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METALS ENVIRONMENTAL RISK ASSESSMENT GUIDANCE

# MERAG

## Marine risk assessment

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**CONTENTS**



*The content of the Metal Risk Assessment Guidance (MERAG) fact sheets reflect the experiences and recent progress made with environmental risk assessment methods, concepts and methodologies used in Chemicals Management programs and Environmental Quality Standards (EQS) setting (soil, water, sediments, …) for metals. Because science keeps evolving, these fact sheets will be updated on a regular basis to take into account new developments.*

## 1. INTRODUCTION

The main focus of most risk assessment methodologies and Environmental Quality Standards (EQS) setting has been on the inland environment considered potentially at risk from urban or industrial development. Because marine ecosystems are a part of the largest aquatic system on the planet, covering over 70% of the Earth's surface including habitats ranging from the productive near shore regions to the barren ocean floor, the extension of the existing risk assessment approaches to cover the marine environment seems to be a logical development. However, it is only recently been recognized by several regulatory bodies that there is indeed a need to extend these principles to assess the potential risks of a substance entering into the marine environment with the main focus on estuaries and coastal zones (OSPAR 1998; ECHA 2008a).

It should, however, be acknowledged that the physico-chemical characteristics of saltwater environments show important differences compared to freshwater environments. For example, seawater is characterized by a higher ionic strength and the observed gradients in abiotic factors such as chlorine content have important consequences on composition, behaviour, physiology, reproductive strategies of species on one hand and could have consequences for the speciation and bioavailability of metals on the other hand (Wright 1995; Verslycke et al 2003; Nriagu 1980). Certain metals express strong tendencies to form chloro-complexes (egCd and Pb) and thereby express lower toxicity profiles in the marine environment. Blust et al (1992) investigated the effect of salinity on cadmium uptake by brine shrimp *Artemia fransiscana* and found a decrease in the cadmium uptake with increasing salinity. At the normal pH of seawater, most of the total amount of lead is precipitated as lead (II) chloride and about 10% is an active ion form (Byrne and Miller 1984). Consequently, marine risk assessments should use, where possible, data generated using a range of ecologically relevant saltwater species tested under conditions prevailing in the marine environment.

**Exposure assessment** aspects are not discussed in this fact sheet. It is, however, noted that analytical accuracy, detection limit and partitioning (as reflected in Kd values) can be quite different in the marine environment thereby causing an additional challenge in marine risk assessments. Subsequently, although general processes are by and large the same as in freshwater, input parameters need to be

specific to the marine environment and should not be cross-read without a proper justification. In the next paragraphs, dissimilarities/similarities between marine/estuarine and freshwater ecosystems that could possibly influence the risk assessment of metals and metal compounds in the marine/estuarine aquatic environment are explored.

## 2. CHARACTERISTICS OF THE MARINE ENVIRONMENT

### 2.1 Abiotic factors

#### *2.1.1 Inorganic composition*

Geochemical conditions in coastal marine waters are vastly different from those of freshwater systems. Table 1 presents a comparison between several factors that have been shown to influence metal toxicity towards freshwater organisms, including pH and the constituents of hardness, $Ca^{2+}$ and $Mg^{2+}$.

**Table 1:** Some selected parameters of typical EU fresh water as compared to typical seawater. All values are in mEq/L except pH (Ni-RAR 2008).

| Parameter | Typical EU fresh water (FW) | Typical seawater (SW) | Ratio SW/FW |
|---|---|---|---|
| pH | 7.5 | 8.1 | $0.3[H^+]/[H^+]$ |
| $[Ca^{2+}]$ | 0.4 | 20 | 50 |
| $[Mg^{2+}]$ | 0.6 | 104 | 173 |
| $[Na^+]$ | 26 | 470 | 18 |
| $[Cl^-]$ | 17 | 550 | 78 |
| $[SO_4^{2-}]$ | 1 | 28 | 28 |
| $[K^+]$ | 0.4 | 10 | 25 |

Seawater is characterized by a higher ionic strength and a relatively constant inorganic composition, with generally a smaller temperature range and a more constant pH (typically 7.8-8.2) and hardness than the freshwater environment. The most important inorganic factors that could influence metal speciation in the marine environment are salinity ($Cl^-$), pH, ionic strength and hardness.

In open seas and oceans, the pH, salinity, hardness and ionic strength are fairly constant. Coastal or intertidal zones are typically characterized by a higher turbidity and more gradients with regard to the parameters mentioned above. Estuaries are even more fluctuating systems with strong gradients of turbidity, pH, and salt concentrations leading to oligo-, meso- and poly-haline conditions. A number of marine environments have very specific conditions, deviating from these more general rules (the Baltic Sea with many gradients, highly productive coral reefs, sub-marine volcanoes with extreme temperatures…). However, the general nature of the enclosed and semi-enclosed seas is essentially dependent on whether or not the freshwater lost through evaporation is more or less than the amount of freshwater input from precipitation and direct runoff from the land. Another important physical feature is the retention time, most relevant to (semi-)enclosed seas.

These variations in physico-chemical parameters can have a pronounced influence on the speciation of metals. In addition to chlorides, suspended solids, manganese, sulfur and oxygen will dominate trace metal distribution/speciation, also in saltwater.

### *2.1.2 Dissolved organic matter/dissolved organic carbon*

One of the most important parameters that may influence metal bioavailability is dissolved organic carbon (DOC). Sometimes the more general parameter dissolved organic matter (DOM) is used to refer to organic material coming from natural sources. DOC is a part of DOM. The river inputs to the coastal zone, together with the intense physical and biological activity in coastal waters, make that part of the marine realm one of the most dynamic in terms of (DOM) and DOC (Cauwet 2002). Unlike the inorganic composition of marine waters, DOC levels may vary considerable between marine water bodies. Baltic Sea, North Sea and Mediterranean coastal waters have DOC levels ranging between 1-10 mg/L. Open Ocean waters usually have lower DOC, ranging between 0.5 and 1.8 mg/L. An inverse relationship between DOC concentrations and salinity was generally observed (Cadée et al 1982; Doval et al 1999; Vignudelli et al 2004; Baker and Spencer 2004), demonstrating the importance of conservative mixing of freshwater and marine DOM. Already in 1992, Druffel et al (in Baker and Spencer 2004) further reported the importance of autochthonous DOM for the marine waters DOM pool.

Globally, riverine inputs of DOM represent about 0.25 Gt C per year representing only 0.03% of the total marine DOC pool. The impact of freshwater DOC inputs on the coastal zone is, however, far from negligible. Furthermore, it is unknown how much is rapidly degraded or persists in the marine environment. A relatively large fraction of that DOM is degraded after mixing with seawater, with turnover times ranging from days to years. DOM behaviour is also modified by the physical-chemical processes occurring in the mixing zone, particularly flocculation and photo oxidation, changing the structure and the biodegradability of the organic matter. In addition to riverine inputs, seasonal autochthonous production contributes to a large amount of DOM present in the coastal zone (Cauwet 2002).

Vignudelli et al 2004 measured DOC concentrations in the Coastal Mediterranean Sea and observed, besides a conservative dilution of DOC, a conservative mixing of humic-like fluorescence. The authors reported an additional “protein like fluorescence” of marine origin (phytoplankton bloom and bacterial decay) and concluded that 60% of the marine DOC in the coastal Mediterranean waters could be considered to be of terrestrial origin, and the remaining 40% was of marine autochthonous origin.

Considering the terrestrial as well as marine autochthonous origin of estuarine and marine DOM, the DOM quality can vary geographically and seasonally along estuarine gradients and coastal zones where the terrestrial versus autochthonous DOM contributions may change. Variation in DOM quality related to sources and characteristics of organic matter has been investigated from DOM absorbance and fluorescence measurements by several authors (Marin 2010; Pempkowiak 1999). A trend was observed with maximum fluorescence at shorter excitation and emission wavelengths for marine samples than for freshwater samples (Coble 1996). Difference in quality of DOC may have a profound impact on the general mitigating effects of DOC. Marin et al (2010) concluded that both differences in complexation and in toxicity observed among samples towards the larvae of the sea urchin *Paracentrotus lividus* were related to the bulk DOC concentration and the optical properties of the biogenic coloured DOM. The importance of the quality and origin of DOC on the bioavailability of metals in marine systems is further discussed in section 4.

