

Original Article

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Bioavailability-Based Sediment Risk Assessment for Nickel

Development of a Bioavailability-Based Risk Assessment Approach for Nickel in Freshwater Sediments

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**ABSTRACT**

To assess nickel (Ni) toxicity and behavior in freshwater sediments, a large-scale laboratory and field sediment testing program was conducted. The program used an integrative testing strategy to generate scientifically based threshold values for Ni in sediments and to develop integrated equilibrium-partitioning based bioavailability models for assessing risks of Ni to benthic ecosystems. The sediment testing program was a multi-institutional collaboration that involved extensive laboratory testing, field validation of laboratory findings, characterization of Ni behavior in natural and laboratory conditions, and examination of solid phase Ni speciation in sediments. The laboratory testing initiative was conducted in 3 phases to satisfy the following objectives: 1) evaluate various methods for spiking sediments with Ni to optimize the relevance

of sediment Ni exposures; 2) generate reliable ecotoxicity data by conducting standardized chronic ecotoxicity tests using 9 benthic species in sediments with low and high Ni binding capacity; and, 3) examine sediment bioavailability relationships by conducting chronic ecotoxicity testing in sediments that showed broad ranges of acid volatile sulfides, organic carbon, and Fe. A subset of 6 Ni-spiked sediments was deployed in the field to examine benthic colonization and community effects. The sediment testing program yielded a broad, high quality data set that was used to develop a Species Sensitivity Distribution for benthic organisms in various sediment types, a reasonable worst case predicted no-effect concentration for Ni in sediment ( $PNEC_{\text{sediment}}$ ), and predictive models for bioavailability and toxicity of Ni in freshwater sediments. A bioavailability-based approach was developed using the ecotoxicity data and bioavailability models generated through the research program. The tiered approach can be used to fulfill the outstanding obligations under the European Union (EU) Existing substances RA, EU REACH, and other global regulatory initiatives. *Integr Environ Assess Manag* 2015;X:000&ndash;000. ©2015 SETAC</ABS>

**Keywords:** bioavailability modeling, field validation, Ni, sediment, Species Sensitivity Distribution</KWG>

## INTRODUCTION</H1>

Recently, a multi-laboratory, multi-phase research project was conducted to provide a scientific basis for a bioavailability-based approach for assessing risks of nickel (Ni) in sediments. This project used sediments that were spiked with soluble Ni to collect laboratory (Besser et al. 2013; Brumbaugh et al. 2013) and field (Costello et al. 2011; Custer 2012) ecotoxicity information. The impetus for this research project was to fill data gaps identified in the European Union's Existing Substances Risk Assessment of Nickel, which was a predecessor of Europe's Registration, Evaluation, Authorisation of Chemicals (REACH). The goal of these legislative initiatives is to assess the risks of ongoing production and use of chemical substances to humans and the environment, including the sediment compartment. Ni is also a priority substance under the European Union (EU) Water Framework Directive (WFD) (Dir. 2013/39/EU) (Official Journal of the European Union 2013), and deriving a sediment Environmental Quality Standard

for Ni is a possible way for managing risks that are identified, e.g., through REACH.

Earlier attempts to develop sediment toxicity data for Ni using laboratory toxicity tests were unsuccessful, largely because Ni spiked into natural test sediments diffused from the sediment into overlying water, resulting in overlying water concentrations sufficiently high to cause toxicity (Vandeghechuchte et al. 2007). This outcome highlights the critical need to ensure sediment spiking methodologies produce results representative of natural field sediment to avoid test outcomes that are related to laboratory artifacts. Laboratory results (Vandeghechuchte et al. 2007) and results of a Ni field recolonization study (Nguyen et al. 2011) indicated the importance of sediment parameters (e.g., acid volatile sulfides [AVS]) as possible mitigating factors for Ni toxicity. The European Commission decided in 2008 that additional information was required before a scientifically sound risk assessment of Ni to freshwater organisms could be made (Official Journal of the European Union 2008).

A recent workshop sponsored by the European Chemicals Agency (ECHA) identified new scientific developments within sediment risk assessment and made recommendations on incorporating these advances into sediment risk assessment guidance (ECHA 2014). Several of the issues discussed at the workshop are specifically relevant for metals, including approaches for introducing metals into test sediments (i.e., spiking) and the development of metal-specific bioavailability models. Other broader issues that were discussed are also applicable to metals, including the identification of important taxonomic groups that should be included in testing strategies, and minimum numbers of species and requisite taxonomic groups that are needed before probabilistic approaches like the Species Sensitivity Distribution (SSD) can be used.

The recently completed Ni sediment research program addressed many of the developments that were discussed at the ECHA workshop and represented an example for how research findings can be implemented into sediment risk assessment. This article describes this research on Ni and its incorporation into risk assessment (Figure 1), including 1) laboratory sediment toxicity testing, 2) development of bioavailability models, 3) determining effects thresholds, and 4) field validation. The first section focuses on obtaining sediments with appropriate characteristics and developing appropriate spiking methods for Ni in sediments. This section will also address issues

pertaining to obtaining sufficient ecotoxicity data to use probabilistic approaches to determine predicted-no-effects-concentrations (PNECs). A lack of specific guidance on the quantity and quality of ecotoxicity data needed for probabilistic approaches and the limited numbers of standardized sediment toxicity test species that are currently available make this an especially challenging issue. The second section describes how relationships between organism response and sediment characteristics were identified and used to develop bioavailability relationships in both the laboratory and field. The third section describes how these components were brought together in a tiered bioavailability-based approach to assess risks of sediment-associated Ni at regional and local scales, and in ways that satisfy the requirements of both REACH and the WFD. Finally, the fourth section shows how field studies evaluated the degree of uncertainty associated with the laboratory-based ecotoxicity data and bioavailability modeling. Key advances in laboratory and field assessments of Ni were achieved and are relevant for other metals.

