present, the physico-chemical properties and many other factors that would help to understand the potential effect of a chemical in that specific environment. However, monitoring and field data can, if performed in a comprehensible way that covers the environment of interest sufficiently both in time and location, be used in order to calibrate multimedia fate models, to estimate partition coefficients, to identify local sources etc., and provide essential validation to any desktop predictions that are typically fraught with uncertainties. If there is field data available for the same substance or similar substances, then this information could possibly be used to evaluate the reliability of the PEC calculations or exposure scenarios/models. It should be noted that field data and monitoring cannot always be assumed to represent the actual environmental exposure and that such data also includes confounding factors (e.g. contribution of the chemical concentration of a substance from degradation processes of other substances and from other natural and anthropogenic sources and processes).

Field data and monitoring data can however be used in a WoE approach when evaluating single substances in a regulatory context. Results from synoptic measurements on biology, chemistry and ecotoxicology as measured with the TRIAD approach²⁶ could be used as a kind of validation. Site-specific information should be taken into account when it is considered to affect the behaviour or fate of the substance. Monitoring, often done only in the water column, needs to include substances expected to distribute into sediments. After that a simple multimedia model could estimate concentrations in sediment. Even better would be a scheduled sampling and analysis of sediments. Of particular importance are monitoring data for incorporating bioavailability-based approaches (e.g. AVS for metals, passive sampling devices for organic chemicals) and data that can be used to validate model-based exposure estimates. Monitoring and field exposure data can also be used in calibrating site-specific models that are often applied to predict future

²⁶ e.g. <http://www.efsa.europa.eu/en/efsajournal/doc/2562.pdf>

risks and in evaluating various management options for risk reduction.

In a standard risk assessment approach (e.g. under REACH), monitoring is a higher tier methodology and limited to substances already on the market. For site-specific assessments, however, monitoring is an essential component in an integrated (e.g. TRIAD) approach.

Sediment serves as “an archive” for many particle associated contaminants and includes all possible routes of depositing material at that specific site. Source characterisation and control is essential, not only in exposure assessment but also in possible remedial actions. The quantity of the emissions from point sources and diffuse sources should be estimated (as far as possible) and if both are considered relevant, then they should both be included in the exposure assessment. To include point source discharges and diffuse sources, one would need to be able to model contaminant transport from these sources to the sediment compartment, and thus evaluate their contribution to sediment contaminant concentrations. As mentioned earlier, such models exist in conceptual form and as computer programs, but they have been seldom validated. This is a challenge for modelling (to be dealt with via emission data/loads, area size etc.).

Measuring will integrate this automatically, that is, if the spatial resolution is sufficiently great to catch point sources. If the location of a point source is known, the campaign can be tuned to this. If point sources cause local concentrations to exceed Sediment Quality Criteria (SQC), local remediations should be performed. The linkage of point and diffuse sources to exposure concentrations and bioavailability in sediment has been performed using mass balance models. Screening-level models for organic chemicals and metals are available and have been used in generic risk assessments. Site-specific models have also been developed and have been used in support of many regulatory programmes. Modelling the transport of contaminants from the point source or diffuse sources requires models coupling hydraulic processes (e.g. advection, dispersion of water and SPM), sedimentological processes (e.g. deposition/resuspension) and chemical processes (e.g. adsorption/desorption). From a modelling point of view, both point source and/or diffuse sources can be included as input data in such integrated models.

Current practice to conduct risk assessments focuses on generic assumptions and exposure scenarios. For industrial chemicals, the sediment compartment is presently assessed with data from the water compartment. It is evaluated on a local scale, where the sources are well identified and on a regional scale where the sources are more diffuse but in terms of the calculation, the characteristics of the receiving sediments are always the same. For pesticides, diffuse sources including spray drift, drainage and run-off are included in the FOCUS SW scenarios and models. Point sources are not included in the exposure assessment for pesticides as the starting point of the assessment is good agricultural practice.

4.2 ELEMENTS FOR DISCUSSION

The following questions were used to initiate the working group discussions:

- What are the main processes to be considered when assessing the environmental fate and transfer of chemicals from water to suspended matter and sediment for local/regional and generic/site-specific²⁷ assessments?
- Which physical-chemical parameters are essential for a proper exposure assessment in the sediment compartment covering release, environmental transfer/partition and within sediment distribution processes (e.g. redistribution, partitioning, ageing, etc.) for the following metals, non-ionic organic

²⁷ Site-specific include the quality status assessment of defined water bodies.

chemicals, ionic organic chemicals, organometallic chemicals, polymers, and nanomaterials?

- Which exposure scenarios²⁸ are currently available for predicting the exposure of sediment organisms including the epi-benthic community?
- What are the best metrics for quantifying sediment exposure? (e.g. total dw or ww sediment concentration, suspended/settled matter concentration, pore water concentration). Is one single metric sufficient or do different ecological receptors require different exposure estimations and/or different metrics?
- How should bioavailability be accounted for in sediment exposure assessment?
- How should degradability and dissipation be considered in sediment exposure estimations?
- How can temporal and spatial variability and uncertainty be assessed and expressed in sediment exposure estimations?
- Which exposure estimations should be prioritised? For example, maximum versus averaged concentrations, realistic versus worst-case concentrations, peak versus averaged concentrations, time-weighted averages adapted to the ecological receptor?
- How can monitoring and field exposure data be used in local/regional and generic/site-specific sediment RA?
- How to include point source discharges and diffuse sources in the sediment compartment exposure assessment?

4.3 OUTCOME OF THE WORKING GROUP DISCUSSIONS

The following sections reflect the discussions from the working groups. Whenever there were different views in the working groups, these are reported.

4.3.1 Release and key environmental fate processes

A high affinity of a substance to bind with suspended matter and sediment was seen by both working groups as a key trigger for conducting a detailed sediment risk assessment. If there is no binding to the sediment/suspended matter (SPM), further testing can already be ruled out. It could, however, also be worthwhile to combine the exposure assessment with the toxicity profile of the substance under scrutiny to assess if a detailed sediment assessment should indeed be conducted. For example, a compound can be of low toxicity so that the exposure would probably not lead to risks. It was also noted that sediment assessments should not be restricted to the settling of the substance into the sediment only but should also consider the potential for re-suspension of sediments given this process could lead to a remobilisation of the contaminant. These release and fate processes are time and event dependent.

²⁸ Exposure scenarios include the environmental release and fate processes allowing quantitative estimations of the expected sediment concentration (including spatial and temporal variability and uncertainty)

4.3.2 Use and limitation of exposure models/exposure scenarios

4.4.2.1 Use of equilibrium partitioning models

The participants of the workshop indicated that the currently available simple partitioning models can be used as a first tier screening approach for both metals and organic substances provided that the correct partitioning coefficients are used. More specifically:

- for metals, care should be taken in selecting a representative K_d value since K_d values for metals may vary several orders of magnitude. For inorganic nano-particles, different methods could apply.
- for organic substances, the usefulness of $\text{Log } K_{ow}$ only as an indicator (i.e. $\text{Log } K_{ow} > 3$) for the accumulation of organic substances in sediment phases, was questioned since binding to organic matter is not the only relevant adsorption process. The use of the current K_{ow} -based EqP models should be limited to non-polar organic substances that typically bind with organic carbon. However, for many polar and ionisable organic chemicals that have not been as commonly monitored in the environment (e.g. perfluorooctanesulfonic acid, PFOS, pharmaceuticals), the use of the conventional K_{ow} -based EqP methods is deemed inappropriate. Indeed, although some ionisable compounds are more polar and have a lower affinity to bind with the organic carbon pool in sediments, the sediment compartment may still be a critical binding phase for some of these substances. For example, positively charged compounds could still have a high affinity to certain sediment constituents (e.g. binding to clay minerals). Other types of substances that cannot be correctly modelled using the classical EqP method are those substances that may form a phase on themselves (e.g. C24 chlorinated substances, polymers, micelle forming chemicals) and do not partition between the solid phase and the water phase in any detectable way but which may still end up in the sediment compartment. Current EqP models may not be applicable to nanoparticles.

For a proper use of simple partitioning methods in a lower tier assessment it is imperative that a conservative but realistic partitioning coefficient should be chosen. Regardless of the choice, a clear justification must be given and the uncertainty should be described in a transparent way. For a generic integrated assessment (sediment and water) the median, arithmetic or geometric mean is typically selected. In that way, none of the distributions of the contaminant in the relevant compartments (aquatic and sediment) is likely to be over- or underestimated. For a local assessment, preference should be given to a site-specific partitioning coefficient or for a targeted sediment assessment, the use of the lower 90th percentiles could be warranted in order to be sure that the assessment is sufficiently protective.

The use of K_{ow} -based EqP models or K_d -based EqP at a higher tier of a risk assessment is deemed less appropriate and if available preference should be given to the use of measured data at that level. For example, the lack of a direct consideration of the contribution or relative importance of the dietary component in the EP models hampers their relevance for higher tiers of a risk assessment (although the assumption that the pore water is the most relevant route to benthic organisms seems to be true for many organic chemicals, e.g. PAH's, PCB's and pesticides and divalent metals). Nevertheless, there is ample room for further improvement/refinement of the underlying concepts of the current models and their parameterisation. The incorporation of concepts such as speciation (metals), biodegradability (organics), probabilistic modelling, use of non-equilibrium conditions/kinetic modelling may be available for future model applications.

4.4.2.2 Exposure scenarios

The use of EqP models is integrated in different exposure scenarios (e.g. REACH, pesticides). The mass balance models used are generally fit for the purpose but sometimes lack a more defined spatial/temporal component (e.g. dealing with spatial/temporal variability). Clearly there is a need to develop more realistic exposure scenarios tailored to the conditions of a specific region, habitat or ecological system (e.g. ecoregions, hydrology (e.g. lakes versus transitional waters) or use pattern of a substance (e.g. spray drift

models). These are generic considerations that apply beyond the sediment compartment. Exposure scenarios for some uses/substances (e.g. biocides, nanoparticles) need further development. Biotransformation and transfer processes from sediments to biota are also fields that need further development before they can be integrated in the existing models. Quite often, the parameterisation, validation and coverage of regional variability are the main fields that should be improved instead of the assumptions used in the different scenarios. This process could include the development of a mechanistic reason for the consideration of additional model parameters as well as a sensitivity analysis that demonstrates the impact of the use of new parameters on the estimate of exposure. In general, a process should be developed in order to recommend that additional parameters be added to existing exposure models. Parameters that could be added are:

- For organics: degradation rates, temperature
- For metals: major ions; major sediment constituents such as Fe/Mn (oxy) hydroxides, organic carbon, (AVS, incorporation of hydrological conditions (particle settling rates, resuspension), cation exchange capacity, interactions with microbial cycling etc.

4.3.3 Accounting for bioavailability/bioaccessibility in sediment exposure assessment

Both working groups discussed the provided definitions in the thought starter on bioavailability and bioaccessibility and in general it was acknowledged that both are operationally defined terms and might warrant more specific and precise wording when doing research, assessment, regulation and management.