## 2.2 Biotic factors

### *2.2.1 Species diversity*

Because the physico-chemical conditions encountered in the marine ecosystems differ from freshwater ecosystems, freshwater and saltwater organisms have developed very different strategies to cope with ion- and osmo-regulatory problems related to living in either very low- or high- dissolved salt concentrations. The observed gradients in ionic strength and dissolved nutrients resulted in the development of very specific biological assemblages in both the marine and the freshwater environment. A key question that has to be answered is to what level the observed differences in species diversity between marine and freshwater ecosystems might influence the vulnerability of the system.

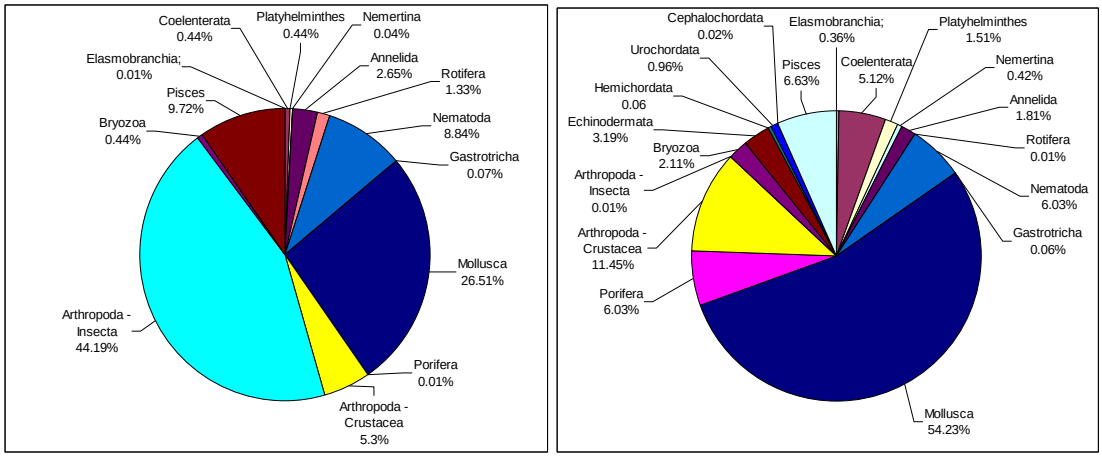
Overall, saltwater environments show more diversity of taxonomic groups compared to freshwater environments (Box 1). However, in terms of relative numbers of individual species, the picture is reversed. While higher species diversity may lead to a sensitivity distribution spanning a wider sensitivity range, there could also be a considerable functional overlap making the system less sensitive to the potential impact of a substance emitted to this environment. Dunne et al., 2004, showed that due to their relatively high connectance (complexity), marine food webs appear fairly robust to loss of most connected taxa as well as random taxa. On the other hand, there also exist distinct scenarios (e.g. brackish systems) with lower species diversity and less apparent sensitivity differences for the species taken up in the sensitivity distribution in the lower end of the salinity range between 5 and 8 promille (eg parts per thousand). Such systems can be more vulnerable due to the ecosystem function dependency on a small number of key species. However, the latter is not marine specific. Based on the observations of Briand (1983) who evaluated the diversity, connections and mean maximum food chain length of 40 food webs, comprising marine, freshwater and terrestrial communities, there is no clear scientific basis to assume that “low species diversity-high ecosystem dependence” is higher in marine systems than in freshwater systems. However, Cohen (1994) and Link (2002) found that linkage and connectivity are higher than non-marine webs. Dunne et al (2004) corroborates with different aspects of previous studies but stated that in most cases marine food webs do fall within previously reported ranges of observed food web properties from non-marine systems. With regard to biomagnification, food chains on average do not appear to be longer in marine ecosystems than in other ecosystems

(CSTEE 2002). In both freshwater and marine ecosystems, it is generally possible to define five basic trophic levels (primary producers, primary consumers, detritus feeders, secondary consumers and degraders). There may exist a potential for one more link in the marine food chain and within the marine environment (although not necessarily exclusively) with larger carnivorous species present (eg sharks). There is potentially a further emphasis needed relating to the impact upon larger marine species of mammal or birds (ie high trophic level species) (ECETOC 2001).

**Box 1: Comparison number of species: taxa in marine and freshwater environments**

ECETOC (2001) evaluated the number of species encountered in freshwater and marine ecosystems. The evaluation was based on gathering phylogenic data on fauna to determine species abundance within an ecosystem. However, when interpreting these results, one has to bear in mind that (1) many species have not yet been discovered, (2) phylologists classify species differently (eg dividing or grouping organisms in greater or smaller categories), and (3) it does not account for species at higher trophic levels being less numerous. Overall, more species groups, but less individual species are present in the marine environment.

An overview of the species diversity as reported by ECETOC (2001) is shown in Figure 1. The phylum *Arthropoda* has been separated into the two classes *Crustacea* and *Insecta* to highlight the differences between marine and freshwater environment. Likewise, elements within the phylum *Chordata* have been highlighted separately.




**A** **B**

*Figure 1: Species composition of freshwater (A) and marine (B) fauna (redrafted after ECETOC 2001).*

In freshwater ecosystems, insects (44.2 %) represent the largest group, followed by mollusks (26.5 %), fish (9.7 %) and nematodes (8.8 %). Crustaceans amount for 5.3 % of the freshwater species. In saltwater ecosystems, mollusks represent 54.2 % of the species, crustaceans 11.5 %, fish 6.6 %, poriferans (sponges) 6 % and coelenterates *(*cnidarians*)* 5.1 %. When comparing the largest groups in both freshwater and saltwater ecosystems, it is striking that only a very limited number of insects are present in the marine environment (0.01 %), while this is by far the largest group of freshwater species. Further, mollusks constitute more than half of the marine fauna, but only a quarter of the freshwater fauna.

Moss (1988) and Barnes (1984) stated that 56 phyla were present in marine waters compared to 41 in freshwaters. Excluding a few groups solely comprising parasites, species of all known phyla (70 to 90 depending on the classification system) are represented in the sea or in the transitional coastal fringe (Moss 1988; Barnes 1984). No phyla are confined to fresh waters only, while 15 phyla are found only in marine waters. Examples of these are the *Echinodermata*, *Ctenophora*, *Polyplacophora*, most *Gastropoda* and *Bivalvia*, *Cephalopoda*, and most *Polychaeta*. Other 'smaller' marine groups include the *Sipunculida*, *Echiuroidea* and *Pogonophora*. In contrast, terrestrial and freshwater organisms represent a smaller range of known phyla and classes. Yet, when one looks at the relative numbers of individual species, the picture is reversed. Using a conservative estimate of 2 to 2.5 million described species of living organisms, 10% of these (250 000) are marine. Of the species occurring in the marine environment, only 2% inhabit the water mass itself, the other 98% live in or on sediments or other substrates (Barnes and Hughes 1988; Janssen 2000).

Overall, although there are more taxa in the marine environment as a whole, there is no evidence that particular communities in the marine ecosystem are consistently more diverse than those in freshwater or terrestrial systems. However, there are a number of phyla and/or classes of organisms which occur mainly or exclusively in marine environments. Examples of these are the *Echinodermata*, *Ctenophora*, *Bryozoa*, *Polyplacophora*, most *Gastropoda* and *Bivalvia*, *Cephalopoda* and most *Polychaeta.* Other 'smaller' marine groups include the *Sipunculid*a, *Echiuroidea* and *Pogonophora*. Alternatively, some phyla and taxa do not occur in marine waters or at least compared to the freshwater or the terrestrial environment: I*nsecta* and *Cladocera*.

### *2.2.2 Species sensitivity*

Freshwater and marine organisms utilize very different ion- and osmo-regulatory strategies to manage the physiological challenges related to living in either a very dilute or concentrated salt environment. Organisms living in estuaries face even more harsh conditions because they live in a salt gradient and have to cope with tidal and temporal fluctuations in salt concentration. Depending on their evolutionary history, organisms have developed different solutions to deal with these physiological challenges. These differences in physiology may also have an impact on metal uptake and elimination processes (Smolders et al 2004).

In general, gills and surface (skin, carapace, epidermis…) are the primary routes of metal uptake for most freshwater organisms. Freshwater organisms normally do not drink because they take up water by passive exchange across the permeable body surfaces. They live in a very dilute environment and have to actively retrieve major ions such as $Na^+$, $K^+$, $Ca^{2+}$ and $Mg^{2+}$ from the environment and the gills and digestive system are actively involved in this process. In contrast, saltwater organisms live in a much more concentrated ionic environment, and depending on the exposure conditions and their ion- and osmo-regulatory physiology, they are either hypo-ionic or hyper-ionic in relation to their environment.