## Sediment selection

The use of natural sediments in the determination of threshold concentrations or development of bioavailability models in either the laboratory or the field setting requires careful consideration of sediment selection. Before selection, natural sediments should be evaluated for several key factors, including geographical relevance (e.g., regional relevance), relevance of physical and chemical sediment characteristics (e.g., pH, total organic carbon [TOC], AVS, Fe), elevated background concentrations, and regulatory considerations. Sediments must be identified and evaluated with the objectives of the testing program in mind. For instance, for determination of a PNEC, a reasonable worst case (RWC) sediment, or sediment representing a potential worst case exposure, should be used. According to REACH guidance, a RWC-PNEC should reflect conditions that represent the 10th percentile of physical and chemical sediment characteristics (ECHA 2008a). Therefore, sediments for which the presence of toxicity mitigating factors (AVS, TOC, and Fe) do not represent a RWC should be excluded from the RWC-PNEC evaluation. The physicochemical characteristics of the RWC sediment in the Ni sediment research program were slightly below the 10th percentile distribution of AVS (AVS <1.0  $\mu\text{mol/g}$ ), TOC (TOC < 1%), and Fe (0.13%–0.34%) for sediments collected from EU surface waters, and hence represent a

RWC sediment exposure for surface waters within the EU.

Alternatively, if the goal of the testing program is the development of models to predict bioavailability and toxicity in the sediment compartment, sediments that span broad ranges of physicochemical characteristics should be considered. Sediments used in the development of the predictive Ni bioavailability model ranged from less than 1.0 to 36  $\mu\text{mol/g}$  AVS and 0.4% to 10.5% TOC. Table 1 identifies the chemical and physical parameters of all of the sediments used in Ni sediment toxicity tests.

#### Appropriate spiking methods

Adding metals to sediments (spiking) is the first critical step in the chemical-specific risk assessment process since they allow concentration–toxicity response relationships to be established for various benthic invertebrate species. Traditional spiking methods involved adding soluble metal salts to sediments without further amendment. These approaches have been revisited recently due to artifacts they produce, including metal hydrolysis that depress porewater pH and subsequently inhibit the binding of metals to sediment solid phases (Hutchins et al. 2007) and because Ni diffusing into overlying water can contribute to toxicity (Vandegheuchte et al. 2007; Simpson et al. 2004). These artifact-driven results highlight the need to develop methods where spiked sediments are more representative of field contaminated sediments.

Brumbaugh et al. (2013) developed a 2-step method for spiking Ni into freshwater sediments based on earlier approaches used for spiking Cu and Zn into marine sediments (Hutchins et al. 2008). The 2-step approach involved adding high concentrations of soluble  $\text{NiCl}_2$  to sediments followed by immediate pH adjustment with NaOH to mitigate effects of hydrolysis. The product of the first step, referred to as a “super-spike,” was equilibrated for 4 weeks. After this equilibration, the super-spike sediment was diluted with unspiked sediment and equilibrated for 6 additional weeks to create a series of Ni concentrations. This concentration series was ultimately used to create gradients of sediment Ni concentrations, which in turn were used to establish concentration–response relationships in toxicity tests. The duration of the second equilibration period was chosen based on time-course data showing that porewater Ni

concentrations reached equilibration by the end of the 6-week period (Brumbaugh et al. 2013; Besser et al. 2011).

Brumbaugh et al. (2013) used a number of diagnostic measures to evaluate the spiked sediments. The first involved comparisons of Ni distribution coefficients ( $K_d$ ) between the laboratory-spiked sediments and field sediments.  $K_d$  represents the ratio of Ni between porewater and solid phases within the sediment. Log  $K_d$  for 2 sediments that reflected extreme ranges in terms of sediment chemistry ranged from 3.5 for a low AVS, low organic carbon sediment (i.e., low metals binding sediment) to 4.5 for a high AVS, high organic carbon sediment (i.e., high metals binding sediment). This range is consistent with the 10th to 90th percentile range (log 3.3 to log 4.2) reported for field contaminated sediments (Allison and Allison 2005).

To evaluate consequences of the spiking approach on overlying water Ni concentrations and ecotoxicological effects, toxicity tests with the amphipod *Hyaella azteca* were performed following standard methods (USEPA 2000; ASTM 2010). Nickel-spiked sediments were placed in sediment toxicity chambers (0.3 L beakers filled with 0.1 L sediment and 0.175 L overlying water). Dissolved Ni concentrations in overlying water were monitored for up to 27 d (6 d before introducing organisms, and 21 d after organisms were added). Overlying water was exchanged at rates from 2 to 8 volume exchanges per day. Dissolved (<0.45  $\mu\text{m}$ ) Ni concentrations remained above reported toxicity thresholds, e.g., the US Environmental Protection Agency (USEPA) Continuous Criteria of 52  $\mu\text{g Ni/L}$  (USEPA 2009) in chambers where overlying water exchange rates were between 2 and 4 volume exchanges per day. Importantly, exchanging overlying water had no effect on total recoverable Ni concentrations in the sediments, indicating that the Ni lost from the sediments represented a small exchangeable fraction of total sediment Ni. Brumbaugh et al. (2013) concluded that an overlying water exchange rate of 8 times per day for the duration of the toxicity test was required to maintain acceptably low Ni concentrations (e.g., <52  $\mu\text{g Ni/L}$ ) in the overlying water while maintaining the target sediment Ni concentrations. Additionally, they recommended that sediments be added to toxicity test chambers at least 1 week before the addition of test organisms to allow the development of an oxic sediment layer, which occurs in situ in most surficial sediments (Boothman and Helmstetter 1992). Another recommendation was for overlying water to be replaced at a frequency of 8 times per day during the 1 week pre-

exposure period. This approach mitigates the flux of Ni to the overlying water during testing, creating concentration gradients with dissolved porewater concentrations as high as 48  $\mu\text{g Ni/L}$  at the end of the incubation period (Besser et al. 2011). All of these steps act to minimize overlying water Ni concentrations and thereby increase the causal relationship between observed organismal response and exposure of Ni in sediment phases (i.e., porewater and solid sediment phases).