Availability begins with physico-chemical considerations (chemical availability). However, clearly this available fraction should be subsequently linked to different ecological receptors, taking the different uptake routes into account. Bioaccessibility was seen as a useful concept that provides an upper limit of the fraction of a substance that could eventually (i.e. present or in the future) be accumulated (e.g. across gut or dermis). The fraction that is really available, after internal distribution/detoxification that could trigger a toxic effect, would then be considered the bioavailable fraction.

Several metrics have been put forward to assess bioaccessibility and bioavailability. None of them can really be singled out to capture all the different aspects in relation to bioavailability of chemicals in general. However, some have a broader and more relevant applicability domain than others (e.g. free metal ion, freely dissolved concentrations/chemical activity, chemical lability/desorption from particles).

- For organic chemicals the most appropriate metric for bioavailability appears to be the "freely dissolved pore water concentration (C_{free})", which is a function of the chemical's activity. Based on the discussions

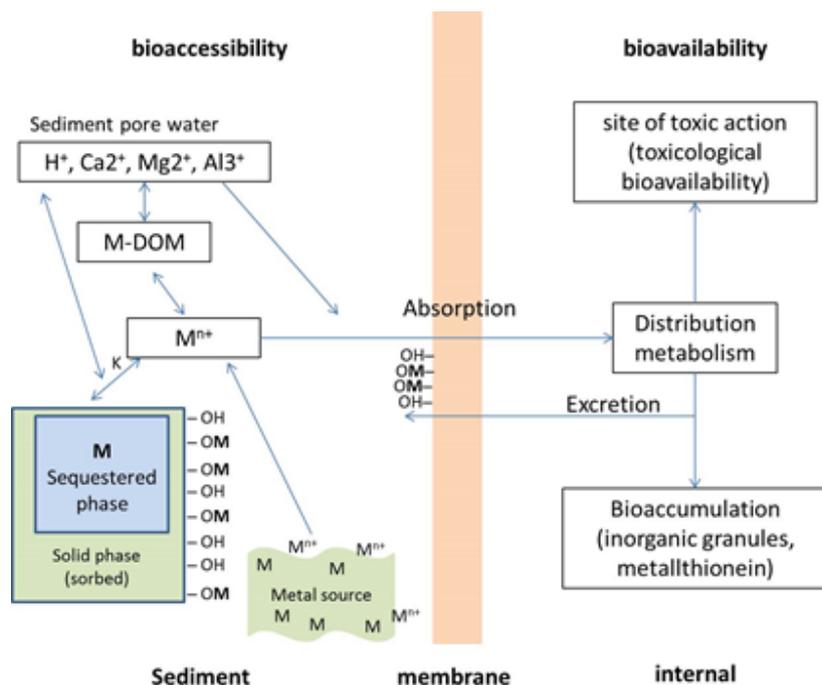


Figure 1: Conceptual outline for metals (after McLaughlin personal communication)

on bioaccessibility/bioavailability there was a general agreement that there is increasing proof and good reasoning behind the use of the pore water concentration as a first main step to improve the assessment of exposure and impact. As conventional pore water measurements may lead to major artefacts, the use of PSDs to estimate the “freely dissolved concentrations” may be a good alternative. However, their usefulness depends on the chemical for which it is used. For non-polar organic chemicals they seem to work the best. For polar compounds it is more difficult to develop suitable PSDs. PSDs also have important limitations. Passive sampling for example, cannot account for dietary uptake. It should also be noted that most of the PSDs experiments performed in the laboratory may not always reflect the actual situation in the field as equilibrium conditions may never be obtained under realistic field conditions. In situ measurement using PSDs could help to better understand these concerns. If the results of PSDs are to be used, there is a need for a better alignment between the exposure parameter and what has been measured in the toxicity test without making the requirements too complex to be used in a regulatory context. The reader is referred to the conclusions and recommendations as formulated at the Pellston workshop for more details on this topic²⁹.

- For metals the free ion and its potential to complex/compete/internal distribution with other organic and inorganic ligands for the available biological binding sites is key to understanding metal bioavailability (Figure 1).

As indicated at the recent Pellston workshop on PSDs, DGT (diffuse gradient in thin films i.e. non-equilibrium devices to measure metal flux) have been less evaluated for assessing the bioavailability of metals in surficial sediments with regard to predicting benthic organism bioaccumulation/toxicity. Further studies

²⁹ Parkerton et al. (2012). Guidance on Passive Sampling Methods to Improve Management of Contaminated Sediments. Summary of a SETAC Technical Workshop, 7-9 November 2012, Southern California Coastal Water Research Project (SCCWRP), Costa Mesa, California, USA.

are necessary to fully evaluate the potential of passive sampling devices for metals by comparing PSDs results with accumulation (tissue residues) or toxicity in organisms. Equilibrium devices such as pore water “peepers” show more promise for those benthic species that are exposed to metals primarily through contact with the porewater. Using the overall composition of the pore water (e.g. pH, hardness, and dissolved organic carbon) it may be possible to perform biotic-ligand calculations to estimate metal toxicity in a similar way to that which has been done for the overlying water.

4.3.4 Accounting for degradation/dissipation in sediment exposure assessment

- **Organic substances:** Laboratory generated degradability data can be helpful to improve the accuracy of modelled exposure concentrations of organic chemicals in sediments. However, laboratory degradation rates may overestimate rates observed in field sediments because the conditions that favour degradation used in laboratory tests (e.g. aerobic conditions) may not occur in the field. The presence of redox profiles in the sediment could also be taken into account. The adjustment of degradability data to actual conditions is probably feasible for the estimation of local exposure, which is for example, required for management decisions during risk assessment of contaminated sediments. For predictive risk assessments, which should be valid on a regional scale, rather standard conditions (which need to be properly defined) seem to be more feasible than using actual conditions. In any case, neglecting degradation at a lower tier would mean a worst-case assumption with regard to the parent compound. Information on the possible generation of metabolites should, however, already be included in lower tiers of the assessment whenever relevant (e.g. because the degradation products may be (more) toxic).
- **Metals:** Long-term chemical and diagenetic processes (e.g. speciation, ageing, burial) are appropriate variables to consider for metals where degradability concepts per se do not apply. Mechanistic modelling (e.g. changes in speciation and potential for reversibility) can be informative. The Ticket-Unit World Model (UWM) (Farley et al., 2011) for example, may provide a good starting point for freshwater sediments. For screening purposes that maximise conservativeness, long-term processes should not be considered because they may underestimate risk. Such approaches are needed as laboratory results from studies with soluble metal salts may differ from field-based studies where the metal forms might be very different.

4.3.5 Dealing with spatial and temporal variability at a regional scale

In general, Mackay type mass balance fugacity models could be used for regional exposure estimations but quite often they lack a well-defined spatial and temporal component. For example, although peak exposures, or in general terms short-term fluctuations, are more likely to occur in the water column they may also happen in the sediment compartment. Flushing, or run-off events may lead to a sudden increase in exposure, which will have the tendency to last longer than in the water column. Its long-term effects will depend on the degradability/reactivity of the compound and its toxicity but may also be influenced by ecosystem characteristics, e.g. the seasonality of sensitive life stages of benthic organisms. Measuring freely dissolved concentration (C_{free}) could already be an important improvement given it has more relevance towards predicting ecotoxicological response than using total concentrations. However, even without sudden events, contaminant concentrations will be patchy and hotspots will always be present. Geostatistics and appropriate sampling strategies should be used to capture this variability. The incorporation of ecoregion/ecotype concepts, as already used for pesticides and metals, could increase realism of the assessment. Another promising tool is the incorporation of spatial and temporal variability using Monte Carlo sensitivity analysis to generate probability distributions of exposure.

4.4 RECOMMENDATIONS

4.4.1 For regulation

- Fate and exposure are key factors that should be considered in the decision making process of any sediment assessment.
- Available exposure assessments tools such as EP are relevant as a first tier for conventional chemicals (e.g. non-polar organics, divalent metals) but should be improved in order to increase realism. The uncertainties, limitations, choice of parameterisation and coverage of regional variability must be transparently reported.
- Exposure scenarios for specific classes of compounds (e.g. biocides) need further development.
- Exposure models should be developed for substances that are currently outside the boundaries of many of the existing models such as polar and ionisable organic substances or for nanoparticles.
- The value of more refined/realistic exposure models should be evaluated for higher tier assessments taking into account biotransformation, dietary exposure and bioaccumulation.
- A proper working definition is needed for the terms bioaccessability and bioavailability.
- Potential metrics from an exposure perspective are related to freely dissolved concentrations (C_{free}), chemical activity, readily desorbing concentrations etc. Although it is acknowledged that these measures of exposure might not capture all situations.
- Both local as well as diffuse source contributions should be considered if relevant for the aim of the assessment.
- Both modelled and measured data have their merits and could be used alone or in combination depending on the regulatory question.
- Information on the formation of contaminant metabolites (the result of biotransformation within organisms) or degradation products (including abiotic/chemical degradation) should already be incorporated at lower tiers of any risk assessment.
- Uncertainty analysis should be performed and presented in a transparent and scientific way (e.g. Monte Carlo analysis).

4.4.2 For scientific research

- There is a need to evaluate the added value of new metrics that may increase the accuracy of predictions of bioaccessability/bioavailability, which would include a demonstration of their relationship with ecotoxicological effects, bioconcentration and bioaccumulation.
- There is a need to better understand the importance of the dietary exposure route in relation to the expression of toxicity and with regard to the uptake mechanisms of contaminants across the gut wall and the relative importance of dietary exposure versus dissolved exposure to substances in pore water.

- There is a need to develop more realistic exposure models taking into account transformation processes, kinetics and different exposure pathways.
- Metal partitioning, speciation and bioavailability in oxic sediments should be better understood.
- Further research is needed on the speciation and diagenetic processes (e.g. ageing, burial) affecting metals in the sediment environment; such processes can have important toxicological consequences and can (at least partly) explain differences observed between laboratory tests performed with soluble metal salts and results from field studies where different forms of metals occur.
- Biodegradability processes under realistic field conditions should be examined.
- More research is needed to examine intracellular distributions of contaminants and its link to toxicity, once a contaminant entered the body via ingestion of sediment particles and/or via pore water.
- Exposure models should be developed that reflect spatial and temporal variability.
- The relative contribution of diffuse source input should be better understood.
- PSD should be developed for polar chemicals.
- There is a clear need for studies that try to link PSD responses in sediment to metal uptake and toxicity responses in benthic organisms.
- The merits of using peepers as an alternative to DET (Diffuse Equilibrium in Thin films) and DGT for metals should be further investigated and validated (see also the specific recommendations and conclusions of the Pellston workshop organised on this topic in 2012).

5. Effect assessment in sediments

5.1 SCIENTIFIC STATE OF THE ART AND RECENT DEVELOPMENTS

Apart from editorial changes, the text below is copy of the original thought-starters sent out to the workshop participants.