Saltwater organisms lose water and have to compensate for this loss by drinking (Prosser 1991; Schmidt-Nielsen 1997; Willmer et al 2000; Smolders et al 2004). This also means that they take in metals in solution via the digestive system. Both the epithelia of gills and gut are important and sensitive targets mainly due to the control of the flux of cations. The observed differences in physiology, however, do not inherently lead to an overall greater sensitivity of marine species and it remains unclear whether the exposure through the digestive track also translates into a higher sensitivity to metals. Indeed, for the same internal metal concentration exposure via the gut does not necessarily result in the same toxic effect as exposure via the gill (Thomann et al 1997; Szebedinszky et al 2001; Campbell et al 2003; Sappington et al 2003). Saltwater species may also have pelagic planktonic stages that can exhibit different sensitivities to chemicals and some reproductive strategies of marine invertebrates are less responsive to changing environmental conditions, which might be expected to lead to differences in sensitivity to toxicants (Hutchinson et al 1998; Smolders et al 2004). Finally, differences in metal sensitivity could also be linked to

differences in osmotic strategy in marine vs estuarine organisms. That is the difference between osmo-conformers and osmo-regulators. For example, marine teleost fish, known as ion-regulators, show low permeabilities of the major cations across the gills, in order to limit the influx of the ions from the seawater across the otherwise strong concentration gradient between outside (seawater) and inside (blood). Most marine invertebrates do not possess such a regulatory system (there are some exceptions). They are more permeable and show rapid equilibration of the circulatory fluid with seawater after transfer from a lower to a higher salinity or vice versa.

Because there are generally fewer toxicity data available for saltwater species than for freshwater species (Hutchinson et al 1998; Leung et al 2001; Wheeler et al 2002)[1] it could be worthwhile to explore on a case-by-case basis if freshwater data can be used in case of absence of relevant marine data for some taxa (see section 3). As stated before, there are a number of important physico-chemical differences between the saltwater and freshwater environment. Furthermore different communities exist in saltwater ecosystems compared to freshwater ecosystems, with a number of taxa restricted only to marine and freshwater environments. Therefore, a relevant question to pose is whether or not marine species are more or less sensitive than freshwater species and if extrapolation from the freshwater compartment to the marine compartment should be allowed for the metal/metal compound under consideration without correcting for these differences. In this regard care should be taken in the interpretation of toxicity data generated with open sea species because these species may come from a metal-deficient area. This may result in increased sensitivity when tested at concentrations of metals occurring in coastal water conditions.

The sensitivity of marine species in comparison with their freshwater counterparts and the sensitivity of unique marine species has been addressed in a limited number of studies only (Box 2). Some of these studies assessed the sensitivity of freshwater versus saltwater species to metals and/or organic chemicals by studying existing effects databases. Other studies deal with a number of individual metals studied in one species.

[1] This is largely because risk assessments have been mainly focussing on freshwater systems and less standard test methods are available for saltwater species.

**Box 2: Comparison sensitivity freshwater/marine species**

Several authors have based their comparison in species sensitivity derived species sensitivity distributions (SSD) from the USEPA's AQUIRE and ECOTOX databases. Leung et al. (2001) and Wheeler et al. (2002) extracted acute median $LC_{50}$ data from the database for a number of chemicals amongst which are cadmium, copper, lead, mercury, nickel, chromium and zinc. No true quality check has been performed on the data retrieved from AQUIRE. Except for zinc, $HC_5$ values were within one order of magnitude for freshwater and saltwater species. In general, the differences between freshwater and saltwater responses, as described by the SSD values, were not large and freshwater species appeared to be more sensitive than saltwater species. The use of freshwater data would thus be protective for saltwater species.

The USEPA ECOTOX database was also used by Smolders et al (2004) without further quality evaluation to calculate HC5 values in freshwater and saltwater systems for different metals (cadmium, cobalt, copper, lead, mercury, nickel and zinc). As an example, the SSD values for lead are given in Figure 2. On a chronic level, both freshwater and marine SSD values almost coincide.

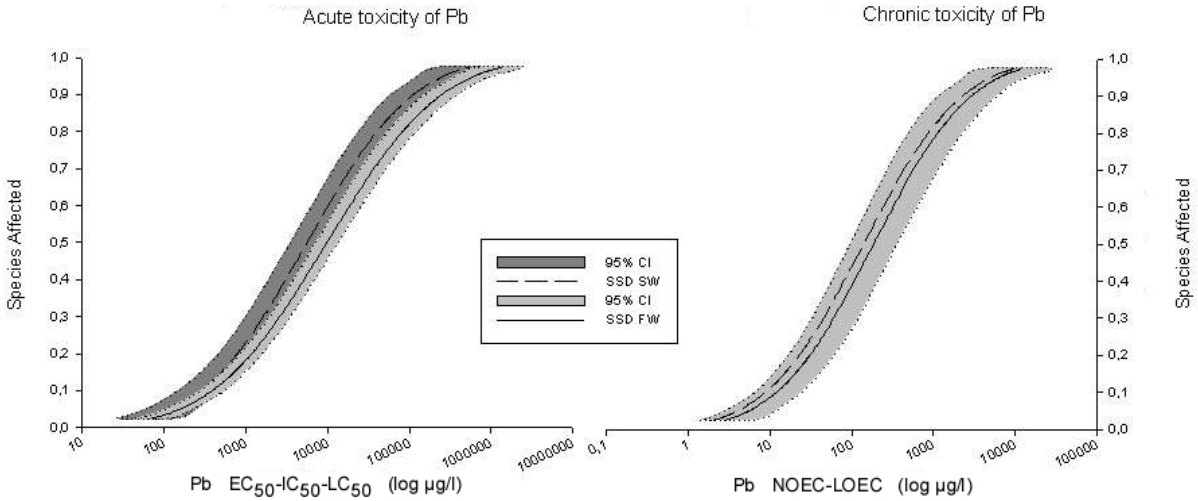



*Figure 2: Comparison between freshwater (FW) and saltwater (SW) organisms for a) acute and b) chronic toxicity of lead (from Smolders et al 2004).*

The authors conclude that there are no clear indications for important differences between freshwater and saltwater organisms in terms of acute and chronic toxicity for

copper, cobalt, nickel, lead and zinc when expressed on a total metal concentration scale, with freshwater species being slightly more sensitive (acute and chronic freshwater and saltwater HC5 of the other metals are all within a factor of 4.4). In the case of cadmium, freshwater species were considerably more sensitive for chronic toxicity. For cadmium, the chronic HC5 value is 13.4 times lower in freshwater compared to saltwater.

Another series of studies has described the European Centre for Ecotoxicology and Toxicology of Chemicals (ECETOC) aquatic toxicity (EAT) database (Hutchinson et al 1998; ECETOC 2003). Freshwater versus saltwater species sensitivities are described and 'general chemicals', 'pesticides' and 'metals' are differentiated. A limited number of metal studies are available and thus the results must be interpreted with caution. Only relatively small differences between sensitivities of freshwater and saltwater species were found. A physiological similarity is suggested between species belonging to similar taxonomic groups regardless of their freshwater or saltwater origin. The authors conclude that the use of freshwater acute effects data instead of or in addition to saltwater effects data for risk assessment purposes is not contra-indicated by the empirical data reviewed.

Although no metals were included in their study, LeBlanc et al (1984) confirmed previous data that relatively little differences in sensitivity exist between freshwater and saltwater species. Much greater differences between different taxonomic groups exist (eg different taxonomic groups of algae) than between related freshwater and saltwater species. Differences in sensitivity of different trophic levels were also as great as or greater than the paired species differences. Other authors concluded that marine species were more sensitive than freshwater species (e. Robinson 1999). Part of the higher sensitivity of invertebrate saltwater species may be attributed to the longer exposure period in saltwater invertebrate tests. Overall, several authors found that differences between freshwater and saltwater species sensitivities for metals and other compounds were generally within a factor of 10 (eg Calleja et al 1994; Dawson et al 1977; Hemmer et al 1992; Sorokin 1999).

Although the used data in the previous studies (Box 2) were not specifically screened for quality, there appears to be a relatively good agreement between the sensitivity of fresh- and saltwater fish. This is partly due to the fact that fish represent only 1 taxon. For invertebrates, less agreement (higher variance) is found, but this is probably

largely due to the fact that several higher taxa are included in 'invertebrates' (contrary to fish). **In general, it can be stated that the results of the different studies do seem to indicate that the differences between freshwater and saltwater response, are not large and freshwater species appear to be even more sensitive than saltwater species.** The use of freshwater toxicity data would thus be protective for saltwater species. It is likely that different sensitivities of freshwater and saltwater species are at least partially a consequence of differences in speciation and bioavailability in the different media. In particular, the greater abundance of "uncomplexed" or free ionic forms of metals under freshwater conditions and the greater ability of saltwater organisms to regulate uptake of some essential metals such as zinc and copper probably contributes to the greater tolerance of these substances by saltwater organisms. Therefore, comparison of 'real' sensitivities between fresh- and saltwater organisms should ideally be performed based on the bioavailable fraction rather than on total/dissolved metal concentrations. More background information on regulation of metals and bioavailability of metals can be found in MERAG (2007).