Time course analysis by Brumbaugh et al. (2013) of the sediments before they were added to the toxicity test chambers showed the proportion of spiked Ni associated with porewater decreased over time, suggesting corresponding increases in binding to solid sediment phases occurred. Extraction with 1 N HCl liberated both AVS and Ni associated with a range of solid phases that included amorphous sulfides, which comprise AVS. This would be consistent with results of a field deployment of Ni-spiked sediments by Nguyen et al. (2011), which showed a protective effect of AVS against Ni re-colonization by sediment organisms. Nguyen et al. (2011) did not neutralize sediment porewater after spiking sediments with Ni, although in situ toxicity tests performed in conjunction with the deployment of the spiked sediments showed no effects to organisms located in the water column just above the spiked sediments. Results of the extraction gave insight into the behavior of Ni in spiked sediments. NiS is not soluble in 1 N HCl (Cooper and Morse 1998); therefore, in instances where molar quantities of Ni exceed those of AVS, there should be no recovery of AVS if all of the spiked Ni reacted with FeS to form NiS. Brumbaugh et al. (2013) observed partial recovery of AVS and concluded that the spiked Ni was not reacting with AVS in a stoichiometric manner, largely because of competitive binding with other sediment phases (such as organic matter and iron oxyhydroxides). This was confirmed in solid phase speciation analyses reported by Brumbaugh et al. (2013) indicating that the spiked Ni was predominantly associated with organic matter, iron oxy-hydroxides, carbonates, and other  $\text{O}_2$ -bearing phases. Costello et al. (2011) used the same spiking approach in 8-week field deployments of Ni-spiked sediments. They observed a progressive increase in partitioning to the solid phase (i.e., an increase in  $K_d$ ) over the 8-week period and also documented a progressive change in the solid phases with which Ni was associated. At the beginning of the exposure, Ni was associated with organic matter. The dominant phase changed over time, and at 8 weeks the majority of solid phase Ni was associated with Fe and Mn oxides. The same phenomenon was

noted in recent studies of Cu in spiking studies where Cu bioavailability and toxicity was tied to a shift in partitioning to the amorphous Fe oxide fractions and decreasing porewater concentrations (Costello et al. 2015). This was also recently noted in similar spiking studies with Ni with increased partitioning to the crystalline Fe oxide fraction (GA Burton, University of Michigan, School of Natural Resources and Environment, Ann Arbor, Michigan, USA, personal communication). Although it is clear that other sediment characteristics that covaried with AVS were probably factors contributing to the Ni partitioning, the role of AVS was illustrated by the consistently low porewater Ni concentration in treatments having negative SEM-AVS values (Brumbaugh et al. 2013). One possible explanation is that porewater Ni and fluxes of Ni in general could be influenced to a large extent by excess AVS present in deeper sediment layers (Di Toro et al. 1992). Among the 8 sediments characterized by Brumbaugh et al. (2013), AVS was highly correlated with TOC ( $r = 0.826$ ), % fines (0.760), and total recoverable iron (0.919). Therefore, an alternative explanation to the strong relationships observed between AVS and Ni toxicity is that AVS is an indicator of the influence of all relevant sediment phases on the partitioning of Ni.

The dynamic nature of Ni in sediments suggests that sediments used in laboratory testing do not account for the natural aging processes in the field that reduce the availability of Ni due to changes in solid phase speciation. Hence, even attempts to create spiked sediments with realistic characteristics will result in worst case exposures and may overestimate toxicity to benthic organisms. Regardless, toxicity testing using laboratory-spiked sediments remains a valid approach for determining interspecies variability to specific metals, which plays an important role in chemical safety frameworks. There is a strong need to harmonize approaches for spiking metals into test sediments for this purpose, and the work of Brumbaugh et al. (2013) for Ni, along with similar approaches described for Cu, Pb, and Zn (Hutchins et al. 2008; Vandegehuchte et al. 2013), indicate that the 2-step approach is preferable to previous methods because it results in sediments that better represent exposure occurring at contaminated sites.

Appropriate strategies for quantifying exposure</H2>

Laboratory and field components of the Ni effects assessments focused on thorough



characterizations of exposure conditions and sediments to demonstrate shifts in Ni partitioning, bioavailability, and toxicity while minimizing experimental artifacts. Nickel associated with solid and porewater sediment phases was measured, as was Ni in overlying water. Porewater was collected using sediment peepers, which collect dissolved porewater constituents less than 0.45  $\mu\text{m}$  via diffusion (Brumbaugh et al. 2013). Additionally, diffusive gradients in thin films (DGT) were used to characterize labile Ni flux and concentrations in situ in laboratory tests (Brumbaugh et al. 2013) and in field deployments (Costello et al. 2012).

Costello et al. (2012) determined that the use of DGT for field-based studies was not a strong predictor of benthic community response compared to SEM-AVS/foc, as DGT appears to overestimate Ni exposure to sediment organisms. However, recent studies on estuarine and marine sediments suggest DGTs do mimic bioavailability and benthic responses (Simpson et al. 2012; Amato et al. 2014). As indicated by Costello et al. (2011), DGTs may, in some cases, overestimate Ni exposure to sediment organisms. This may be due to the resin that comprises the gel within DGTs, which may actively mobilize Ni from solid phases that are not available to sediment organisms. Additionally, DGTs can bind metals associated with dissolved organic carbon (Zhang 2004), whereas DOC-bound Ni is believed to be unavailable to aquatic organisms (Deleebeeck et al. 2008). Hence, analysis of Ni porewater exposures via DGT in field studies should be carefully evaluated for validity.

#### Collection of ecotoxicity data

Increasingly, regulatory programs are establishing data quality criteria that encourage the use of standardized test methods and good laboratory practices. The aim of this initiative is to increase the quality and reliability of ecotoxicity data used for regulatory decision-making. However, this practice may decrease the number of taxonomic groups that can be used in the determination of effects thresholds. This is especially true for sediment risk assessment, where relatively few standardized toxicity test species have been established. The availability of a low number of standardized test species creates potential boundaries for considering the use of probabilistic tools like the SSD, where the number of species included in the analysis is one factor determining statistical confidence. Furthermore, no guidance is available on the number of species and taxonomic groups that are needed to represent an adequate database of benthic

species for the determination of reliable sediment effects thresholds.