5.1.1 Identification of relevant ecological communities and endpoints in the risk assessment for the sediment compartment

Distinguishing between epi-benthonic/benthonic and lotic/lentic communities could be largely assumed as an issue of exposure assessment and not necessarily effect assessment with the caveat, of course, that the exposure influences the effects not only in terms of the relevant exposure pathways but also in terms of bioavailability and uptake and community structure. For example, truly benthic organisms have a greater exposure to pore water and the actual sediments, which may result in a different contaminant exposure relative to epi-benthic organisms which are predominantly exposed to overlying water and suspended (or recently deposited) particles. In addition, published exercises indicate that for water-only exposure there are no differences in HC5 for a number of insecticides for lentic and lotic species, and these include species or taxonomic groups that are suitable/recommended for the sediment compartment. For copper, final chronic

values derived using SSDs (species sensitivity distributions) are within a factor of 2-3 (not significantly different) when using data sets comprising both pelagic and benthic species, or comprising sole benthic species life stages.

There are several reasons justifying the need to cover all these communities accounting for relevant differences. First, in most ecosystems these different communities are connected and interact in complex ways. In lakes, for example, pelagic community processes influence the flux of organic matter to benthic communities. The biochemical processes controlling bioavailability and exposure differ between benthic and pelagic communities. Second, many key species are “part” of different communities in different life stages, and could therefore have distinct contaminant exposure histories and transfer contaminant burdens from one community to another. For example, an organism that spends part of its life in the benthos (where it would have an exposure history unique to that environment) and then spends a part of its life in the pelagic zone (again, with unique exposure) could effectively transfer contaminants from one community to the next. Obviously, the relevance of this process depends on many factors; for example, in historical contaminated sites where there are persistent and bioaccumulative substances (Dioxins, DDT, Mercury, PAH) the main ecological process is the transfer in the foodchain of the contaminants. Finally, services and values derived from communities differ greatly among ecosystems, which have a large influence on the societal relevance to sediment contamination. For example, contaminated sediments in the benthic zone of a deep, fishless oligotrophic lake are unlikely to have the same societal significance (e.g. human exposure) as contaminated sediments in a shallow estuary that is a nursery for seafood and shellfish. Clearly, the connections and uniqueness of these different communities must be distinguished in any sediment-effects assessment.

The relevance of the contaminant exposure needs to be considered in evaluating the need for a sediment assessment. For instance, exposure of benthic organisms to contaminants in a lotic system is expected to be primarily associated to the dissolved phase and freshly deposited sediments, and therefore to actual emissions, while in a lentic system additional factors may be relevant, including actual and previous emissions, ageing processes, and distribution within the sediment. For generic assessments, it is likely to be counter-productive to try and assess flowing and still waters separately (owing to the amount of studies required) and therefore the best approach is probably to include both in freshwater assessments. Both epibenthic and benthic communities should be assessed. It is even more important to make a distinction between life strategies and feeding strategies. In conclusion, both epi-benthonic and benthonic organisms should be represented in the effect assessment. Since they are characterised by different living and feeding modes they should both be represented in a base set. The Ecotoxicologically Relevant Concentration may differ between epi-benthos and infauna (certainly important in the risk assessment). Another approach could be to distinguish among differences in functional ecology (trait-based approach like differences in feeding mode; filter feeder versus deposit-feeder) rather than on epi-benthonic versus in fauna.

Regarding freshwater and marine assessments, in principle they should be separate owing to likely differences in sensitivity and ecology. Marine and transitional waters (estuarine) assessments are probably not required to be separate but some account should be taken of the salinity tolerance of test organisms; combined marine/estuarine data sets should include studies from both groups or include organisms that live in both estuarine and marine environments. Beyond this, a range of routes of exposure are required (e.g. feeding on sediment particles, sediment ingestion, filter feeding, etc.) and this may mean that organisms from different micro-habitats are required (e.g. on and within the sediment). Due to differences in the sensitivity, bioavailability, and community structure, marine and freshwater species require independent evaluations; however, if evidence exists to indicate that there is no difference in sensitivity/tolerance, combining the data sets may be a consideration, although other factors, such as the ecological relevance of the database for addressing the assessed biological community, should be considered. An EFSA review is available for pesticides³⁰.

³⁰ <http://www.efsa.europa.eu/en/supporting/pub/357e.htm>

Thus, from a scientific perspective the effect assessment should distinguish between different communities. Nevertheless, considering the tests available in the regulatory dossiers (PPP, BP, REACH...), and the validated guidelines, rules for using, pooling or not, refining the available data should be investigated. A guidance document on these rules could be relevant. For organic chemicals with a narcotic mode of action, the species specific distributions available at the moment show no specific differences in sensitivity between marine and freshwater organisms. Therefore, data from the freshwater sediment compartment can be used to assess the marine sediment compartment. For chemicals with other modes of action, specific evaluations are needed. Regarding the relevance of the database for assessing the overall community, in the Risk Assessment for REACH and biocides, when setting the generic AFs a larger factor is proposed for the marine environment because of the overall higher diversity (higher number of taxonomic groups in general, although this is not necessarily the case for specific ecosystems/locations) in the marine environment compared with freshwater environments, although the possibility for demonstrating equivalent sensitivities is also mentioned. In addition, there are issues that may be taken into account in a semi-generic way, for example the reduction of solubility in seawater for non-ionising substances (exposure) or differences in bioavailability between epi-benthic and benthic organisms and physiological adaptations such as osmoregulation (biology).

In conclusion, all relevant communities should be covered but there are several ways for getting this coverage:

- Conducting complementary assessments for different communities.
- Focusing the assessment in the ecologically-driven (habitat, feeding strategy, etc.) exposure differences, if similar sensitivities among the relevant groups can be assumed (e.g. narcotic or other modes of action not leading to particular sensitivities for organisms only represented in a particular community). This can be further developed by exposure corrections (e.g. based on internal dose), but this approach requires setting the scientific basis for these corrections.
- Selecting the most sensitive groups by combining the potential for exposure and sensitivity (e.g. the risk lines approach).
- Applying extrapolations (e.g. freshwater to marine) based on corrections for exposure/bioaccessibility and a second consideration for the relevance of the dataset regarding the overall biological community.
- Considering the services and values derived from the communities. These differ greatly among ecosystems, which have large influence on the societal relevance to sediment contamination. For example, accounting for the different societal significance (e.g. human exposure) of sediment contamination in a shallow estuary that is a nursery for seafood and shellfish versus a deep, fishless oligotrophic lake.

Effects assessment on strictly benthic organisms might be more relevant to exposure scenarios where contaminants sorb to and persist within the sediment compartment. Appropriate species can be selected to assess the worst-case effects of the contaminant (i.e. via a combination of exposure routes – sediment contact, sediment ingestion and pore-water). In comparison, epi-benthic organisms may be exposed to lower concentrations in the pore water, with a greater contribution of exposure from the overlying water. Being more associated with the uppermost sediment layer, epi-benthic organisms are likely to be exposed to sediment with comparatively smaller and less dense particle sizes, where both quantity and quality of the organic carbon component may differ markedly. They may be exposed to, and be feeding on, newly deposited sediments particles, with more potential for exposure to transient sediment contaminants and, perhaps, less exposure to accumulated contaminants forming in the deeper substrate layers. Conversely, however, bioturbation may result in contaminants being released from the deeper bed sediments and becoming more

bioavailable to epi-benthic organisms.

On the issue of relevance, many of the internationally accepted test methods advocate the use of artificial soil or sediment recipes as the solid matrix for benthic effects assessment, on the basis that results will be more standardised if sediment components are well controlled. This approach to standardisation may be at the expense of environmental realism, whereas the introduction of standard (reference sediments) may provide a more realistic alternative for risk assessment purposes. Standardised test methods have little consideration for the impact of sediment aging processes occurring in the environment. Temporal changes in toxicity due to the formation of non-extractable residues (NERs) or their release over time are rarely accounted for in the effect-endpoints generated. Guidance on methods and approaches (when/how) to assess these temporal changes would improve realism in risk assessments for the sediment compartment.

The sediment effects assessment should evaluate the impact on the sediment ecosystem/community structure, not on single benthic or epi-benthic species. Effects assessments should be considered for benthic and epi-benthic organisms for substances with expected high toxicity to sediment organisms, substances with different toxicity in the aquatic versus sediment compartment, or substances with high accumulation potential in sediment.

Both benthic and epi-benthic organisms are important in effect assessment for sediments and thus all benthic (e.g. oligochaetes, polychaetes, some bivalves), and epibenthic species (e.g. amphipods, copepods and numerous meiofauna at the sediment-water interface), including benthic fish, should be considered. They should be the object of protection as they often form the basis of food chains for many aquatic ecosystems. In addition, they alter the structure of the sediment through sediment processing, burrowing and re-suspension. The uniqueness of exposure pathways present at the sediment-water interface, and the physiological, morphological diversity of the species that occur in this habitat should be taken into account. All organisms that are in contact with sediments will be exposed to the contaminants within those sediments from both dissolved (porewater, burrow water, overlying water) and particulate sources (sediments, food sources – algae, detritus).

The degree of exposure from each source contributes to the net exposure, but this is not always characterised by the definitions of what are benthic and epi-benthic organisms. Some benthic species utilise sediments almost solely as their 'home', and the major contaminant exposure route is via the overlying waters. For other benthic species, both the dissolved phase and particulate phase (dietary, while feeding) are significant contaminant exposure routes. The dominance of an exposure route (water or particulate) may change, depending on the organism's behaviour and life stage. There exist both benthic and epi-benthic species that ingest large amounts of sediments (dietary exposure) while feeding, however as pointed out above the materials/particles ingested by different organisms may be very different, leading to very diverse dietary exposures. Epi-benthic algae may also experience a different exposure regime than rooted macrophytes that occupy a deeper sediment layer but are also exposed via the water column. For assessments, it is important to ensure that all the possible exposure routes are assessed, and in terms of the use of bioassays, it is important to use a range of organisms with an adequate range of (characterised) exposure routes. For regulatory assessment, it is interesting to have a list of the different organisms and their relevant uptakes of substance such as water or ingestion of sediment to link this information with the behaviour of the substance in water/sediment systems.

There is a need to address the typical 'variability' in sediment ecotoxicology results. Even for the most robust methods (and same laboratories), variability in single tests can be 20-30%, and is often greater for tests with longer durations. Non-contaminant factors (food availability, sediment type) often contribute to the variability.

Benthic and epi-benthonic organisms are an important ecological element, since they comprise a very high number of species with different ecological roles and they cover all trophic levels, from primary producers to consumers. Living in direct contact with the bottom sediments, they are an important link between detrital deposits and higher trophic levels. Moreover, their presence and assemblage can reflect eventual environmental changes occurring in the ecosystem, integrating the information provided by the chemical characterisation. Due to considerable variation in sensitivity among species, community composition and the distribution and abundance of species are useful measures of ecological integrity. For these reasons, these organisms have been included in many biomonitoring programs and are considered by the WFD as Biological Quality Elements for the assessment and classification of the ecological status. In particular, for what concerns toxic contamination, the WFD aims for the protection of the whole ecosystem, and has introduced a novel approach to assess ecosystem integrity, using results related to the whole-community response. Following this approach, benthic and epi-benthonic communities are being studied in response to gradients of contamination, producing the first effective toxicity indices. A key element for further discussion is how the experience of these integrated approaches may be used in the design and implementation of prospective risk assessments, including those related to generic marketing authorisation (e.g. REACH, biocides and pesticides).