Differences in sensitivity between similar freshwater and saltwater species within a taxon also seem to be smaller than different between species belonging to different taxa. Hence, it is likely that extrapolating from freshwater to saltwater species will introduce less uncertainty than extrapolating between non-related taxa.

### *2.2.3 Conclusions*

Although there are more taxa in the marine environment as a whole, there is no clear evidence that particular communities are consistently more diverse than those in freshwater or terrestrial systems, and that there are consistent differences in sensitivity between marine taxa and those in other environments. Most marine effects databases generally lack data on certain key marine taxa (echinoderms, mollusks), which make it difficult to judge that such phyla are potentially more sensitive and that any effects assessment conducted in the absence of such data may not capture this sensitivity. From our growing knowledge of data sets that become available for metals (e.g. Cu, Zn, Ni, …), however, no specific indications that species from (key) marine taxa are consistently more sensitive than freshwater species (to the contrary), and the same critique can also be leveled at the freshwater effects database which similarly lacks abundant information relating to key taxa such as mollusks and insects.

## 3. DERIVATION OF ECOTOXICITY THRESHOLDS (PNEC OR EQS) FOR MARINE SPECIES

Deriving an ecotoxicity threshold (PNEC or EQS) for the marine environment should follow the same principles as for the freshwater environment. This means that all available effects data for marine species belonging to different taxa have to be gathered, screened for quality and handled by appropriate statistical techniques to derive a PNEC or EQS. Because there are only a limited number of standard guidelines on toxicity testing in the marine aquatic and sedimentary environment, mostly fewer species mean NOEC values/$EC_{10}$ values will be available for marine organisms than for freshwater organisms.

In appraising toxicity data for the development of water quality guidelines (WQG and EQS) or Predicted No effect Concentration (PNEC), two approaches can be used (Warne 1998 in Batley et al 1999). The first and traditional approach uses assessments- or safety factors applied to toxicity data. This empirical approach is based largely on intuition, factors that have typically been assigned order of magnitude numbers such as 10,100, 1000. These factors represent a typical example of the precautionary principle and as such are conservative and over-protective in most cases. In the EU, even higher assessments factors have been suggested in order to account for the presence of key marine sensitive taxa (TGD 2003). The second and scientifically preferred method involves the fitting of all available and acceptable data to a statistical distribution, known as the Species Sensitivity Distribution (SSD) approach.

If sufficient marine ecotoxicological data are available to build a saltwater Species Sensitivity Distribution (SW SSD), the use of the statistical extrapolation method is recommended (Figure 3). However, due to the paucity of reliable marine data (for some metals it could be worthwhile to explore on a case-by-case basis if freshwater data can be used in the absence of relevant marine data for some taxa. In those cases it could be evaluated whether or not freshwater ecotoxicity data can be pooled with marine ecotoxicity data in order to increase the size of the marine database and thereby allowing the use of the SSD approach for deriving a PNEC or EQS. If there is proof that freshwater species exhibit a similar sensitivity or are even more sensitive than saltwater species, pooling both databases as a hybrid SSD can be applied. Pooling of freshwater and marine data should, however, only be considered when

one dataset is not sufficiently robust to derive an SSD on its own. Pooling freshwater data with a less robust marine database is appropriate, but the inverse should not be performed, as this will increase uncertainty in the ecotoxicity threshold for the freshwater. Also, care should be taken to avoid pooling freshwater taxa that do not occur in marine ecosystems (eg amphibians) or are unlikely to occur in strict marine ecosystems (eg insects). Criteria for determining the adequacy of taxonomic coverage for marine databases have not yet been addressed but the initial criteria of the 2001 London workshop can be used as a starting point[2].

Alternatively, to overcome the issue of data scarcity one could focus on the sensitive tail of the distribution only as is being done in the derivation of water quality criteria in the US (US-EPA), which may be helpful to overcome the issue of data scarcity.

Usually the data are not there to assess the similarity between the sensitivity of freshwater and marine species. In case not enough marine data are available and the evidence of the comparative sensitivity evaluation is not conclusive to allow cross-reading between the saltwater and freshwater data, then the assessment factor approach may be the only alternative. An assessment factor should be applied on the lowest marine data point. In the latter case, because there is no scientific evidence that marine ecosystems are more sensitive for metals than freshwater systems, the size of the assessment factors applied should be similar to the ones used for the derivation of a freshwater ecotoxicity threshold[3].

[2] The London 2001 workshop provided criteria for the use of SSD analysis for mainly freshwater databases. While these criteria are in general applicable to the marine environment too, the detailed guidance provided for the freshwater system needs careful consideration because some taxa are represented in marine and not in freshwater environments. For example, insects are an essential freshwater taxonomic group according to the London criteria; however, insects do not live in strict marine environments. Likewise, representative marine taxonomic groups such as echinoderms do not occur in freshwater environments. It was therefore suggested at the EU level to apply the London criteria in a comparative way substituting typical freshwater taxa by typical marine taxa (eg echinoderms and ….)

[3] In some legislative systems the application factors for the marine environment have been raised (TGD 2003). But as also indicated by the Scientific Committee on Toxicity, Ecotoxicity and the Environment (CSTEE), there are no scientific grounds for raising the assessment factors (CSTEE 2002)

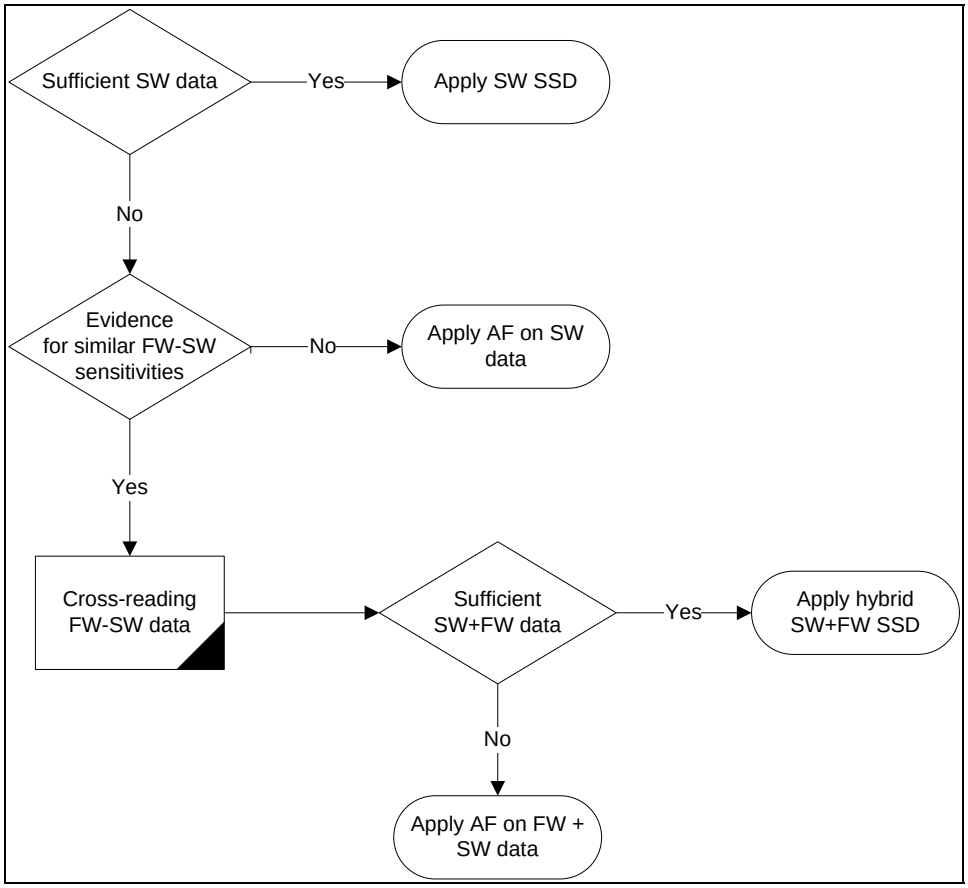



*Figure 3: Methodology outline for the derivation of marine risk assessments (PNEC derivation). AF = assessment factor, SSD = species sensitivity distribution, SW = saltwater, FW = freshwater.*

The PNEC derivation for the marine environment for molybdenum is worked out as an example in detail in Box 3.