The approach taken for the Ni sediment toxicity research project was to use as many species in toxicity tests as possible. The REACH regulation risk assessment approaches are based on chronic ecotoxicity data, so only chronic toxicity tests were considered. Testing was performed in 2 phases, and both of these phases followed the 2-step spiking procedure described by Brumbaugh et al. (2013). First, 9 species of benthic invertebrates were tested at the US Geological Survey laboratory in Columbia, MO: amphipods (*Hyalella azteca*, *Gammarus pseudolimnaeus*), mayfly (*Hexagenia* sp), oligochaetes (*Tubifex*, *Lumbriculus variegatus*), mussel (*Lampsilis siliquoidea*), nematode (*Caenorhabditis elegans*), and midges (*Chironomus dilutus* and *C. riparius*) (Besser et al. 2013). Characteristics of the sediment toxicity tests are included in the Supplemental Data (Table S1). Data for the nematode *C. elegans* were not included because of low control survival in several of the sediments tested (Besser et al. 2013). Additionally, results of tests with *L. siliquoidea*, *C. riparius*, *C. dilutus* and *T. tubifex* resulted in unbounded NOECs; that is, the test organisms showed no response at the highest sediment Ni concentration. Therefore, the first phase of testing resulted in the availability of 4 chronic EC10 values.

To broaden the database and increase the statistical confidence in the SSD model, additional species were tested in a second phase, which took place at the Laboratory of Environmental Toxicology and Aquatic Ecology at Gent University, Belgium. Test organisms included 2 previously untested species including a bivalve (*Sphaerium corneum*) and a mayfly (*Ephoron virgo*), and also included retesting 2 of the species that were unresponsive in the first testing phase, including *T. tubifex* and *C. riparius* (Vangheluwe and Nguyen 2014) (test characteristics shown in Table S1).

For both phases, tests included sediments with broad ranges of parameters known or suspected to influence Ni bioavailability (from the 10th to 90th percentile of the distribution in European freshwater sediments) (Table 1). Importantly, 3 of the sediments (SR, Dow, and Braekel) satisfied the definition of a RWC, i.e., sediments reflecting conditions that represent the 10th of parameters affecting Ni toxicity (ECHA 2008a). Each species was tested in at least one of these

sediments.

Species comparisons in high bioavailability, low AVS sediments that showed responses varied by nearly an order of magnitude, with the amphipod *H. azteca* showing the lowest EC10 of 149 mg Ni/kg dw for the biomass endpoint and the oligochaete *T. tubifex* showing the highest EC10 of 1100 mg Ni/kg dw, also for the biomass endpoint (Figure 2). Sediment chemistry clearly influenced ecotoxicological response. For example, EC10 values for *H. azteca* in Spring River (AVS = 0.7  $\mu\text{mol/g dw}$ ) and Dow Creek (AVS = 0.9  $\mu\text{mol/g dw}$ ) were 160 and 140 mg Ni/kg dw, respectively. Similarly, the EC10 for *S. corneum* in Braekel 1 sediment (AVS = 1 to 2  $\mu\text{mol/g dw}$ ) was 388 mg Ni/kg dw (Figure 2). These 3 sediments showed the lowest AVS concentrations and were near the 10th percentile value of AVS distributions in EU surface waters of 0.8  $\mu\text{mol/g dw}$ . In sediments with higher AVS concentrations, the EC10 values for these 2 species increased substantially. For example, EC10 values for *H. azteca* in sediments with AVS concentrations greater than the 50th percentile value of 9.1  $\mu\text{mol AVS/g}$  were at least 970 mg Ni/kg dw (Figure 2). Likewise, the EC10 for *S. corneum* in the Lampernesse sediment (AVS = 29 to 30  $\mu\text{mol/g dw}$ ) was 2300 mg Ni/kg dw. In contrast, EC10 values for *T. tubifex* differed little between the low AVS Braekel 1 sediment (AVS = 1 to 2  $\mu\text{mol/g dw}$ ; EC10 = 1100 mg Ni/kg dw) and the high AVS Lampernesse sediment (AVS = 29 to 30  $\mu\text{mol/g dw}$ ; EC10 = 1500 mg Ni/kg dw). General patterns of Ni sensitivity among the different sediment toxicity test species were similar to those observed in water and soil ecotoxicity databases for Ni. For water and soil, crustaceans were among the most sensitive species. The gastropod mollusk *Lymnaea stagnalis* has been demonstrated to be among the most sensitive species in dissolved water-only exposures (Schlekat et al. 2010; Niyogi et al. 2014), but gastropods are not infaunal organisms and are not typically used in sediment testing. Bivalves were included in sediment testing, but were not among the most sensitive species. *Sphaerium corneum* ranked 4th out of 7 species, whereas *L. siliquioda* was unresponsive at the highest exposure concentrations. Although this suggests data from the bivalve species will yield a threshold concentration protective of these groups, it also suggests sediment risk assessments should be performed in conjunction with assessments focusing on pelagic exposures to ensure gastropods, for which overlying water may be more important than exposure to sediment phases, are protected.

A workshop on sediment risk assessment sponsored by ECHA (2014) identified several taxonomic groups that should be considered for future sediment toxicity test developments. For freshwater systems, rooted macrophytes, benthic algae, and microbial processes were suggested because of their importance in supporting benthic communities and their roles in critical geochemical processes. Both individual microbial species and critical microbial processes (e.g., respiration) are sensitive endpoints within soil ecotoxicity databases compiled for Ni and other metals (McLaughlin et al. 2011). Likewise, vascular plants (i.e., *Lemna gibba*) are among the most sensitive taxa in terms of dissolved Ni exposure (Schlekat et al. 2010). At this point, however, tests on these taxonomic groups have not been adapted for sediment exposures, which limits the Ni database to invertebrate species.