5.1.2 Selection of taxonomic groups and relevant ecological functions

Both ecosystem functions (decomposition, primary production, and nutrient cycling) and structure (covering at a minimum survival, growth and reproduction) should be considered. An integrated functional approach focusing on ecosystem services could be ideal, but measuring functions is not straightforward. In addition, species can be redundant so the local loss of a species or groups of species may be compensated by species performing similar functions. From a testing perspective, microcosm and field studies can be used to assess community function more effectively than single species toxicity tests, which can more effectively evaluate ecosystem structure. Endpoint selection should be driven by protection goals (e.g. population parameters for rare/endemic/commercially important species; community properties (e.g. taxon richness, diversity, trophic indices) for general protection).

Both the macro and meio-benthos in sediment should be considered. Generally, insufficient information is available about potential keystone species in many meio and macro benthic communities to pinpoint these. There is no one species or genus that is most important but testing species from as wide a number of families, orders, classes, phyla as possible is supported. Ideally, testing up to the community level should be performed, but this requires higher tier mesocosm and field studies.

The following groups should be considered as part of a sediment toxicity database:

- Micro organisms (including algae, bacteria) – growth, community composition/ abundance/function (decomposition, primary production, and nutrient cycling).
- Sediment rooting macrophytes (e.g. *Myriophyllum*, *Zostera*), growth/photosynthesis endpoints. Seagrass (*Posidonia oceanica*) meadows; it should be noted that this group is linked to specific habitat conditions and is also exposed via the water column.
- Invertebrates:
 - Sediment ingesters and facultative suspension feeders. Feeding strategies: filter, deposit, detritus, scavengers, burrowing.
 - Benthic: Bivalves, oligochaetes, polychaetes, nematodes. Epibenthic: Amphipods, gastropods, midge

and mayfly larvae, cladocerans.

- Additional species might be added as follows: a) where specific toxicological modes of action are suspected, e.g. mollusc (FW, estuarine or marine species) for endocrine disruptors. b) Echinoderms (only present in the marine compartment) and may not be sufficiently protected using the traditional invertebrates given above.
- Insecta (Ephemeroptera, Plecoptera, Trichoptera), Mollusca, Crustaceans in freshwater lotic ecosystems; Diptera, e.g. Chironomidae, Oligochaeta, Mollusca, Amphipods in freshwater lentic ecosystems
- Slow-moving fish inhabiting bottom waters; larval stages of organisms could also be particularly important since many live on or in the sediment (e.g. some fish and bivalve molluscs).
- Top carnivores.

The endpoints depend on the objective, scope, and limitations of the assessment. In the first step, the most important taxonomic groups, feeding strategies and micro habitats of organisms inhabiting the sediment should be summarised and sensitive endpoints and ecosystem functions be analysed. Then, the assessment should be based on tests performed with representative species. These species should differ in taxonomic group, feeding strategy and micro habitat (e.g. porewater). The test species and the test design should be selected in a pragmatic way taking into account sensitivity, practicability, reproducibility, etc. A pragmatic approach should be applied to perform a sediment assessment on the basis of limited available information. Substance properties and mode of action are also important parameters to consider when selecting appropriate test organisms. In addition to the endpoints measuring the adverse effects directly (e.g. reproduction or growth), the use of early-warning signals may be considered. Biomarkers and in particular genomic-based biomarkers and the new approaches related to the adverse outcome pathways (AOP) are promising tools but the ecological relevance of the observed response must always be considered.

For monitoring programmes, if the objective is to detect an ecological change that is potentially attributable to contaminants, a large number of measures of community composition are available from which to select an endpoint. Depending on the ecosystem and the contaminants in question, certain sub-groups of organisms are likely to be the most sensitive. Thus, the selection of appropriate indicators should be based on a basic conceptual understanding of contaminant transport and fate, and especially of community dynamics. Key to detecting any ecological change is an understanding of baseline, or reference condition, which is the expected natural or pre-disturbance/contaminated condition. This understanding of baseline condition should especially include an estimate of natural variability in the ecological endpoint of interest, as well as the expected variability associated with sampling. Without this basic understanding of baseline conditions, inference is limited to merely variation in observed conditions, which may or may not be within the bounds of natural spatio-temporal variability. Change in an endpoint that is beyond the range of natural variation is likely to have real ecological consequences, and therefore be a meaningful measure of ecological effect due to sediment contamination. Assessments should not be limited to merely detecting ecological change. Even if a significant change in an ecological endpoint can be attributed to sediment contaminants, more thorough assessments are required to truly understand the potential consequences of this change to other components of the ecosystem, including humans. De novo in-depth ecological studies are often not feasible, but additional assessments targeted to key ecosystem components will provide clues about the broader effects of changes in community composition. Included in these follow-up assessments are key measures of processes such as growth, reproduction, population dynamics, and primary production. Process-based measures are usually necessary to understand the broader implications of contaminant-induced changes in community composition.

Within a biomonitoring framework, the most studied aquatic organisms are at present:

1. **Macrobenthic invertebrates:** benthic and epi-benthonic groups, with a very high number of species with different ecological roles. They cover all trophic levels among consumers (grazers, shredders, gatherers, filterers, and predators) and they can be found in all micro-habitat types in lotic and lentic ecosystems. Benthic invertebrates are exposed to contaminants in water, sediment and biofilm, providing a direct pathway to higher trophic levels. Different species are characterised by different resilience and resistance traits, providing a large spectrum of ecological adaptations to cope with environmental stress. Relevant taxonomic groups include Insecta (*Ephemeroptera*, *Plecoptera*, *Trichoptera*), Mollusca, and Crustaceans in freshwater lotic ecosystems; *Crustaceans Gammarus and Diporiea spp*, *Diptera* e.g. *Chironomidae*, *Oligochaeta* and *Mollusca* in freshwater lentic ecosystems. Crustaceans are important indicators in marine waters. Riverine, lacustrine and marine communities are major biological quality elements to be assessed within the EU-WFD for evaluating the ecological status of aquatic systems.
2. **Biofilms:** among epi-benthonic organisms, biofilms are composed by green algae (diatoms and cyanobacteria) forming the autotrophic component and by bacteria, fungi and protozoa composing the heterotrophic part. Due to their omnipresence, their important role in primary production, in nutrient fluxes and trophic cascades as well as their sensitivity to organic and inorganic pollutants, biofilms have been recognised as proper indicators of integrated ecosystem health. Fluvial biofilm communities are one of the major biological quality elements to be assessed within the EU-WFD for evaluating the ecological status of aquatic systems. Multiple endpoints have been developed to assess both structure and function of macrobenthic and biofilm communities. Community abundance and composition are considered within most biomonitoring programs. Moreover, species sensitivity to different environmental stressors is often included as ecological weights of single taxa. Besides, functional endpoints are also considered, including biological (e.g. life cycle, respiration mode, reproduction, body size, etc.) and ecological (e.g. feeding habits, habitat preference, tolerance to stressors, etc.) traits of species. Most of the functional endpoints developed focus on functions directly linked with processes essential for the whole aquatic ecosystem, such as primary production, cycling of nutrients, flow of energy etc. Using a well-defined set of measurements these organisms may allow capturing both acute and chronic effects of a toxicant. The response of functional molecular biomarkers is expected to be quicker than community composition or growth, but the ecological relevance of these responses must be assessed. At site scale, micro-habitats characterised by fine sediment deposition, such as riverine pool habitats, may be preferred to assess the effects caused by toxic contamination of sediments.

A recent development in aquatic ecology is the characterisation of the communities according to their functional composition. The advantage of using functional traits instead of taxonomic composition of communities is bound to the *a priori* predictable response of traits to individual stressors. For example, this approach was adopted to study the effects of toxic contamination on invertebrate communities in running waters. The trait approach has been used as framework for deriving species sensitivity to toxicants. For example, Archambault et al. (2010) developed a multimetric index based on the benthic macroinvertebrate community described in terms of 22 biological and ecological traits, considered as sensitive to sediment toxicity. Community composition at each site was thus described as relative abundance of trait categories. Based on sets of selected trait categories, a statistical procedure was used to allocate sites to toxic quality classes from the attributes of its benthic macroinvertebrate community. Similarly, the SPEAR (SPECies At Risk) index, based on species traits, was shown to be highly sensitive to particular groups of toxicants, such as pesticides. The index is calculated as the proportion between sensitive (SPEAR) and less sensitive (SPENotAR, "SPECies not At Risk") species, on the basis of some traits which were considered sensitive to organic toxicants and on life cycle traits responsible for recovery. The index is applicable across different biogeographical regions in Europe.

For regulatory assessments, the current Guidance recommends different taxonomic groups and feeding

strategies but a logical format, such as the one for pelagic assessment (primary producers, primary consumers and secondary consumers), is missing for sediment assessment. A deeper understanding of keystone species and FW ecosystem structure with read across if possible to other compartments would be a good start. At the moment of drafting this paper Wageningen University is running an Long-Range Initiative project (sponsored by the European Chemical Industry Council CEFIC) with new trophic levels included, such as plants and micro-organisms. Other species that could be considered and are frequently found in the literature are *Gammarus*, *Asellus*, insect larvae and molluscs. These organisms would dramatically increase the diversity and usefulness of current options. Endpoints with too high a variability such as predator-prey interactions might not be useful and preference should be given to reproductive, growth and biomass endpoints already used. The reality is that few test methodologies exist for addressing a broad range of taxonomic groups. Therefore, at this point extrapolations to these groups must be made based on the available data. A tiered pragmatic approach, depending on the mechanism of action is proposed.

There are many experimental tools available depending on the objectives and limitations of the assessment. A review of those relevant for pesticide assessment has been published by EFSA³¹.

Currently, the EPM is the most widely used tool. Quantitative Structure Activity Relationships (QSARs) could also be used but need to have more data to be validated. It is also important to note that data on marine sediment organisms are scarce. Due to this small amount of available data on sediment organisms in dossiers used in regulatory risk assessment, it will be worthwhile to investigate what is the best way to derive a $PNEC_{\text{marine_sediment}}$ via $PNEC_{\text{marine_water}}$ or $PNEC_{\text{freshwater_sediment}}$.