**Box 3: Derivation PNEC molybdenum for the marine compartment**

Chronic ecotoxicity data for molybdenum (as molybdate) for ten different marine species have been reported in the Chemical Safety Reports (http://apps.echa.europa.eu/registered/registered-sub.aspx#search) for molybdenum and molybdenum compounds. The database includes a broad representation of temperate marine organisms, including unicellular algae, macroalgae, invertebrates, and fish (Table 2 and 3). In terms of ecological diversity, the database includes primary producers, filter feeders, grazers, deposit-feeders, predators, and omnivores. These ten test organisms represent eight taxonomic classes that are relevant and typical for the

marine environment. Echinoderms, for instance, can only be found in the marine environment, and more than 93% of all mysid species live in the marine environment (Porter et al 2008).

| Number of species | Individual species in Mo database |
|---|---|
| 1 | *Ceramium tenuicorne* (algae: red macroalgae) |
| 2 | *Dunaliella tertiolecta* (algae: green flagellate) |
| 3 | *Phaeodacgtylum tricornutum* (algae: diatom) |
| 4 | *Strongylocentrotus purpuratus* (echinoderm: sea urchin) |
| 5 | *Dendraster excentricus* (echinoderm: sand dollar) |
| 6 | *Mysidopsis bahia* (crustacean: mysid) |
| 7 | *Mytilus edulis* (mollusc : bivalve) |
| 8 | *Cyprinodon variegatus* (fish: family Cyprinodontidae) |
| 9 | *Acartia tonsa* (crustacea: copepod) |
| 10 | *Crassostrea gigas* (mollusc: bivalve) |

*Table 2: Individual species covered in the Mo marine ecotoxicity database.*

| Number of Classes | Individual Classes in the marine Mo database |
|---|---|
| 1 | Florideophyceae (*Ceramium tenuicorne*) |
| 2 | Chlorophyceae (*Dunaliella tertiolecta*) |
| 3 | Bacillariophyceae (*Phaeodactylum tricornutum*) |
| 4 | Echinoidea (*Strongylocentrotus purpuratus, Dendraster excentricus*) |
| 5 | Malacostraca (*Mysidopsis bahia*) |
| 6 | Bivalvia (*Mytilus edulis, Crassostrea gigas*) |
| 7 | Actinopterygii (*Cyprinodon variegatus*) |
| 8 | Maxillopoda (*Acartia tonsa*) |

*Table 3: Individual classes covered in the Mo marine ecotoxicity database*.

A log-normal distribution has been fitted through the ten data points (Figure 4)

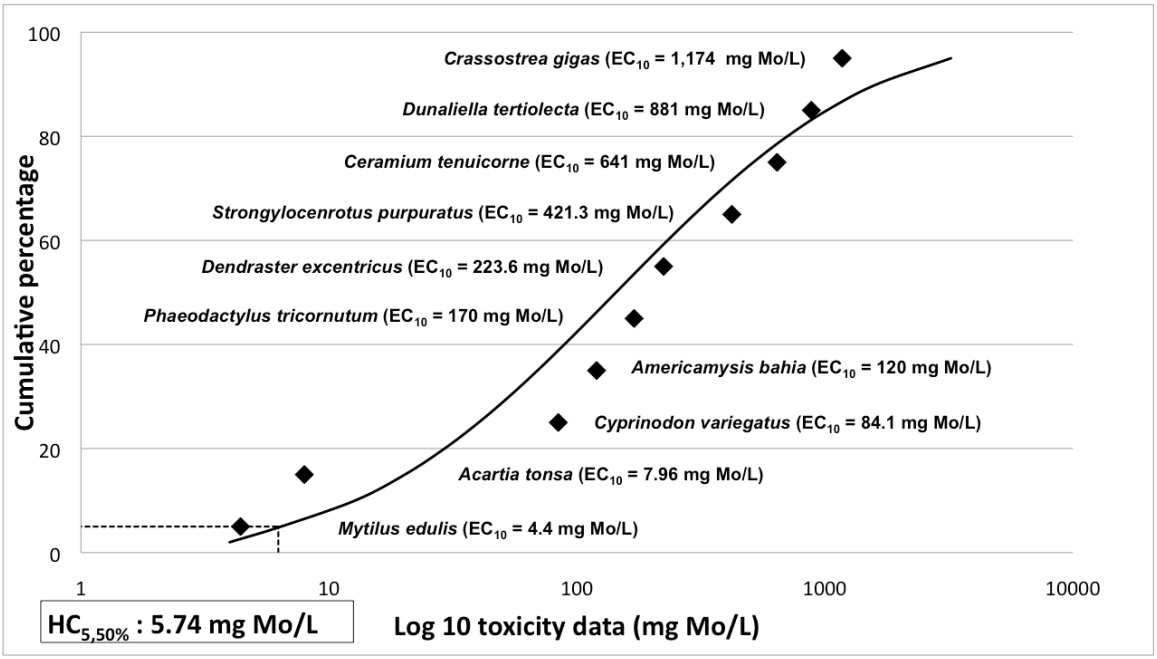



*Figure 4: SSD relationship for chronic Mo marine test data using a log-normal distribution. Relationship shown for median hazardous concentrations as estimate of the hazardous concentrations. $HC_{5(50\%)}$ = 5.74 (0.58 – 21.0) mg Mo/L.*

Chronic effect levels for the ten marine species are situated between 4.4 mg Mo/L ($EC_{10}$ for *M. edulis*; Morgan et al 1986) and 1,174 mg Mo/L ($EC_{10}$ for *C. gigas*; Kools and Vanagt 2009), which is a difference of a factor of 267 between the most and the least sensitive species. It is noteworthy that different types of molluscs are found on either side of the sensitivity spectrum: the mussel *M. edulis* proved to be more sensitive that the oyster *C. gigas*, and this by more than a factor of 250. This large variation in response towards metal exposure among molluscs is not uncommon, and was also noted for lead. Both echinoderms (*D. excentricus*, *S. purpuratus*) belong to the lesser sensitive organisms that were evaluated, with $EC_{10}$ values of 233.6 and 325.8 mg Mo/L, respectively. All tested marine micro- and macro-algal species also belong to those species that show a larger resistance to elevated Mo-levels.

Most ecotoxicological effect levels were more or less within one order of magnitude; only the mussel *M. edulis* and the copepod *A. tonsa* were at least one order (and up to almost three orders) of magnitude more sensitive compared to the eight other species. Unlike what has been observed for some other metals, the teleost fish *C. variegatus* was not distinctively less sensitive towards molybdenum when compared to other species, and more specific marine invertebrates. In fact, *C. variegatus* was the third most

sensitive species of the SSD and proved to be more susceptible to adverse effects of molybdenum than typical marine taxonomic groups like echinoderms and mysids.

This atypical property of molybdenum could be related to the fact that molybdenum is present as an anion (i.e., $MoO_4^{2-}$) and not a cation, and that regulation processes may be somewhat different. Secondly, molybdenum has a very low toxicity when compared to other metals (2-3 orders of magnitude) and the absence of effects at low exposure levels could make the impact of different regulation mechanisms redundant.

The log-normal distribution yielded an $HC_5$ (50%) value of 5,74 mg/L. Based on uncertainty considerations, an additional assessment factor on the 50% confidence value of the 5$^{th}$ percentile value (thus PNEC = 5$^{th}$ percentile value (50$^{th}$ ci)/AF), with an AF between 1 and 5 has to be applied, to be judged on a case-by-case basis [ci = confidence interval]. For molybdenum it was felt that the most appropriate AF would be 3. Therefore, hence the $PNEC_{marine}$ is proposed to be 1.91 mg Mo/L.

## 4. INCORPORATION OF BIOAVAILABILITY

As a general rule, total/dissolved metal concentrations in marine environments should be 'normalised to sea-values'. That is, the bioavailable fraction of the metal considered should be calculated for the saltwater environment under consideration. In general, different metals will act differently on increasing saltwater concentrations and this should be accounted for on a case-by-case basis (eg Turner et al 2002; Pohl and Hennings 1999; Tipping et al 1998; Toteja et al 2001).