### Species Sensitivity Distribution

A number of possibilities exist for obtaining a sediment threshold value for Ni that protects sediment-dwelling organisms. One current probabilistic method aggregates all relevant and reliable ecotoxicity data in a SSD. The SSD approach has been recognized as a viable method for substances with ecotoxicity data for multiple species and taxonomic groups because it recognizes the susceptibility of organisms to contaminant exposure is broadly distributed and, as such, does not occur as a dichotomous threshold. The SSD has greater ecological relevance than simpler alternatives, such as assessment factor (AF) approaches, where the PNEC is calculated by taking the most sensitive ecotoxicity value for a given chemical substance and dividing by an AF. The magnitude of the AF is subjective and is determined based on data type (acute vs chronic), data quantity (i.e., the number of species for which data are available), data quality (i.e., measured test concentrations), and habitat (i.e., freshwater vs marine) (ECHA 2008b). If the AF approach were used for the Ni sediment database under current REACH guidance, the PNEC would be calculated by applying a 10-fold AF on the lowest available EC10 (ECHA 2008b). This approach would yield a PNEC<sub>sed</sub> value of 14.9 mg Ni/kg dw. Given that the ambient Ni sediment concentration in Europe ranges from 9 to 36 mg Ni/kg dw (Swennen et al. 1998), managing Ni in sediments using a PNEC of 14.9 mg Ni/kg dw would not be feasible.

The SSD approach has been accepted in the EU in the determination of PNECs for freshwater pelagic systems (ECHA 2008b). The traditional approach in the EU framework uses the

Aldenberg–Slob approach for fitting a log-logistic distribution to the available chronic ecotoxicity data and to then solve for the 5th percentile of the distribution, a value that is referred to as the hazardous concentration at the 5th percentile, or the HC5. The HC5 theoretically represents a concentration below which 95% of organisms should not be affected by exposure to the toxicant in question. For the Ni database, application of the log-logistic distribution to the ecotoxicity data from the RWC sediments yielded an HC5 of 136 mg Ni/kg dw (Figure 3). The principle behind the SSD is that it serves as an integrated representation of the ecosystem. De Vries et al. (2010) concluded that HC5 values from SSDs based on mortality endpoints should be protective of community structure and function. Furthermore, these authors suggested HC5 values from SSDs based on more sensitive sublethal endpoints, such as the one developed for Ni in this assessment, represent an even more conservative threshold. This suggests the RWC HC5 of 136 mg Ni/kg dw should be protective of benthic communities in most sediments.

To be truly representative, however, the database used to populate the SSD and to determine the HC5 should include a broad range of species and functional groups. Although clear recommendations are made on which freshwater pelagic species should be tested in order to use SSDs, no guidance is currently available for what species would represent an adequate database of sediment organisms. The chronic sediment effects data set generated for 8 benthic species exposed to Ni spiked sediment is representative of different sediment exposure pathways, as well as a variety of feeding strategies and taxonomic groups. The test species include 8 different sediment-dwelling invertebrates, belonging to 4 different orders (i.e., oligochaetes, mollusks, crustaceans, and insects) with different feeding habits and ecological niches. Additionally, testing with *C. dilutus* resulted in an unbounded NOEC because this species did not respond to the highest test concentration. Although it is not feasible to use unbounded NOECs in the SSD, it is clear that the HC5 is protective of this species. To our knowledge, the Ni sediment toxicity data set is the largest chronic data set available for any chemical substance. In summary, the RWC HC5 of 136 mg Ni/kg dw can be seen as a robust and broadly protective threshold concentration.

Bioavailability normalization</H2>

Assessing risks from metals for the sediment compartment are often hampered by the fact that no clear relationship has been established between measured total concentrations of metals in sediments and their potential to cause toxic effects on aquatic life (Di Toro et al. 1992). As a result, comparing total concentrations expressed on a dry or wet weight basis with an established threshold concentration has the potential to result in an under or overestimation of the associated risk. Therefore, bioavailability determinations using sediment chemistry have been broadly recommended as a more accurate approach to establish relevant risk assessments of metals. The SEM-AVS concept was developed to predict situations in which toxicity from sediment-associated metals should not occur. Naturally occurring Fe and Mn mono sulfides have higher solubility products than other metals (e.g., Cd, Cu, Ni, Pb, Zn) and can be displaced by these metals on a mole-to-mole basis, forming insoluble sulfide complexes that decrease porewater metal exposures and exposure of sediment organisms to metals in porewater (Di Toro et al. 1990, 1992; Ankley et al. 1996). In general, metals in sediment will not be toxic if the molar concentration of AVS is higher than that of SEM (SEM/AVS ratio smaller than 1) or if the difference between the molar concentrations of SEM and AVS (SEM-AVS) is used (Hansen et al. 1996) the molar SEM-AVS difference is less than 0.

The applicability of the AVS model to Ni and other metals has been demonstrated in acute responses to field-contaminated (Ankley et al. 1991) and laboratory-spiked (Di Toro et al. 1992; Doig and Liber 2006) freshwater sediments, acute responses to marine laboratory spiked sediments (Pesch et al. 1995), chronic responses to laboratory-spiked sediments for freshwater organisms (Vandegheuchte et al. 2007; Besser et al. 2013), and benthic recolonization of spiked sediments placed into freshwater (Costello et al. 2011; Nguyen et al. 2011) and marine (Boothman et al. 2001) habitats.

Although useful in determining situations where toxicity should not occur, the AVS approach is limited in terms of predicting toxicity. Likewise, the suitability of the AVS approach for oxic sediments and for situations following resuspension events has been questioned because of the lack or reduction of AVS in these situations. Nevertheless, many field studies have documented the utility of the AVS approach, supporting its use by the USEPA (Burton et al. 2005; USEPA 2005; Nguyen et al. 2011). Field studies showed that the AVS approach was conservative and

that SEM Ni needs to exceed AVS by 2 to 8 times in the investigated field sediments before toxicity was observed. This can be explained by the added partitioning of metals to Fe oxides (as discussed above). Predicting toxicity for all sediment types is particularly important for regulatory frameworks like REACH that are based on probable no effects scenarios. To this end, Vangheluwe et al. (2013) evaluated relationships between sediment parameters and Ni ecotoxicity endpoints for 4 sediment toxicity test organisms tested in sediments with widely different ranges of chemical parameters, including the amphipods *H. azteca* and *G. pseudolimnaeus* and the mayfly *Hexagenia* sp. (*T. tubifex* was included in these experiments but no statistical relationship was observed in this round of experiments).