Among the basic and simple tools, standardised sediment toxicity tests can be used as the first tool, supported by additional lines of evidence and higher tier studies when needed. The available tests include a broad number of different species, taxonomic groups with different feeding strategies and exposure routes. Insects and midge larvae, mainly *Chironomus sp* for which different testing methods are available (OECD), and crustacean amphipods such as *Hyalella* (USEPA 2000) and the most common in Europe *Gammarus sp*, oligochaetes (*Lumbriculus variegatus* OECD), and nematodes (*Caenorhabditis elegans* ISO) were already present in the 2003 guidance document. These organisms would provide complementary data that is most suitable in a base set for sediment toxicity. Additional tests include the rooted macrophyte *Myriophyllum aquaticum* (OECD and ISO under development), ostracods (*Heterocypris incongruens* (ISO/DIS)), a sediment contact assay with early life stages of fish is also extensively considered for sediment assessment using different endpoints. Polychaetes, amphipods, molluscs such as bivalves are recognised test species for the estuarine and marine environment. Test methods are available for *Arenicola marina*, *Corophium volutator*, *Leptocheirus plumulosus*, and *Amphiascus tenuramis*, and tests with early life stages of sea urchins or bivalves that would be more representative of the sediment-water interface. Larval mollusc and echinoderm tests are often water only tests, the potential for exposure from suspended matter depends on the experimental conditions. Criteria for establishing the relevance of the test organisms and experimental exposure conditions for sediment RA need to be developed. Marine benthic microalgae have been also used in sediment-contact tests and should be considered. Some tests designed to measure water toxicity may also be useful in assessing sediments (e.g. embryo-larval or fish early life stage tests) if the test organism satisfies relevance criteria, i.e. the sensitive life stage is in contact with sediment-associated contaminants. Regarding standardisation, the development of OECD test guidelines offering a proper coverage of species/organisms and endpoints is a priority.

The comparison of the relevant groups previously discussed with the current availability of standardised tests indicates an obvious need for more validated and standardised single species laboratory test methods. The validation process is essential in all cases, while the standardisation is particularly relevant in the

³¹ <http://www.efsa.europa.eu/en/supporting/pub/337e.htm>

regulatory context. Taking into account that the standardisation of a test method requires a significant investment, there is a clear need to identify the current coverage and gaps, to be followed by a careful selection and prioritisation of key tests requiring further development and standardisation.

Experimental systems with greater environmental realism have been developed for some forms of benthic communities: mesocosms and microcosms; transplants and in situ caged and colonisation studies; or standard benthic community analyses. The greater ecological realism of these approaches is a clear advantage but it is often associated with the specific conditions of the studied community, and this may create difficulties regarding the extrapolation of the results to other ecological conditions. This extrapolation may be solved in a weight of evidence approach leading to a better understanding of the ecotoxicological profile of the substance and the remaining uncertainties; in some cases, there are also limitations regarding the statistical power of these approaches due to the reduced number of replicates. Whole-sediment toxicity tests, whole-sediment bioaccumulation tests, pore-water toxicity tests with field-collected sediments or with contaminants spiked into sediments are also available, but these tools should not be used alone for measurement and prediction, rather in a weight of evidence approach.

Collectively, all experimental tools available for sediment-contaminant assessments have limitations and should therefore not be relied upon alone. The most defensible approach to measure and predict effects in risk assessments includes a combination of carefully designed observational studies and experiments in a WoE approach that are targeted to demonstrate key mechanisms and linkages.

5.1.3 Accounting for inter-species sensitivity in the effect assessment

Inter-species sensitivity can be considered in Species Sensitivity Distributions (SSDs) and can also be considered based on mode-of-action. Inter-species sensitivity is the reason why community-level ecological responses to contaminants are observed. A species' sensitivity to a particular contaminant is influenced by its physiology, behaviour, life history, food preferences, and a host of other traits. Knowledge of these traits, in addition to the chemical properties of the contaminants, is needed to identify appropriate ecological endpoints and predict the ecological consequences of sediment contaminants. It may be possible to take into account inter-species sensitivity to some extent using approaches along the lines of critical body burden. Some of the differences may be due to the relative bioavailability and therefore time to reach equilibrium of the substance in the organisms, which depends on both uptake and metabolism/elimination processes. For metals, homeostatic regulation and storage process may play a role. An alternative approach using biological traits showed that organisms' sensitivity to stress is a function of their biology, and can be predicted from species traits such as morphology, life history, physiology and feeding ecology. This approach showed that four species traits (skin respiration, insect/crustacean, life-cycle duration, gill respiration) explained 71% of the variability in sensitivity to toxicants within a group of 12 species exposed to 15 chemicals. This approach could revolutionise the SSD concept, showing which species within the community are most susceptible to specific toxicants.

For the sediment assessment, interspecies sensitivity is difficult to resolve using standard bioassays because of the limited suite of organisms for which sediment data are available. Field data and mesocosm experiments are more likely to yield information needed for characterisation of interspecies variation. However, mesocosm studies typically have lower statistical power than laboratory toxicity tests; and when several exposure pathways are relevant, the "apparent" inter-species sensitivity may be influenced by the role of each pathway under the specific experimental conditions. Thus, it is important to consider laboratory, mesocosm, and field approaches as complementary tools. When quantitative understanding of interspecies variability in responses to sediment contaminants is not available, the most conservative approach would be to use the most sensitive species in the effects assessment, addressing the additional uncertainty using appropriate assessment factors.

In general, SSD principles can be applied to sediment communities but the complexity of the exposure pathways would require careful screening of data to standardise or otherwise control the influence of bioavailability on any endpoint used to construct an SSD. This approach would be implemented as per aquatic SSDs although targeting species that are applicable to the sediment risk assessment. With regard to the minimum species requirements in order to apply the SSD concept, some recommendations can be formulated for the aquatic compartment only (covering at least eight taxonomic groups, containing at least 10 NOECs and preferably more than 15 for different species, etc.). It can be even questioned if the same criteria developed for the aquatic compartment should be imposed on the sediment compartment. Applying the same criteria would ignore: 1) the expected differences in species richness between sediment and water ecosystems, 2) the different exposure conditions and feeding behaviour of the organisms in the sediment (ingestion of sediment, body wall contact, exposure through pore water and overlying water). In addition, very few standardised toxicity test methods exist for benthic species, creating additional difficulties. Extrapolating the aquatic guidance to sediments may therefore not be appropriate. The focus in establishing an SSD for sediment should instead be based on obtaining a reasonable cross section of the feeding behaviour of all benthic species. The use of fewer species than for the aquatic compartment (but representing different living and feeding conditions) can be covered by the complementary use of other lines of evidence (e.g. mesocosms).

Minimum requirements would depend on the end use of the data (i.e. allowing a substance to be used versus clean up criteria). A broad range of taxa (different trophic groups, physiologies, feeding mechanisms, reproductive strategies) including plants, animals and microbial composition/function is needed. However, in practice for most chemicals the data is lacking, which makes the approach not feasible. Using an SSD to calculate an HC5 would require at a minimum ~10 species, otherwise such an approach would often be extrapolating a value beyond the range of the data. It is implicit to the HC5 concept that if the number of species is sufficient for ensuring intrapolation instead of extrapolation, the HC5 should be expected to be higher than the lowest NOEC or EC10; nevertheless, this issue has created some discussions in the regulatory context. For most chemicals, there is not enough data to employ the SSD approach. Whenever you are estimating extreme values within the tails of a distribution like an HC5 you are only likely to get an accurate estimate if you have a lot of data. Additional generic issues associated to the SSD include pooling of data (within species, duration of test, endpoint, etc.), developing SSDs covering all species in a compartment or SSDs using only similar types of organisms, goodness of fit, choice of fit functions, confidence limits, among others. The SSD approach is also only protective for the community if the species within the SSD are representative of the community. With the limited suite of organisms for which data exists for a given chemical it is unlikely that those organisms are a good representation of the community which is the protection target. Despite these limitations, the capacity of SSD approaches, when properly applied, for refining the effect assessment has also been recognised for other compartments in the regulatory context. Thus, it should be important to consider which specific adaptations and developments are needed for setting guidance on its applicability in sediment risk assessment.

As a first step, emphasis is needed on choosing relevant species for inclusion in the SSD. A more conscious choice of test organisms is needed to represent the actual risk to benthic communities. Elements to be considered include aspects such as exposure potential (e.g. related to choice of habitat or feeding strategy), biotransformation capability (for organic compounds; inefficient biotransformers are generally more susceptible to chemical exposure), ecological importance (i.e. species that are crucial for certain ecosystem functions) and/or the expected mode-of-action of the chemical in question (if this is known) in cases where the chemical has a mode-of-action that targets particular taxonomical groups. These elements should be addressed when presenting the SSD outcomes, and the development of generic guidance would be very useful in the regulatory context.

Even more important are the metrics for constructing the SSD. As stated above, different organisms are exposed by different routes (and combinations of routes) and the distribution of the chemical among the

different sub-compartments may be highly influenced by the experimental conditions. If not corrected for bioaccessibility/bioavailability, the SSD may reflect artificial distributions linked to conditions of each test, and even when corrected for bioaccessibility, the metrics used for the correction will affect the sensitivity of each species within the SSD. Therefore, there is a need to either construct separate SSDs for sediments with different properties (low versus high AVS, DOC, sand-silt) or construct SSDs using effect thresholds that account for variability in sediment properties. A possible approach is:

1. First make SSDs for a standard situation relating to relevant bioavailability parameters, then conduct tests to quantify bioavailability normalisation functions on all relevant types of species. 2) Make spot tests on species not used for building the normalisation approach.
2. Apply the normalisation approach on all species and thereby transform the SSD towards different but relevant abiotic factors determining the bioavailabilities toward the different species.
3. Take account of uncertainty for bioavailability read across (from species with known bioavailability dependence to those only spot checked).

5.1.4 Minimum requirements and use of information from non-sediment dwelling organisms

The minimum requirements should (as noted above) cover a specified range of ecologies/ feeding strategies and taxonomic groups. The PNEC should be based on long-term data as any exposure of the sediment compartment is a long-term exposure.

In some current regulatory systems (e.g. REACH and biocides), a PNEC screening can be derived without using a single sediment toxicity data through the EPM, and a PNEC based on assessment factors can be derived from just one long-term test. The higher tier methods can be a mesocosm study or field-based considering that the most sensitive species is tested, and the analytical measurements are available.

Equilibrium partitioning theory (EqP) is often applied to predict sediment organism toxicity from pelagic organism data using the theory that exposures via water or dietary pathways are in equilibrium with freely dissolved pore water concentrations. Equilibrium partitioning between pore-water and sediment is often modelled using properties that predict binding potential, e.g. $\log K_{ow}/K_{oc}$, to predict binding of non-polar organics to the organic carbon in sediment. The sorption behaviour for some substances is less predictable though (e.g. ionisable compounds). The method also assumes that the sensitivity of sediment-dwelling species is not significantly different to that of pelagic species as long as they are physiologically and ecologically similar.

The assumptions have not been validated for a broad range of sediment-contaminants or for organisms at different trophic levels or with different feeding types. Uptake via ingestion of sediment particles may become more important for highly adsorbing chemicals and to account for these uncertainties, compounds with $\log K_{ow} > 5$ or correspondingly high adsorption/ binding behaviour in the case of metals and binding mechanisms not related to lipophilicity, require specific considerations for uptake via ingestion. Even for lipophilic compounds with very high $\log K_{ow}$, binding, bioavailability and bio-accessibility may vary widely according to the actual K_{ow} value and other properties. The organism feeding behaviour should also be considered, at least between total sediment ingestion and more selective feeding approaches. In laboratory tests with artificial sediment, the partitioning process may be different than that expected for natural sediments, and this issue should also be considered.