In marine waters, the pH is typically stable in the range of 8.1 to 8.4. The stability of the pH is due to the high buffering capacity of seawater. The marine concentrations of $Mg^{2+}$ and $Ca^{2+}$ are also stable, and are typically 800 and 2,200 mg/L, respectively. The stability of pH, $Ca^{2+}$, and $Mg^{2+}$ reduces the need to normalize marine toxicity data, as long as the toxicity tests are performed on seawater at salinities between 28 and 34 g/L and as long as DOC concentrations are not excessively high. Large differences in salinity and dissolved organic carbon that can be encountered in estuarine/coastal zones, however, may play an important role in altering the bioavailable fraction of metals. Decreasing toxicity with increasing salinity, probably due to a decrease in bioavailability, has been observed by a number of authors (eg, Sundae et al 1978; Blust et al 1992; Verslycke et al, 2003; Hall et al 2008). Although each metal may react differently to increases in salt concentrations, free ion concentrations of, for instance, cadmium, zinc, copper and nickel tend to decrease with increasing salt concentrations, most probably by complexation with (chloride) ions (Nriagu 1980; Sadiq 1992; Verslycke et al 2003; Wright 1995). Hence, the free metal ion, which is most bioavailable, is more abundant at lower salinities because of the reduced formation of chloro-complexes (e.g. AgCl, $CdCl_2$, $CoCl_2$). Other metals, however, are less influenced by salt concentration. Lead for instance, is mostly precipitated as lead(II)chloride at the normal pH of seawater and is less influenced by salinity. In open ocean, salinity is constant and variations in dissolved organic matter (DOM) will be the most critical parameter governing metal bioavailability.

It is theoretically possible to run for instance a BLM for the specific saltwater conditions. However, until now, no validated chronic BLM values for marine environments exist (Niyogi and Wood 2004). Arnold et al (2005) developed a BLM model for copper using the bivalve *Mytilus sp*. (the most sensitive taxa in the US EPA

saltwater copper criteria database). From the results, it is clear that the BLM predictions are to a high degree related to the presence of DOC and the BLM model could in fact be interpreted as a kind of DOC regression model.

DOM in general is considered to decrease metal bioavailability in aquatic environments by binding metal ions and thus reducing the free ion concentration, in accordance with the Free Ion Activity Model (FIAM) (Campbell 1995). Several authors using commercial fulvic and humic acids, algal exudates or DOM pre-concentrated by reverse osmosis have confirmed that the FIAM works for both freshwater and saltwater organisms exposed to Cu (Brooks et al 2007; Arnold 2005; Kim et al 1999; Lorenzo et al 2006). Contrasting results have been observed for Pb, the next metal ion with higher affinity for DOM, depending on the DOM type used and the organism tested. Results range from a lower than expected decrease in lead bioavailability (Lamelas et al 2005; Lamelas and Slaveykova 2007) to an increased bioavailability in the presence of DOM (Sanchez-Marin et al 2007; Schwartz et al 2004). The apparent contradiction with FIAM has been attributed to an additional effect caused by the direct interaction of DOM with the cell membrane (Galvez et al 2008; Vigneaul et al 2000).
Next to the importance of the direct effects of increased quantities of DOM present in the marine/estuarine system, metal-DOM binding capacity may also vary in coastal/marine waters due to differences in origin and quality of estuarine, coastal and marine DOM. Therefore some authors have suggested including other DOM parameters that in addition to the amount of DOC may improve the predictions of aqueous metal toxicity (Playle 1998; Ryan et al 2004).

Very few studies have included the study of optical properties of DOM for the evaluation of metal toxicity in seawater. Pempkowiak et al (1999) made a first attempt to relate spectroscopic and chemical properties of DOM to metal bioavailability in seawater, but using DOM extracted from different freshwater sources. They found that 60% of the differences in copper accumulation were explained by the carbon content in organic matter, while DOM aromaticity explained 13% of the variance. The differences in copper and lead complexation properties of seawater samples enriched with DOM of contrasting origins (natural seawater, effluent of a sewage treatment plant and two sediment elutriates) were studied by Sanchez-Marin et al (2010) by means of the *Paracentrotus lividus* embryo-larval bioassay. Differences in DOC complexation capacities were reflected in copper and

lead toxicity. In contrast to copper where toxicity was reduced for all DOC sources, lead toxicity was less affected by the organic matter present in the samples, and the observed effects were different (protecting, enhancing or not affecting toxicity). Good correlations were found between DOC and copper $EC_{50}$, while the complexing capacity correlated better with the fluorescence of marine humic substances, stressing the importance of characterising not only the amount but also the quality of seawater DOM to improve predictions.

In freshwater, more work has been done including DOM quality measurement for the improvement of bioavailability models (Ryan et al 2004; De Schamphelaere et al 2004; Richards et al 2001; Swartz et al 2004). All of these studies postulate that autochthonous DOM, with lower aromaticity, bound less metal per unit DOC than allochthonous DOM. Overall the effects of DOM quantity is more important in explaining variability in the test results than DOM quality.

Nevertheless, because DOM quality plays a significant role, it is recommended to evaluate carefully the source of the DOM used in the toxicity tests selected for the PNEC derivation. The applicability of laboratory studies using artificial DOC is doubtful in the case of seawater, given the fact that commercially available DOM is isolated from soil or freshwater rather than marine sources. When used, the actual binding capacity of the artificial DOC needs to be compared and supported with actual field data of metal speciation in marine waters. An example of the use of DOC as a normalisation factor for copper is given in Box 4.

**Box 4: use of DOC as normalisation parameter in the PNEC derivation of copper for marine environments (VRAR Cu 2006)**

In an assessment of a modifying factor in copper toxicity, Arnold (2005) undertook an extensive analysis of the relationship between DOC and toxicity of copper to the most sensitive saltwater genus in the U.S. EPA criteria database, *Mytilus*, proving that dissolved copper $EC_{50}$ values are highly correlated ($r^2 = 0.71$, $n = 54$, $p < 0.001$) across a wide range of sample DOC concentrations (0.3–10 mg C/L) and are explained by the equation $EC_{50} = 11.53DOC^{0.53}$ (Figure 5)

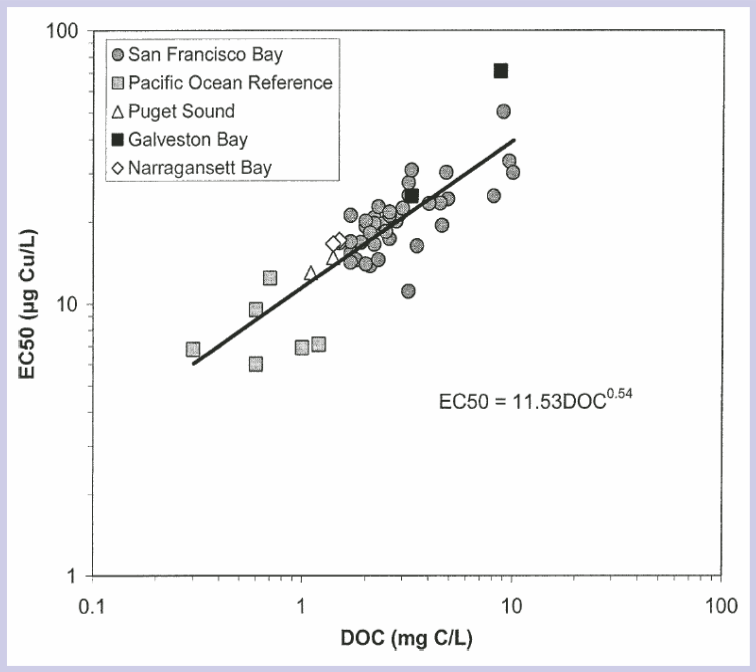



Figure 5: Dissolved copper EC50 values for embryos of *Mytilus galloprovincialis* as a function of dissolved organic carbon (DOC) in a range of water samples (n=54, R2=0.71, P<0.01).