EC20s expressed as either total recoverable Ni or SEM<sub>Ni</sub> showed significant relationships with a range of sediment parameters, including AVS, total recoverable Fe, TOC, cation exchange capacity, silt, total recoverable Mn, and SEM<sub>Mn</sub>. The importance of sediment phases other than AVS indicates that the relationships should be relevant for oxic sediments as well as anoxic sediments. For all species tested, the sediment parameter showing the strongest linear relationship was AVS. Subsequent experiments with the bivalve *Sphaerium corneum*, the insect *Chironomus riparius*, and the oligochaete *Tubifex tubifex* were performed to determine the extent of the AVS relationships with other species (Vangheluwe and Nguyen 2014). Each of these species was tested in sediments ranging in AVS from 1 to 32  $\mu\text{mol/g dw}$ . Chronic ecotoxicity endpoints for each species were significantly related to sediment AVS concentrations (Table 2).

Although the effect of decreasing toxicity with increasing AVS was consistently observed for all species, the magnitude of the effect was not similar among species, and these differences appear to be linked with organism behavior. The strongest mitigating effects of AVS are observed for those species with an epibenthic lifestyle such as *H. azteca*, *S. corneum* and *G. pseudolimnaeus*, with slopes ranging from 0.358 to 0.492 (Table 3). The relationships (i.e., slopes ranging from 0.125–0.180) are less pronounced for the benthic species *T. tubifex*, *C. riparius*, and *Hexagenia* sp that exhibit more burrowing activity and subsurface feeding. Chandler et al. (2014) observed a similar pattern in exposures of marine invertebrates to sediment-associated Ni where active bioturbating amphipods showed greater oxidation of AVS and greater susceptibility to Ni exposure in sediment phases compared with less bioturbative copepods.

The empirical relationships between sediment toxicity endpoints and AVS concentration (Table 2) allow Ni ecotoxicity data to be normalized to different sediment scenarios. For example, if a RWC PNEC is required, then the ecotoxicity data can be normalized to the 10th percentile of AVS that is reported for European freshwater sediments, which is 0.77  $\mu\text{mol AVS/g dw}$  (Vangheluwe et al. 2008). The process of bioavailability normalization begins with the normalization of ecotoxicity values (e.g., EC10 values would be used for REACH) from each test to the target AVS concentrations (e.g., 0.77  $\mu\text{mol/g dw}$  for the RWC scenario). For species that were tested in multiple sediments, the geometric mean of normalized ecotoxicity values were calculated. The log-normal distribution of normalized geometric mean data was then determined using the ETX program (van Vlaardigen et al. 2005), and from this distribution the HC5 was calculated. When the RWC AVS of 0.77  $\mu\text{mol/g dw}$  was used, the calculated HC5 was 136 mg Ni/kg dw. The impact of bioavailability normalization was evaluated by using AVS concentrations from the 8 sediments chosen by Besser et al. (2013) to represent ranges of AVS that are typically encountered in European surface waters (Figure 3). The HC5 for the highest AVS concentration of 38.4  $\mu\text{mol/g dw}$  was 437 mg Ni/kg dw, which is 3.2 times higher than the RWC HC5. This range of HC5 values offers the same level of ecological protection, and hence serves as a flexible management tool that can be used to address challenges created by naturally varying sediment characteristics.

## Field and mesocosm data

Single-species laboratory tests offer the advantage of controlled laboratory environmental conditions and organism parameters (e.g., life stage). These advantages contribute to statistically robust results, which in turn increase the confidence in the reproducibility of effects thresholds and bioavailability predictions. However, applying laboratory results to natural field conditions is not straightforward, as field conditions vary substantially from laboratory settings. For example, changes in sediment chemistry can occur through natural disturbance events such as storms, which may result in sediment resuspension, oxidation of AVS, and increased availability of metals to infaunal organisms. Also, organisms in natural settings may be subject to additional stress associated with the dynamic environmental conditions that occur in the field, which include: diurnal fluctuations in temperature, pH, and dissolved  $\text{O}_2$ ; food quality and quantity; and



ecological interactions such as predation and competition for habitat and food. Finally, field settings may include organisms that are more sensitive than currently available laboratory test species. Therefore, testing laboratory based effects thresholds through field exposures is an important component in sediment risk assessment.

Threshold concentrations and bioavailability models developed from laboratory tests can be validated by performing exposures in natural field settings. Several field studies have specifically examined effects of Ni exposure to natural benthic communities (Burton et al. 2009; Costello et al. 2011, 2012; Nguyen et al. 2011; Custer 2012; Costello and Burton 2014). These studies were performed with a range of different sediment types, were conducted during different seasons, and were carried out in different geographical locations (Europe and North America) and in different types of systems (lotic and lentic), with varying water quality and abiotic parameters. These studies confirmed Ni binding to AVS, organic carbon, and Fe oxides fractions in both laboratory and field exposures, as discussed above.

A streamside experiment (Burton et al. 2009; Custer 2012) performed on a low binding sediment resulted in benthic community effects at the 500 mg/kg dry wt treatment level, but not at 100 mg/kg dry wt. The lowest NOEC of an earlier colonization study performed in Europe in 2005 (Nguyen et al. 2011) resulted in a NOEC of 100 mg Ni/kg dw. Effects were observed at 500 mg Ni/kg dry wt (only 3 spiking levels were used—100, 500, and 1000 mg Ni/kg dw).

The 2 most recent field studies were conducted over a time period of 2 months (Costello et al. 2011) to 9 months (Nguyen et al. 2011), and the colonization of the deployed spiked sediments were followed over time. The results of these studies converge in a range of effects concentrations that are protective of the toxicity results seen in the laboratory sediment testing. No evidence exists to show that field data are more sensitive than laboratory-based HC5 values. To the contrary, these data and similar data for benthic macro-invertebrates and pelagic communities show that field and/or mesocosm data are less sensitive than results of laboratory tests despite exposing a wider range of benthic invertebrates. Results of the colonization study by Costello et al. (2011), performed on the same sediments used by Besser et al. (2013), indicated a field NOEC of 230 mg Ni/kg dw. In this field study, effects on recolonization (expressed with

macroinvertebrate indices) were measured after 28 and 56 days. Effects attributable to Ni exposure were only observed at the 28-day sampling period. Substantial amounts of Ni were lost from sediments over the course of the study, and the sediment factors with which Ni partitioned changed over the course of the experiment as well. However, Ni concentrations at 56 days remained greater than 4500 mg Ni/kg dw in some treatments, which is far higher than the laboratory-based thresholds expressed as total recoverable Ni. Notably, no effects on the composition of the benthic communities were measured at the Day 56 sampling period. The decrease in toxicity was accompanied by a shift in the geochemical phases with which Ni was associated. Together, these observations indicate that Ni undergoes an aging process in sediments, which is a phenomenon that needs to be considered in the application of laboratory-based effects thresholds to field situations.