The currently applied EPM approach under REACH and biocides was developed over a decade ago taking

into account the very limited availability of data. The regulatory experience on the EPM suggests that a re-thinking is needed. Basically, for generic prospective risk assessments, the use of EPM in the chemical safety assessment produces the same RCR (risk characterisation ratios) for water and sediment for substances with $K_{ow} > 5$, while for higher K_{ow} values, the difference is just related to a pragmatic generic decision assumed to be conservative. An additional issue frequently observed for substances with very low water solubility is that a PNEC aquatic cannot be derived, or that the information suggests that aquatic exposure is of very low relevance. Those are typical cases for substances particularly relevant for a sediment assessment, and the application of the EPM, even with an additional assessment factor, is highly questionable when exposure via water is assumed to be of low relevance.

A weight of evidence approach is needed to determine the minimum data requirements. An SSD with a lower number of species but with corroborating field data has less uncertainty than an SSD alone, the uncertainty reduction depends on the relevance, comprehensiveness, power and type of field data. At a minimum, an effects assessment should consider multiple taxonomic/functional groups and ecological niches for determining the appropriate method for PNEC derivation.

Specific approaches are required for metals. The equivalent approach to organic substances is the derivation of a screening PNEC using pelagic ecotoxicity data combined with K_d values. However, in the Ni case study sediment toxicity test organisms were tested in both water-only exposures and in sediment exposures. Using sediment-specific K_d s, water-only toxicity data were used to estimate sediment toxicity. These estimates were both higher and lower than the toxicity measured in sediment exposures. This places great uncertainty on the use of pelagic data in combination with K_d values for estimating toxicity via sediment exposure. A weight of evidence approach combining data from sediment, pelagic and soil organisms has been suggested based on:

1. Evaluation of the benthic sediment ecotoxicity data, recognising the importance of organic carbon and the Acid Volatile Sulphide (AVS) pool to control the chronic toxicity of Me^{2+} towards sediment-dwelling organisms. The derivation of the freshwater HC5-50sediment (benthic SSD) can be based on the organic carbon normalised dataset, using only low AVS sediments (e.g. the retained database includes six species-specific data points representing 62 NOEC values at various sediment chemistry (OC)).
2. Using the EqP approach, HC5-50sediment (EP) values can be derived for a range of EU scenarios, representative for the physico-chemical characteristics of EU surface waters (e.g. the EU scenario's defined in the aquatic effects section using the aquatic BLM). The scenario-specific HC5-50sediment (EP) values can be calculated from the scenario-specific aquatic HC5-50 values and the application of respectively, the EU median K_d suspended solids, the EU median K_d sediment and the scenario-specific K_d values as calculated from WHAM VI (K_d WHAM).
3. Considering sediments as "wet soils" allows for a comparison between the HC5-50 values, derived from sediment NOECs with OC normalisation and the HC5-50 values derived from soil NOEC data and soil bioavailability models (pH, OC and CEC normalisations).

However, the applicability of this approach has not been checked. Some conceptual limitations to this approach are mentioned below:

- The anaerobic sediment conditions (AVS binding) are not yet considered in the above approach.
- Soil SSDs are often dominated by ecological processes with little relevance to aquatic/sediment communities and these factors are not covered by bioavailability corrections.
- Bioavailability relationships for metals in soil are governed by CEC and pH, whereas for sediments these involve sulphides, organic carbon, and Fe/Mn oxides.

If sediment RA is to be carried out in a tiered approach, the lower tier could be addressed with individual

level toxicity testing as is the case for current RA procedures, taking into account issues outlined above. Additional tiers may cover field and microcosm studies which address semi-realistic community structures and/or the new approach for population effect models. It should be noted however, that at each tier, the statistical power of the test to predict individual effects is reduced.

The extrapolation to population level effects using mechanistic effect models is receiving significant attention. These types of models have in recent years become increasingly recognised in the scientific community for their potential in predicting the risk of chemicals at the population level. Several new models with different degrees of complexity have been developed during the last few years, and guidelines for good modelling practice are now available. So far the models are not in routine use, but certain regulatory authorities seem to be slowly opening up for the possibility of including them as one out of several different tools for RA of plant protection products (PPPs). As the models cover all environmental compartments a generic discussion on this approach is out of the scope of this workshop; however, it should be noted that some currently available models address sediment organisms.

In principle, information for terrestrial organisms might be used for screening in a similar way but this approach has been validated to an even smaller extent. Reasonable correlation has been found between freshwater and sediment effects while the correlation with soil was not so clear. In a recent assessment, a volatile substance resulted to be totally absent in the soil compartment while it was retained in the sediment compartment due to its poor water solubility. Thus, it is not necessarily simply to read across between soil and sediment assessments due to differences in fate and physical properties. Nevertheless, an option to be considered is the use of this information in WoE for supporting the development of the testing strategy, e.g. high toxicity on soil microbial functions could trigger the need for testing microbial sediment functions, while indications that soil invertebrates are much more sensitive than terrestrial plants and soil microbial functions would trigger a testing strategy focusing on sediment invertebrates.

5.1.5 Addressing bioavailability and uncertainty in sediment effect assessment.

Bioavailability data can reduce uncertainty by providing more relevant info on exposure concentrations. This leads to a more realistic exposure assessment compared to the conservative assumptions derived from bulk sediment chemistry alone. Bioavailability is determined by the chemical/physical properties of the compound and the environment-which would presumably be evaluated in the exposure assessment. In addition, bioavailability is a function of many biological/ecological conditions such as life stage and feeding habits, which should be evaluated in the effects assessment. Thus, bioavailability needs to be considered for both exposure and effects assessment, as does bioaccessibility.

For the effects assessment, the biological responses associated with tolerance/detoxification and the relative costs of any tolerance (acclimation and adaptation) must also be considered. Wherever possible, it is preferable to include consideration of bioavailability for each receptor in the effects assessment. Bioavailability would best be dealt with on a local scale with site- specific measurements. Acknowledging that this type of information is not always at hand, a more generic bioavailability correction using realistic worst-case conditions could be used as a first tier. It is likely that a generic or at best semi-generic assessment is all that will be possible at this time. As mentioned in section 5.1.1, the bioavailability of a substance between marine and FW compartments can change due to salting out. Such information could be included in a semi-generic assessment.

It may be possible to get a rudimentary understanding of the difference between bioavailability of a substance to epi-benthic organisms in a lotic and a lentic system or between benthic and epi-benthic organisms to help obtain a series of risk assessments without multiplying the number of studies. As mentioned earlier, deposit-feeding organisms have developed mechanisms, which make them efficient

in extracting chemicals out of the sediment. Therefore, some sediment bound chemicals may be more bioavailable to deposit-feeders as a group compared to benthic organisms with other feeding strategies and to an even higher degree when compared to pelagic organisms. Subsequent tiers can be evaluated by increasing levels of bioavailability normalisation. Substances known to have complex interactions, such as biotic ligand interactions, should be evaluated on an individual basis.

Since bioavailability of sediment-associated contaminants are quantitatively and qualitatively different for different feeding groups, it is necessary to apply different dosimetry for feeding groups. The use of freely dissolved concentrations clearly applies to the exposure assessment (PEC derivation) process, but is also vital for effects assessment. The uncertainty in long term chronic testing derived from, for instance, sediment aging processes or biodegradation is an important factor that should be considered in toxicity testing. The use of passive sampling methodologies to determine equilibrium concentrations in the sediment and true exposure concentrations during the test is key, and will lead to reduced uncertainty in sediment toxicity testing.

There is significant measurement uncertainty in many ecological endpoints, and steps should be taken to quantify this uncertainty during the data collection phase and propagate this uncertainty through the analysis phase. Assessments of ecological effect based on departure of some observed condition from an expected reference condition should express the natural temporal and spatial variability of that reference condition, and incorporate that variability in the assessment itself. Other assessment approaches can use bootstrapping or Monte Carlo simulations to generate distributions of parameter estimates or confidence intervals on predictions. Developing guidance for incorporating results of field-based data is of particularly high importance, given the debate over the use of such data in recent discussions of substances under the Water Framework Directive.

In addition to general tools accounting for uncertainty in any effect assessment, specific elements should be considered for sediments. Qualitative methods to address the uncertainty of sediment effects assessment would be to make some assessment (or critique) of the quality/relevance of tests selected to derive the PNEC, for example, by answering the following questions:

- Was the species selection and test design likely to have assessed exposure to the sediment contaminant by all the major pathways?
- For each species used, was the sediment appropriate for the organism e.g particle size distribution, organic carbon quality/quantity?
- Was the food incorporated into the sediment or untreated and could this have influenced the endpoint substantially?
- Was the sediment spiking method suitable and were interfering effects of any solvent (carrier) apparent/likely?
- What is known about species sensitivity for the contaminant or class of contaminants in question?
- Is there a mode of action that has not been properly addressed by the species and endpoints selected?
- Are other species likely to be more sensitive or at greater risk of exposure in the receiving environment, for example, if bioturbation might influence bioavailability to epi-benthic and pelagic organisms?
- Are there factors related to the binding mechanism for the chemical that may suggest different species, inhabiting different sediment types (different particle size, mineral component, organic carbon types)

may be at greater risk?

5.2 ELEMENTS FOR DISCUSSION

The following questions were used to initiate the working group discussions:

- Should the sediment compartment effect assessment distinguish between the epi-benthonic/benthonic, lotic/lentic, marine/estuarine/freshwater communities?
- What is the relevance of the effect assessment for benthic and epi-benthonic organisms?
- Which benthic and epi-benthonic taxonomic groups, feeding strategies, micro habitats, endpoints and ecosystem functions should be considered?
- Which experimental tools are available for measuring and predicting the effects on benthic and epi-benthonic organisms?
- How should inter-species sensitivity be considered?
- Are the principles for Species Sensitivity Distribution approaches applicable to sediment communities? How can this approach be implemented in practice? Please mention applicability, minimum requirements and limitations.
- What should be the minimum data requirements for establishing a Predicted No Effect Concentration? Which lower and higher tier methods can be used?
- How can ecotoxicological information on pelagic and terrestrial organisms be used for screening and assessment purposes on sediment organisms?
- Is a generic assessment of bioavailability under the exposure assessment sufficient or should bioavailability be part of the effect assessment and discussed independently for each ecological receptor?
- Which ways are available for investigating and expressing the uncertainty of the effect assessment?

5.3 OUTCOME OF THE WORKING GROUP DISCUSSIONS

The following sections reflect the discussions from the working groups. Whenever there were different views in the working groups, these are reported.

5.3.1 Toxicity data selection

Toxicity data selection and compilation should not solely represent an array of taxonomic groups but should also aim for a balanced and realistic representation of functional attributes, including – but not limited to – functional traits. A number of criteria should be fulfilled when selecting and compiling toxicity data in order to result in a realistic and relevant risk assessment for the sediment compartment. More precisely, regarding invertebrates different exposure conditions and feeding strategies should be represented by a variety of life strategies:

1. Surface deposit and/or filter feeders;
2. Sub-surface feeders;
3. Burrowing species with a combined surface and subsurface feeding behavior.