A similar trend in the relationship between measured DOC (added as humic acids) and toxicity has been seen by Brooks (2006) and Brooks et al (2007). In these studies, the effects of copper exposure to *Fucus vesiculosus*-zoospore growth (Chromophycota, "bladderwrack") and to *Crassostreas gigas* - embryo development (Mollusca, "Pacific oyster") were assessed at different levels of added humic acids – DOC. The studies demonstrate a clear relationship between the dissolved copper NOEC/EC50 values and the DOC measured in the test media. Supporting information on copper toxicity to embryo life stages (48 hour tests) of *Mytilus galloprovincialis (*Mollusca, "Mediterranean mussel"), *Dendraster excentricus* (Echinodermata, "Sand Dollar") and *Strongylocentrotus purpuratus* (Echinodermata, "Purple Sea Urchin") are also available which show this relationship between DOC and toxicity elicited by copper (Table 4).

| Test Media | DOC (mg/L) | Dissolved Cu $EC_{50}$ value in µg/L (95% confidence limits) | | |
|---|---|---|---|---|
| | | *Mytilus galloprovincialis* | *Dendraster Excentricus* | *Strongylocentrotus purpuratus* |
| GCML | 1.2 | 10.9 (10.8-11.0) | 18.9 (18.7-19.2) | 14.8 (14.6-15.1) |
| DOC I | 2.1 | 21.0 (20.8-21.1) | 36.4 (35.8-36.9) | 24.3 (24.1-24.4) |
| DOC II | 3.5 | 31.6 (31.3-31.9) | 46.2 (45.4-47.0) | 30.2 (29.8-30.6) |

| | | | | |
|---|---|---|---|---|
| SF Bay | 5.0 | 37.2 (37.0-37.5) | >75.8 (NA-NA) | 46.4 (45.7-47.2) |
| NSDB | 1.3 | 14.5 (14.3-14.6) | 27.2 (26.7-27.8) | 16.6 (16.4-16.9) |
| SSDB | 1.8 | 9.2 (9.1-9.2) | 28.3 (27.9-28.7) | 17.4 (17.2-17.6) |

*Table 4: Summary of measured DOC and dissolved Cu EC50 determinations for ambient water samples for Mytilus galloprovincialis, Strongylocentrotus purpuratus, and Dendraster excentricus testing performed*

As some of the experiments were carried out in natural seawaters while others involved the addition of humic acid DOC to natural seawaters, the binding capacity of the DOC will vary and it is therefore assumed that 50% of the natural seawater DOC and 100% of the DOC added as humic acids is actively binding. This assumption is supported by copper speciation data in marine waters (Hiemstra and Van Riemsdijk 2006).

It can be concluded that when comparing the protective effects of active (i.e. available for copper detoxification) DOC, there exists a statistically proven relationship between the fitting curves for the data sets of the six species, indicating the degree of protection provided by the DOC is similar (power function), with the differences in sensitivities described by the multiplier. This correlation is expected, because the reduction in toxicity by binding to dissolved organic carbon is an extra-cellular function, and should not be species specific.
The correlation was based upon $EC_{50}$ data, because this provides a statistically stronger description of toxicity than the NOEC, which is a function of concentration range selection. However, logically, because the complexation is an external mechanism, the correlation between DOC and the consequent reduction in toxicity will in practice be the same whether it be applied to the $EC_{50}$, the $EC_{10}$ or the NOEC. Therefore, because the $EC_{50}$ value is statistically stronger than NOEC values, normalisation of NOEC data based upon the correlation derived from $EC_{50}$ data is considered to be the most scientifically justified approach to provide a protective PNEC.

Because the six data sets are statistically equivalent, it is appropriate to combine them for derivation of an overall descriptor of the protective effects of DOC. The data are presented graphically in Figure 7, normalized to the most sensitive species in the data set. Such normalisation is done by dividing the average sensitivity of the species (at coastal water DOC of 2 mg/L) by the average sensitivity of the most sensitive species (*M. edulis* at DOC of 2 mg/L).

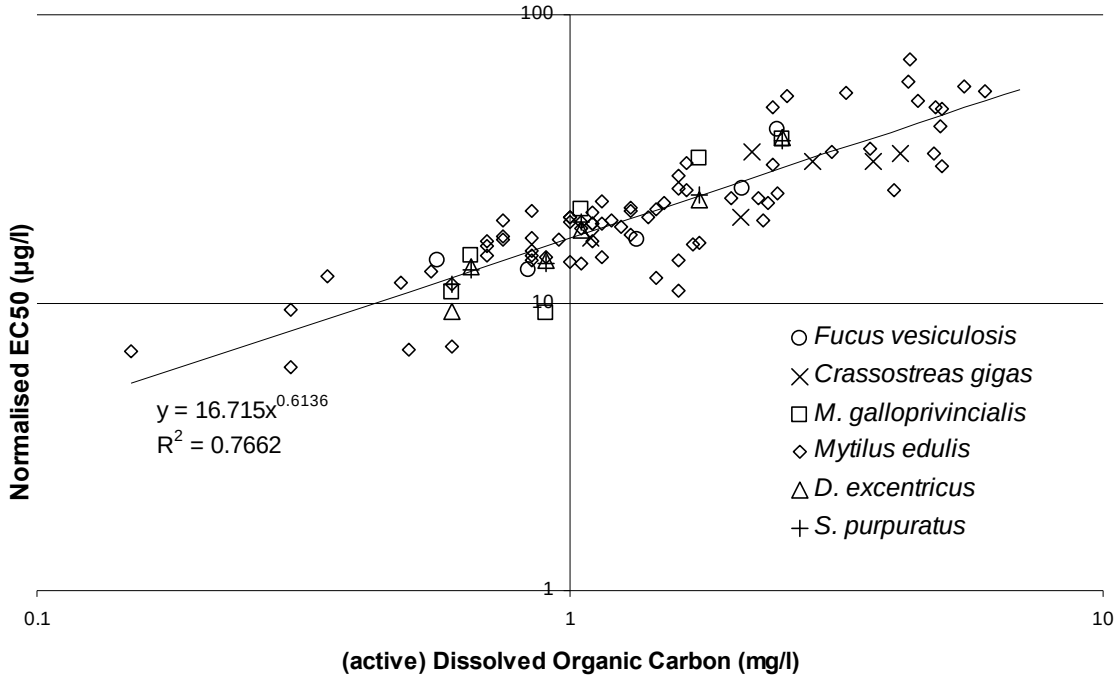



*Figure 6: Log-Graphical representation of the correlation of $EC_{50}$ (normalised to the most sensitive species in the data set) with active DOC*

In conjunction with the statistical assessment of the predictive power of the DOC correlation, all calibration data were plotted against the predicted $EC_{50}$ data**).** A graphical representation of this analysis (Figure 7) shows clearly that the combined DOC descriptor has the capacity to predict effects over six species representing three diverse phyla (*Chromophycota, Mollusca, Echinodermata),* indicating its applicability in normalising data from the high quality data set in order to define a chronic PNEC for the marine environment.

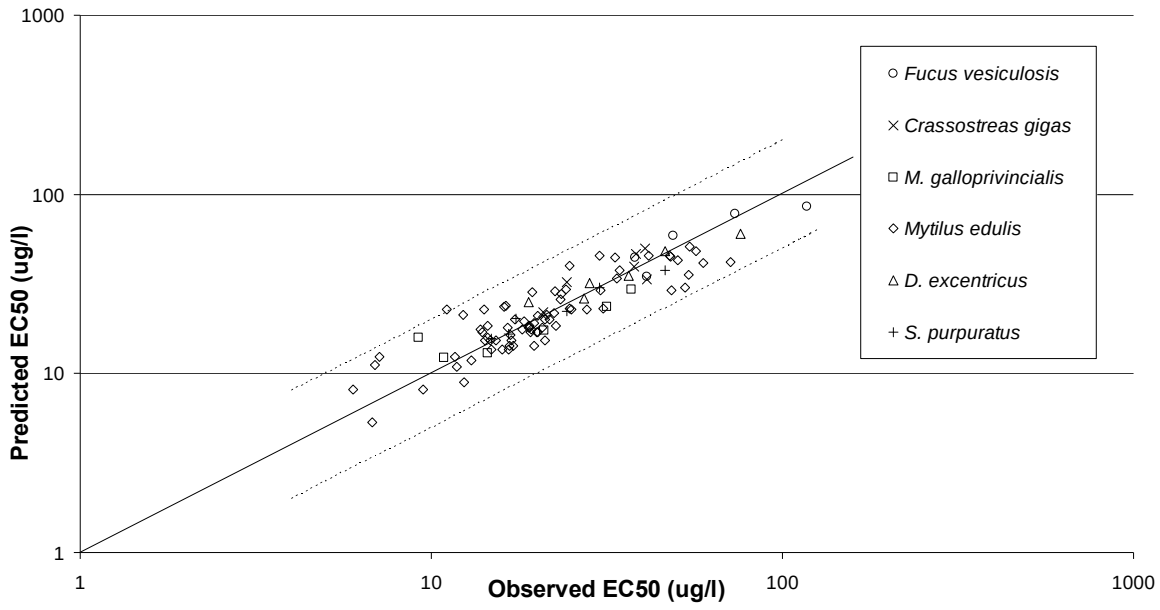



*Figure 7: Predictive capacity as shown by observed vs. predicted effect levels ($EC_{50}$, as dissolved Cu) of the species and endpoint specific models. Dotted lines indicate the range $EC_{50} \div 2$ to $EC_{50} \times 2$.*