## Implementation into risk assessment</H2>

Incorporating the information on bioavailability into a practical application for regulatory risk assessment requires a bioavailability-based tiered risk characterization approach. This approach can be used for local or regional scale risk characterization under REACH or for other regulatory purposes, e.g., delineation of contaminated sites. The first tier of the approach is based on a RWC bioavailability scenario, where the RWC is defined as the 10th percentile of sediment AVS concentrations for the region in question (Figure 4). As indicated previously, using the RWC case AVS concentration for EU surface waters of 0.77  $\mu\text{mol AVS/g}$  yields an HC5 of 136 mg Ni/kg dw. Risk characterization at this tier requires determining the predicted environmental concentration (PEC) of Ni, which is expressed as mg Ni/kg dw. The PEC can be obtained from measuring ambient Ni sediment concentrations, or by modeling sediment Ni concentrations using multimedia fate models. The actual risk characterization is simply a comparison between the RWC HC5 and the PEC. The HC5 is considered to be a concentration below which no effects are expected. Therefore, if the PEC is greater than the RWC HC5, then risk is a possibility, and a more detailed characterization is required in the subsequent tier (Figure 4). For this detailed analysis, site-specific AVS concentrations are used to determine a site-specific HC5 value. As indicated previously, the site-specific HC5 can range from 136 mg Ni/kg dw (for the 10th percentile AVS) to greater than 437 mg Ni/kg dw (for the 90th percentile AVS). If ambient Ni

sediment concentrations are greater than the bioavailability normalized HC5, then risk is indicated, and the need to consider appropriate risk management steps is established. When the goal of risk assessment is to predict the Ni concentrations that affect a specific proportion of species, which may be the case in identifying reasonable clean-up goals for highly contaminated sediments, alternative point estimates can be determined. For example, the HC25 would be a concentration protective of 75% of the species represented by the distribution.

To implement the bioavailability-based tiered approach, the following sediment parameters need to be available: total recoverable Ni;  $\Sigma$ SEM (simultaneously extractable metals); and, AVS (acid volatile sulfides). High quality AVS monitoring data are scarce in most areas of the world, meaning that these concentrations may need to be measured to determine the site-specific HC5. Vangheluwe et al. (2013) show that 200 of 338 samples available for the EU were taken from Belgian surface waters. This general approach can be used in other geographical regions if region-specific data required for the normalization process (e.g., AVS) are collected.

## SUMMARY AND CONCLUSIONS

The assessment approach described in this article can be used to support the primary goal expressed in EU regulations such as the Water Framework Directive, which is maintenance or enhancement of biodiversity. For larger data sets, the use of the HC5 is considered to be protective of 95% of species, and therefore is relevant to management goals related to protecting biodiversity (De Vries et al. 2010). The Ni sediment database used to determine the HC5 is admittedly small relative to databases for the surface water compartments, e.g., the freshwater pelagic database includes chronic ecotoxicity data for 31 species. However, the sediment database covers different and important taxa, ecological niches, and functional groups. From a practical standpoint, it also represents the largest chronic sediment toxicity database for any chemical substance. Finally, the HC5 is statistically significant and can therefore be protective of at least 95% of species for the exposure conditions that were used to generate the underlying ecotoxicity data.

Because the HC5 is based on laboratory data, legitimate questions can be raised about the degree

of protectiveness that it provides for natural benthic communities. The field data available for Ni and the behavior of Ni spiked into sediments indicate that the laboratory-based approach is protective of possible effects in natural systems. First, both the HC5 and the most sensitive single-species EC10 value are below threshold effects concentrations that were observed in the field when the same 2-step spiking method was used. Second, proportions of freely available and exchangeable Ni decrease over time, as indicated by Costello et al. (2011). This indicates that the laboratory-based HC5 is a truly conservative estimate of effects, as it reflects a situation of maximum bioavailability that may not account for processes occurring in nature over time scales that extend beyond those used in laboratory tests.

The experience in performing the Ni sediment toxicity research program provides a number of recommendations for future studies with the goal of determining effects of Ni on sediment organisms:

Using the 2-step method described by Brumbaugh et al. (2013) for spiking Ni into sediments because it results in sediments that closely resemble exposure conditions occurring at contaminated sites

Choosing sediments that take geographical, bioavailability, and regulatory considerations into account

Fully characterizing sediments for critical parameters, such as AVS, organic carbon, Fe and Mn oxides, Ni concentrations in solid and porewater sediment phases, and, during toxicity testing, Ni concentrations in overlying waters

Maximizing the taxonomic diversity of sediment toxicity test organisms as broadly as possible

Evaluating relationships between sediment parameters and organism response to Ni exposure

Comparing results of laboratory toxicity tests and laboratory-based bioavailability relationships with results from field studies, and ensuring that such comparisons include taxonomically similar organisms in both laboratory and field exposures

These recommendations are reflected in ECHA (2014), are appropriate for risk assessments of

other metals and should form part of future sediment risk assessments.

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<abstract type="short">Key Points

<zaq;1><BL><B1>A comprehensive, representative sediment toxicity database is available to support risk assessment of Ni in freshwater sediments.</B1>

Sediment Ni ecotoxicity data were gathered from studies that used spiking approaches that resulted in Ni-enriched sediments resembling naturally contaminated sediments, thus increasing their relevance.</B1>

Bioavailability of Ni in sediments, which is controlled by acid volatile sulfides (AVS), varies among different species, with actively bioturbating species showing a lower slope in the relationship between decreasing toxicity with increasing AVS.</B1>

A bioavailability-based tiered approach is presented, where the first tier involves comparison of ambient total Ni concentrations with a RWC threshold value of 136 mg Ni/kg. Site-specific AVS can be used to calculate a site-specific threshold if ambient Ni is greater than 136 mg Ni/kg.</B1></BL></abstract>

**Figure 1.** Conceptual model of the integrated bioavailability-based approach for assessing risks of Ni to freshwater sediment ecosystems.