These different exposure routes and feeding behaviours imply differences in sediment ingestion rates, in the degree of contact with the sediment, and in the exposure through porewater and overlying water. Additionally, the relevance and role of non-invertebrate taxonomic groups and their functions should be considered.

Apart from considerations such as life strategy and different sediment types affecting sediment communities, more practical restraints should be taken into account. Selected data should include species 1) with a good taxonomic identification, 2) that are culturable, 3) that are generally sensitive (also in consideration of the chemical's mode-of-action), 4) that maintain genetic diversity when cultured, and 5) smaller species should not be overlooked as they may be particularly sensitive.

One important limitation to establishing a set of toxicity data that represent various life strategies is the scarcity of standardised sediment toxicity test methods to assess the sensitivity of benthic species. In view of this constraint, data generated through non-standard tests can be considered but need to produce new insights into how traits connect to exposure routes and physiology and thus to toxicity. In addition, it is recommended that the validation (including ring-tests where possible) of relevant non-standard species tests be conducted. In general, data reliability and relevance should be screened on a case-by-case basis for non-standard and standard test species.

When facing data scarcity, relative "similarity" in the toxic response between different communities can be assumed when the mode of toxic action is non specific (e.g. narcotic). If relevant information is available, field data can be used to identify similarities between toxic responses.

Candidates amenable to toxicity testing include, amongst others, rooted plants, aquatic insects, meiobenthos, and microbial organisms or communities. The latter are especially crucial elements of benthic ecosystems because they are at the base of the local food webs. However, no hazard profiles are currently available for these organisms or communities, and these are necessary to decide on whether or not to incorporate such endpoints in routine test strategies. Whether or not to include fish species, and which species to include, will depend on the life style of its different life stages, and on ethical constraints.

Currently, the most sensitive endpoint measured is used in regulatory effect and risk assessment. The endpoints typically measured relate to survival, growth, development and/or reproduction and these endpoints are hence normally regarded as environmentally relevant. It may be envisioned, however, that in future one endpoint per species could be selected that best represents the contribution of this species to essential functions in benthic ecosystems. To this end, it is crucial that future research efforts are targeted at identifying which functions are essential for sediment ecosystems and communities.

Scarcity of sediment toxicity data may be addressed as a first tier by using equilibrium partitioning and pelagic toxicity data. However, equilibrium partitioning should be used only with care. There are boundaries within which equilibrium might be applicable as a first tier:

- Narcotically acting chemicals; although for some chemicals with specific toxicity (beyond narcosis) equilibrium partitioning might also be applied if this specific toxicity is covered by the pelagic dataset.
- Substances with a $\log K_{ow} < 5$

As a first tier, no biodegradation is assumed. However, it should be noted that substances with a (very) high $\log K_{ow}$ – with a (very) low bioavailability – might break down into compounds that are of higher concern than the parent compound. Further, the contribution of the dietary route to toxicity is not fully understood. Such factors increase the uncertainty associated with using screening approaches such as equilibrium partitioning. Therefore, for some chemical groups, this approach is not suitable (e.g. high MW-chlorinated paraffins, polymers, micelle forming chemicals, compounds that are ionised at environmental pH levels). At higher risk assessment tiers, equilibrium partitioning is generally not applicable, but if it is used, it should be accompanied by uncertainty analyses and/or probabilistic modelling. For metals in particular, speciation models need to be run, if equilibrium partitioning is used beyond lower tier explorations.

5.3.2 Bioavailability normalisation

By ‘normalisation,’ we mean the conversion of a toxicity data point from a given water and sediment chemistry to a local water and sediment chemistry, e.g. using bioavailability models. Such normalisations can be recommended whenever possible. Potentially, there is a need for standardised reference matrices – with a known chemistry – for testing. Thus, the parameters that influence the bioavailability of the considered test substance need to be standardised in toxicity testing. (Bio)availability correction is recommended if feasible, for all types of chemicals.

A tiered (bio)availability correction can be proposed. At a lower tier, the available worst-case sediment composition (mainly AVS, SEM, hardness, pH and DOC for metals, polar and ionic substances; CEC, DOC, pH, salinity, particle size, clay content for organic apolar chemicals) should be combined with chemical properties (sediment or suspended solids – water partitioning coefficient, K_d , or organic carbon – water partitioning coefficient, K_{oc} , for metals; octanol – water partitioning coefficient, K_{ow} , or K_{oc} for organic chemicals) to predict bioavailability. For metals, specific tiered bioavailability normalisation approaches exist. In lower tier scenarios, total concentrations of the metal are measured. In a higher tier, physico-chemical speciation and availability is taken into account, e.g. by estimating the amount of metal bound to organic carbon, Fe/Mn oxy hydroxides, and/or sulphides. Binding to sulphides is estimated using the SEM-AVS concept, where SEM stands for simultaneously extractable metals and AVS for acid volatile sulphides. In the SEM-AVS concept, the activity of most divalent metals (Zn, Ni, Cu, Pb, Cd...) in sediments is controlled by the amount of AVS present in the sediment matrix. Only non-bound metals are potentially bioavailable.

Laboratory-based taxon-specific BCFs and BAFs are candidates to refine bioavailability estimations for organic chemicals. If needed, experimental efforts to assess bioavailability should start by straightforward and short-term testing approaches. In that respect, setting up water-only experiments may be a first approach to screening the bioavailability of the substances at various physicochemical water characteristics.

5.3.3 Derivation of effect thresholds

Specific recommendations on the derivation of effect thresholds are:

1. When a PNEC aquatic cannot be derived (because of low solubility or lack of (acute) effects), this does not imply there is no need for threshold derivation (and thus a sediment risk assessment). For poorly soluble substances or substances with low toxicity, it may not be possible to derive a PNEC for pelagic organisms. These substances may, however, accumulate in sediments. Such accumulation may justify performing a sediment risk assessment on these substances.
2. Regarding minimum requirements, the (EPM was seen as a useful tool at the screening level. For organic chemicals, the extra AF of 10 applied on top of the risk characterisation ratio in order to cover the

dietary route as is done in some regulation was questioned by some but may be a pragmatic approach in a regulatory context for others and some participants felt that a $\log K_{ow}$ based magnification correction of the AF would be a better approach. Pelagic studies could also inform about the importance of dietary uptake.

3. In principle, for organic chemicals, a $\log K_{ow} > 5$ should trigger some additional sediment tests (for example, long-term and/or bioaccumulation studies in sediment organisms where all exposure routes are considered). Similarly, $\log K_{oc}$ or $\log K_d$ based triggers can also be used.

In theory, SSD modelling can be considered applicable to obtain effect thresholds for the sediment risk assessment process, although the practical applicability of this technique should be carefully evaluated on a case-by-case basis. No general guidelines can be followed to judge whether a chemical is amenable to SSD modelling or not, except that the number of data points has to be considerably above three to avoid curve-fitting issues. For cases where SSDs are judged applicable, the following recommendations on the actual use of the SSD approach for the benthic compartments can be made:

1. The more (ecologically distinct) taxa – representatives of different feeding strategies and micro-habitas and life forms – that are contained in the SSD, the lower the AF should be that is used to obtain a PNEC from the HC5. The underlying motivation for this recommendation is that adding more information to the SSD automatically reduces uncertainty.
2. Often, no separate SSDs can be constructed for infauna and epifauna because of general data scarcity for the benthic compartment. Generating more information seems to be the only scientifically sound solution currently as pooling the data is not considered to be appropriate.

5.3.4 Exposure routes

A thorough understanding – and quantification – of the different routes of exposure is vital to a realistic effect assessment of benthic communities. More research quantifying the importance of the different exposure routes is needed for species for which such information is lacking. However, it should be noted that measuring chemical uptake through water might be hampered by the difficulty of measuring pore water concentrations for some chemicals. Related to this issue, attention should be paid to developing standardised testing protocols for quantifying the contributions of the different exposure routes to overall toxicity. It should be noted that effect assessment and exposure assessment are tightly linked. At present, no experimental approach exists that integrates both aspects of risk assessment. Therefore, it can be noted that future research efforts could address this shortcoming by developing such integrative approaches.

5.3.5 Biological entities

Trait-based approaches are increasingly becoming a useful tool for species selection and more research is needed to understand how traits translate to effects on benthic species. The functional importance of a species needs to be further emphasised.

Biological agents that are crucial to the functioning of benthic ecosystems include rooted and non-rooted primary producers, microbial communities, oligochaetes and insects with aquatic (sediment-dwelling) life stages. Rooted primary producers are important candidates as focal species in future research efforts because of their direct contact with the sediment, potentially acting as a contaminant sink. Non-rooted primary producers such as periphyton are crucial because of their basal position in the food web. Microbial communities are responsible for many ecosystem functions, or at least significantly contribute to them.

Nitrification, denitrification, nutrient cycling, and detritus decomposition are examples of such functions. However, toxicity testing with such communities poses a number of scientific challenges that need to be resolved by future research.

Finally, methods for assessing biodiversity and community composition, i.e. higher-level endpoints of benthic ecosystems, require further development. Here, the response to contamination is generally unknown and, consequently, unpredictable, especially in prospective risk assessment. A relationship between ecosystem services and protection goals, including aesthetic values, is desirable.

5.3.6 New approaches

The feasibility and potential scientific value of new approaches or crucial additions to existing approaches need further evaluation:

1. Measuring pore water concentrations during any test design would increase the information content of the resulting toxicity value. However, it should also be acknowledged that for some chemicals, this can be challenging and both the costs and benefits should therefore be duly considered.
2. Gene expression studies and metabolomics, in general 'systems ecotoxicology', are examples of promising new approaches that have the potential to considerably advance effect assessment science. An element that may promote the success of such approaches is the translation of the resulting (sub-) individual effects to higher-level effects that relate to ecological risk assessment protection goals (e.g. at population level). Establishing the link between (sub-) individual effects and higher-level effects needs more research effort.
3. The use of standardised ('artificial') sediments is useful for quality control purposes, i.e. to compare toxicity data across laboratories or to evaluate the quality of toxicity testing. However, artificial sediments can considerably differ from natural sediments and are, therefore, less preferable to replace actual testing with 'real sediments' that are kept as intact and appropriately characterised as possible.
4. Exploring the use of mechanistic effect models for the effects assessment of the sediment compartment would be useful. At the moment, population and community models are being increasingly used and developed, especially related to pesticide applications for pelagic communities. Guidelines for modelling and model validation, good modelling practice similar to GLP guidelines, are available. The success of these models demonstrates that similar efforts would be useful for sediment communities as well.
5. Developing spiking and evaluation methods for contaminants that do not have typical $\log K_{ow}$ partitioning behavior would be useful. Evaluation methods should be sensitive enough to also detect effects from contaminants with specific modes of action. In addition, testing methods should encompass higher levels of biological organisation such as the population and community level.
6. Development of *in silico* models, such as QSAR-based computational approaches, for specific modes of action of chemicals for sediment organisms may be an additional new avenue to explore.