Incorporating this DOC normalisation into the high quality NOEC data set, for the largest datasets (*Crassostreas gigas*, n = 6, *Fucus vesiculosis*, n = 5), the DOC normalisation was able to reduce the uncertainty in the range of NOEC values. In small datasets (n = 2) where the range was originally <2, the incorporation of DOC had an overall improvement of the data comparison (average factor 1.6 before normalisation, 1.4 after normalisation), but the results were less conclusive (Table 5)

| | Range(µg/L ?) before normalisation | Factor | Range(µg/L ?) after normalisation | Factor |
|---|---|---|---|---|
| *Crassostreas gigas* | 10.4 – 47.1 | 4.5 | 7.0 – 12.8 | 1.8 |
| *Fucus vesiculosis* | 11.0 – 46.0 | 4.2 | 12.4 – 25.0 | 2.0 |
| | Range(µg/L ?) before normalisation | Factor | Range(µg/L ?) after normalisation | Factor |
| *Paracentrotus lividus* | 8.8-16.5 | 1.9 | 9.3-16.5 | 1.8 |
| *Phaeodactylum* | 3.1- 5.7 | 1.8 | 4.1- 4.9 | 1.2 |

| | | | | |
|---|---|---|---|---|
| *tricornutum* | | | | |
| *Mytilus edulis* | 6.0- 6.2 | 1.0 | 6.0- 7.2 | 1.2 |

*Table 5: Comparison between the interspecies variability in NOEC data before and after normalisation*

For marine sediments, similar bioavailability parameters play a role as what has been encountered in freshwater sediments. Both Acid Volatile Sulfides (AVS) as organic carbon may mitigate metal toxicity in marine environments. Di Toro et al (1990) introduced and proved even his SEM-AVS concept for the first time using 10 d acute sediment toxicity tests with the marine amphipods *Ampelsica abdita* and *Rhepoxynius hudsoni* and using cadmium as model toxicant.

## 5. RISK CHARACTERIZATION FOR THE MARINE RISK ASSESSMENT

### 5.1 Derivation risk characterization ratios

The impact of metals and metal compounds on the marine environment that are released from point and diffuse sources over a wider area can be assessed in a similar way as for the general methodology outlined for the freshwater environment that involves the comparison of the PEC with the Predicted No Effect Concentrations (PNEC) or more advanced, probabilistic risk contributions.

This should be done separately for each of the following environmental marine protection targets: aquatic ecosystem; and, predators and top predators.

The PNEC values that potentially need to be derived (ECHA 2008b Chapter E) are shown in Table 6.

| **Local** | **Regional** |
|---|---|
| Water: PEClocalseawater/PNECsaltwater | Water: PECregionalseawater/PNECsaltwater |
| Sediment: PEClocalsediment/PNECmarine sediment | Sediment: PECregionalsediment/PNECmarine sediment |

| |
|---|
| Predators<br>[(PEClocalseawater,ann + PECregionalseawater) · 0.5 · BCF[4]fish · BMF1]/PNECoralpredator |
| Top predators<br>[(0.1 · PEClocalseawater,ann + 0.9 · PECregionalseawater) · BCFfish · BMF1 · BMF2]/PNECoraltop predator |

*Table 6: Overview of PEC/PNEC ratios considered for marine risk assessment **

** These ratios are derived for all stages of the life-cycle of a compound. The regional risk characterisation for each compartment is based on the sum of regional ratios (RCR values) for all life-cycle stages. The PEC-local is based on the sum of the local concentration and the PEC-regional (sum).*

The derivation of the PNEC and the metal specific considerations that need to be taken into account has been discussed in previous chapters. For the exposure, mostly general guidance for the calculation of marine PEC values applicable for most substances is given below. Only a limited number of metal- specific guidances can be given for this section.

Indeed, metals for which PNEC Freshwater/marine > 1 and don't express a risk at FW level (or less than 10) can be assumed as not requiring further RCR guidance because they will not be capable of expressing risk.Those metals expressing a risk in the FW environment and especially those with FW PNEC/Marine close to or smaller than 1 deserve particular attention.

### 5.2 Calculation of PEC regional for the marine aquatic compartment

Within Chemicals management frameworks, the potential impacts of multiple point and diffuse sources of substances entering the marine environment (eg from a river plume entering in coastal sea water) are evaluated. According to eg REACH guidance provided, a marine regional generic environment is defined as an area of coastal sea that receives all the water from the rivers from the regional system. This seawater compartment is exchanging substances with the continental seawater compartment by dispersion and advection (a current of seawater flowing in a certain direction). The size of the coastal compartment in EUSES for example, is 40 km long,

[4] BCF (bioconcentration factor) and BMF (biomagnification factor)

10 km wide and 10 m deep. In addition to the input from the regional river water, it receives 1% of the direct releases from the inland sources that is supposed to represent a relevant fraction of the sources that are located near the sea and also have direct releases into the seawater compartment. Most of the relevant characteristics of the coastal compartment are similar to the freshwater compartment apart from the suspended matter concentration that is set to 5 mg/L.
This and other comparative scenarios can be modeled with a multi-media fate model that is also used for the freshwater PEC calculations, modified to allow dispersive exchange between the coastal zone to the continental sea water and specific for metals ignoring biodegradation and volatilization. By default, mixing of river water into the coastal seawater gives a dilution factor of approximately 10. As a result, concentrations in coastal seawater are expected to be a factor of 10 (for conservative substances) or more (for substances that react or sediment) lower than in river water.

The calculation of $PEC_{regional,marine}$ according to this standard scenario may be sufficient for generic risk assessment. If additional information is available on sources and releases and site-specific information on the suspended matter concentration, the flow rate and the dispersion velocity, the generic assessment can be made more site-specific by overriding some of the default parameters or can even be replaced by site-specific models. The dispersion velocity greatly affects all calculated concentrations, while in addition the suspended matter content further affects the dissolved concentration in seawater. The ionic composition of seawater also has a considerable influence on both solubility and partitioning of metals and metal compounds. In the absence of marine specific data, there might be sufficient information available on a case-by-case basis to allow the relevant partition coefficient in seawater to be calculated from the freshwater data. Otherwise, measurements under marine conditions may be necessary. For charged chemicals, including many trace metals and their species, models indicate a general reduction in partitioning from river to sea, despite an accompanying increase in pH of about 1-2 units, because of competitive adsorption and complexation with seawater ions.

For the marine environment, more tailor- made models are available that can be used to assess the concentrations in certain specific compartments (bays, estuaries, regions) of the marine environment to which specific industrial sites discharge wastewater.

### 5.3 Calculation of $PEC_{local}$ for the marine aquatic compartment

The use of local marine exposure scenarios can be necessary for specific sites releasing directly into the sea. In such cases, potential local releases to the marine environment can occur and, hence, it is necessary to perform a local exposure estimation for the local marine environment. Dilution and the presence (or absence) of secondary treatment plant (STP) parameters have large influences on the local concentration in seawater (Clocalseawater). The calculation needs to consider whether effluents are treated in an STP or not. For discharges to a coastal zone, local dilution will be greater than in a freshwater river. First, initial dilution may occur if the density between the effluent and the saline receiving medium differs (Lewis 1997). The initial dilution factor is usually around 10. Further dilution due to currents can also be assumed, particularly if the point of release is subject to tidal influences. In the Baltic or the Mediterranean sea, where there are almost no tidal influences compared to the Atlantic Ocean or the North Sea, only initial dilution may occur on calm days, but normally, further dilution due to currents is probable. Dilution factors of more than 500 have been determined from model simulations (based on current measurements) in the North Sea, 200 m away from the discharge point (eg Pedersen et al 1994). In “site-specific” assessments, due account can be taken of the true dilution available to the given emission as well as the true partitioning coefficient for the marine environment under consideration.

A realistic worst case dilution factor for discharges to a coastal zone of 100 may be assumed if no further information is available. The same estimation method as for inland exposure estimation can then be used to obtain the local concentration in seawater (Clocalseawater). For estuaries, which are influenced by currents and tidal movements, it is assumed as a first approach that they are covered by either the inland or the marine risk assessment. Specific approaches (using higher tier models) can be used if needed.

### 5.4 Calculation of $PEC_{local}$ for the marine sediment compartment

The concentration in freshly deposited sediment is taken as the PEC for sediment; therefore the properties of suspended matter are used. The concentration in bulk sediment can be derived from the corresponding water body concentration, assuming a thermo-dynamic partitioning equilibrium (Di Toro et al, 1991).

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