5.4 RECOMMENDATIONS

5.4.1 For regulation

- Effect assessments should be based on toxicity data compilations representing a balanced and realistic representation of species traits regarded as important for the benthic community in question, not of taxonomy *per se*.
- Rooted plants, microbial processes, meiofauna, and aquatic insects should also be included in effect assessments for the sediment compartment.
- For certain chemicals, toxicity data scarcity can be addressed by combining pelagic toxicity data with equilibrium partitioning models.
- Contaminant bioavailability should be assessed and included where possible.
- SSD modelling is in principle applicable to sediment effect assessments (as a higher tier option). If SSD modelling is applied, ecologically distinct species should be included.
- For organic chemicals, a $\log K_{ow} > 5$ can be used as a trigger for bioaccumulation testing on sediment organisms, not just the use of additional safety factors.

5.4.2 For scientific research

- The contribution to effects of the different routes of exposure needs to be assessed, e.g. by including methods for spiking food in toxicity tests and methods to spike high $\log K_{ow}$ compounds into sediments. Standardised testing protocols need to be developed to facilitate such assessments. The dietary contribution compared to other exposure sources requires specific attention.
- The strong relationship between exposure and effects in sediment risk assessment indicates that it could be valuable to develop integrative experimental approaches.
- The contribution of species to ecosystem functions needs to be better understood, possibly using the functional trait concept.
- Apart from traditionally used test organisms (crustaceans, oligochaetes, molluscs...), test data on rooted plants, periphyton microbial processes, and aquatic insects are recommendable. By preference, all data should be obtained using standardised tests/protocols. Attention should be paid that tested organisms are feeding on sediments and not exclusively on mainly “clean food”.
- Especially in retrospective assessments where a specific sediment system is investigated, the sensitivity of higher-level endpoints such as biodiversity and community composition need to be assessed.
- Establishing the link between (sub-) individual effects and higher-level effects needs more research effort.
- Mechanistic effect models for the sediment compartment need to be further developed and their potential to predict effects on the population and/or the community level needs to be explored.
- Due to the differences in species’ vulnerability and the functional redundancy of ecosystems, there is a need to better integrate recovery potential into risk assessment, both in retrospective ERA and in higher tier prospective ERA.

- Standardisation for the dietary exposure route needs attention and development.

6. Main outcomes

A significant progress in the scientific understanding of the impact of chemicals on the sediment community has been achieved during the last decade, due to a combination of both scientific and regulatory actions. This progress should allow a better definition of the risk assessment problem and the development of improved conceptual models for prospective and retrospective risk assessments. Nevertheless, some gaps and limitations have been identified and specific recommendations for each of the three main topics addressed during the workshop have been included in the previous sections.

Based on the combination of the break-out and plenary discussions a set of issues of generic interest have been compiled and are presented below.

Basic elements and conceptual model

- A clear presentation of the conceptual model is highly desirable. It should consider the traits, functions, services and their indicators for protection. Specific components of the Conceptual Model to be included are the sources, transport, exposure and key receptors/effects. Generic models should also include a list of desirable traits to be protected. An adequate “suite” covering the “population diversity” that describes the structural and functional integrity of the sediments, including relevant communities that live within the gradient from the Pelagic-Epibenthic-Benthic community, needs to be included.
- As all relevant sediment exposure routes should be considered in a sediment assessment, specific attention to the coverage of the different types of exposure pathways needs to be given (dissolved, contact and feeding). The main difference between the pelagic and the sediment compartment is the higher potential for oral uptake as well as mixed exposures in the sediment compartment. Both “aquatic ventilation” and “sediment ingestion” may contribute to the “body load” of a contaminant with potential different uptake kinetics for each. Under some circumstances, for instance for high K_{ow} nonionic organic contaminants, the EqP approach may not sufficiently consider dietary exposures.
- Sediment assessment should be triggered by a combination of specific factors instead of a single trigger. Triggering should include elements such as exposure routes not covered by the pelagic assessment, interstitial water concentrations, bioavailability (including sediment ingestion), partitioning and persistence.
- It should be noted that some organisms (receptors) in both the sediment and pelagic environments are exposed to contaminants from several or even all exposure pathways (overlying water, pore water, sediment contact and diet) receiving an aggregated exposure to the same chemical from different routes.
- The selection of the relevant receptors should consider taxonomic groups and their ecology together with habitat, distribution, feeding strategy and physiology as well as how the organism may influence their microhabitat impacting uptake and bioavailability of chemicals. There is a need for higher species/ taxa diversity in testing (plants, fish, biofilm, periphyton). Some relevant microbial functions should also be considered.

Freshwater versus marine assessment

- There are different views regarding the extrapolation of freshwater ecotoxicity data for covering marine

organisms (and the opposite). Some experts considered that this is simply not scientifically acceptable, while others accepted this extrapolation providing that differences between the two environments are addressed. For example the following should be considered: the role of phyla that are not represented in freshwater (or marine) environments; the differences in water composition affecting the chemical solubility, speciation, (bio)availability and so on, and any other relevant differences. Limited science on transitional waters is available therefore science based risk assessment is not currently possible for these waters.

Equilibrium conditions and equilibrium partitioning approaches

- Equilibrium conditions in generic local and regional assessment can be used as a starting point. However, these should be improved through the use of probabilistic approaches of exposure and effects (and when relevant consider also other processes such as resuspension).
- One or more relevant K_d -values (overlying water – sediment) are needed for using EqP as a first tier. Transparency is important in the derivation of K_d values at any level. It is also important to make sure that there is equilibrium and that the relevant sorption processes are properly characterised (examples: PFOS – ionised/ ionisable compounds), other surfaces, such as clay minerals, should also be considered. For generic assessments, it is recommended to either make a sensitivity analysis on the impact of the K_d on the EqP or to employ a range of relevant K_d s for the substance. A measured K_{OC} or estimated K_{OC} based on a free-energy relationship with K_{OW} can in some cases be used in place of K_d , but it must be very clear how the K_{OC} was derived.
- There are specific chemical groups for which the EqP is not appropriate, for example, high MW-chlorinated paraffins, polymers, micelle forming chemicals. There are also other generic boundaries when the EqP should not be used (e.g. lack of pelagic toxicity info, (potential) metabolites should be individually assessed as they are not covered by EqP applied to the parent substance).
- At higher tiers, EPM is generally not applicable, but if it is used, it should be accompanied with greater clarity by, for example, uncertainty analysis, speciation and/or probabilistic modelling.
- Kinetic processes should be considered at higher tiers. Experimental K_d -values instead of generic ones, site-specific information like sorption characteristics, and considerations of degradability also need to be considered.

Risk characterisation and impact assessment

- Water and sediment compartments are interrelated and hence they should be evaluated together. The sediment should be considered as a part of the aquatic system as it provides structure/habitat for organisms. However, from a pragmatic point of view, risk characterisation for prospective risk assessments should be performed separately in order to facilitate the decision making process.
- Even for screening purposes, a more integrated assessment than the current approach, covering the diet exposure of benthic invertebrates and other taxonomic groups, is needed.
- Test guidelines should be adopted to include the variability of taxonomic group, lifestyle, dietary route (including spiking of food when relevant) and feeding behaviour in an ecosystem. Further tests need to be developed to cover a wide range of traits and functions. The need for sediment microbial inhibition standard guidelines/testing protocols should be considered.
- In prospective risk assessment it is difficult to include issues relevant for the impact assessment (such as biodiversity, species richness, endemism, etc.) due to the variety of systems that need to be covered. This may be easier in retrospect where a specific system is being investigated. A relationship between

ecosystem services and protection goals, including aesthetic values, is desirable. Under some conditions, the assessments may require special considerations in addition to the standard risk paradigm; for example, in some circumstances the bioaccumulation assessment (in addition to PBT assessment, secondary poisoning assessment etc.) may require additional BCF/BMF sediment organism testing (*Lumbriculus*). Additional research is necessary for selecting triggers and conditions.

Uncertainty assessment

- Uncertainty in the weight of evidence should include lack of knowledge, general biological variability and measured variability.
- The options for supplementary or alternative analysis should be evaluated. These include methods currently developed for pesticides but also potentially applicable to other substances (e.g. Spear, trait assessment, geometric means, etc.). Some recommendations are provided in the previous chapters.
- Improved interactions between the risk assessor and risk management are needed.

GLOSSARY

AA	Annual Average
AF	Assessment Factor
AOP	Adverse Outcome Pathways
AR	Applied Radioactivity
AVS-SEM	Acid Volatile Sulphides - Simultaneously Extracted Metals
BAF	Bioaccumulation Factor
BCF	Bioconcentration Factor
BLM	Biotic Ligand Model
BMF	Biomagnification Factor
BP	Biocidal Products
CBR	Critical Body Residue
BSAF	Biota-Sediment Accumulation Factor
CEC	Cation Exchange Capacity
CEFIC	European Chemical Industry Council
CLP	Classification, Labelling and Packaging
DET	Diffuse Equilibrium In Thin Films
DGT	Diffusive Gradient In Thin Films
DOC	Dissolved Organic Carbon
EC	Effect Concentration
ECHA	European Chemicals Agency
EDA	Effect Directed Analysis
EFSA	European Food Safety Authority
EPM	Equilibrium Partitioning Method
EqP	Equilibrium Partitioning
EQS	Environmental Quality Standards
ERA	Environmental Risk Assessment
ERC	Environmental Release Category
EUSES	European Union System For The Evaluation Of Substances
FOCUS	FORum for Co-ordination of pesticide fate models and their USE
GD	Guidance Document
GIS	Geographic Information System
GLP	Good Laboratory Practice
HC	Hazardous Concentration
IPPC	International Plant Protection Convention
ISO	International Organization for Standardization
LC	Lethal Concentration
MAC	Maximum Allowable Concentration
MCDA	Multicriteria Decision Analysis
NER	Non-Extractable Residue
NOEC	No Observed Effect Concentration
OC	Organic Carbon
OECD	Organisation for Economic Co-operation and Development
PAHs	Polycyclic Aromatic Hydrocarbons
PBT	Persistent Bioaccumulative Toxic
PCB	Polychlorinated Biphenyl
PE	Polyethylene
PEC	Predicted Environmental Concentration
PFOS	Perfluorooctane Sulfonate
PNEC	Predicted No Effect Concentration

POC	Particulate Organic Carbon
POM	Polyoxymethylene
PPP	Plant Protection Products
PPR	plant protection products and their residues
PSD	Passive Sampling Device
QSAR	Quantitative Structure Activity Relationship
RA	Risk Assessment
RCR	Risk Characterization Ratio
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals
SC	Scientific Committee
SPEAR	Species at Risk
SPM	Suspended Particulate Matter
SPME	Solid Phase Micro Extraction
SQCs	Sediment Quality Criteria
SQG	Sediment Quality Guidelines
SS	Suspended Solids
SSD	Species Sensitivity Distribution
STP	Sewage Treatment Plant
SW	Surface Water
TER	Toxicity Exposure Ratio
TG	Test Guideline
TGD	Technical Guidance Document
TIE	Toxicity Identification Evaluation
TWA	Time Weighted Average
US EPA	Unites States Environmental Protection Agency
vPvB	very Persistent very Bioaccumulative
WFD	Water Framework Directive
WoE	Weight-Of-Evidence
WWTPS	Waste Water Treatment Plants

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