**Figure 2.** Nickel EC10 values (mg Ni/kg dw) as a function of acid volatile sulfide (AVS,  $\mu\text{mol AVS/g}$ ) for 7 ecotoxicity test organisms. The vertical lines represent the 10th (red), 50th (blue), and 90th (green) percentiles of AVS within European freshwater surficial sediments.

**Figure 3.** Species–sensitivity distributions for 9 sediments after normalization of ecotoxicity data using relationships based on sediment acid volatile sulfide (AVS) concentrations. Symbols represent EC10 values (mg Ni/kg) that have been normalized based on AVS concentrations of each sediment. Sediments include a hypothetical reasonable worst case (RWC; AVS = 0.8

$\mu\text{mol/g}$ ); Dow Creek (Dow; AVS = 0.9  $\mu\text{mol AVS/g}$ ); US Geological Survey Pond #30 (P30; AVS = 9.5  $\mu\text{mol/g}$ ); Raisin River Site 2 (RR2; AVS = 4.8  $\mu\text{mol/g}$ ); Raisin River Site 3 (RR3; AVS = 7.2  $\mu\text{mol/g}$ ); St. Joseph River (STJ; AVS = 2.7  $\mu\text{mol/g}$ ); Mill Creek, South Tributary (STM; AVS = 22  $\mu\text{mol/g}$ ); Spring River (SR; AVS = 0.9  $\mu\text{mol/g}$ ); and West Bearskin Lake (WB; AVS = 38.0  $\mu\text{mol/g}$ ). Lines represent log-logistic distributions fitted to normalized EC10 values.

**Figure 4.** Tiered approach illustrating the implementation of bioavailability normalization for assessing risk of Ni to freshwater sediment ecosystems at local or regional scales.

**Table 1.** Characteristics of Ni-spiked sediments used during all laboratory studies

Method	Spiking	SR	TOC (%)	Fines (%)		AVS ( $\mu\text{mol/g}$ )		Ni treatments ( <i>n</i> )	Highest Ni spiked Targeted
				silt + clay	TR-Fe (%)	Unspiked			
Method development <sup>a</sup>	equilibration; water addition comparison	SR	0.8 (0.1)	nm	nm	0.7 (0.1)	2	500	
		WB	10.3 (0.8)	nm	nm	38.3 (0.6)	2	3000	
								2	1000
Toxicity testing 1 <sup>b</sup>	Species sensitivity	SR	0.4 (0.1)	21.4 (1.4)	0.78 (0.01)	0.9	5	705	
		WB	10.5 (0.6)	88.3 (2.9)	5.10 (0.10)	38.0	5	8500	
Toxicity testing 2 <sup>b</sup>	Bioavailability assessment	DOW	1.2 (0.1)	13.8 (0.8)	0.64 (0.01)	0.9	5	1267	
		STJ	1.9 (0.1)	17.9 (0.2)	2.29 (0.09)	2.7	5	2667	
		RR2	4.1 (0.6)	28.2 (0.8)	1.05 (0.01)	4.8	5	2667	
		RR3	8.1 (0.9)	25.1 (0.2)	1.49 (0.06)	7.2	5	2667	
		P30	1.8 (0.0)	90.0 (0.6)	1.58 (0.04)	9.5	5	2667	
		STM	8.1 (0.2)	46.3 (0.4)	2.64 (0.35)	22.0	5	4800	

Toxicity testing 3 <sup>c</sup>	Species	Braekel 1	1.4	44.0	0.48–0.68	1.0–2.0	5	1000–1800–3200	730 (3)
	sensitivity and	Braekel 2	1.7–2.0	nm	0.53–0.67	4.0–6.0	5	1800–3200	11
	bioavailability assessment	Lampernesse	4.0–5.5	nm	0.78–0.92	29.0–30.0	5	3200–5600	24

SR = Spring River, USA; WB = West Bearskin Lake, USA; DOW = Dow Creek, USA; P30 = US Geological Survey Pond 30, USA; RR2 = Raisin River (site 2), USA; RR3 = Raisin River (site 3), USA; STJ = St. Joseph River, USA; STM = south tributary Mill Creek, USA; Braekel 1 = Belgium; Braekel 2 = Belgium; Lampernesse = Belgium;

nm = not measured; TR = total recoverable.

Values are means with standard deviation in parentheses.

<sup>a</sup>Brumbaugh et al. (2013).

<sup>b</sup>Besser et al. (2013).

<sup>c</sup>Vangheluwe and Nguyen (2014).

**Table 2.** Overview of all available regression models relating the toxicity of Ni to AVS in sediment

Species	Model	R <sup>2</sup>
<i>Hyalella azteca</i>	Log EC20 total Ni (mg/kg dry wt) = 2.65 + 0.492 Log AVS (μmol/g dry wt)	0.74 (p < 0.05)
<i>Gammarus pseudolimnaeus</i>	Log EC20 total Ni (mg/kg dry wt) = 2.8 + 0.358 Log AVS (μmol/g dry wt)	0.62 (p < 0.05)
<i>Hexagenia</i> sp.	Log EC20 total Ni (mg/kg dry wt) = 2.35 + 0.175 Log AVS (μmol/g dry wt)	0.59 <sup>a</sup> (p = 0.07)
<i>Sphaerium corneum</i>	Log EC20 total Ni (mg/kg dry wt) = 2.73 + 0.478 Log AVS (μmol/g dry wt)	0.99 (p < 0.05)
<i>Tubifex tubifex</i>	Log EC20 total Ni (mg/kg dry wt) = 3.05 + 0.125 Log AVS (μmol/g dry wt)	0.99 (p < 0.05)
<i>Chironomus riparius</i>	Log EC10 total Ni (mg/kg dry wt) = 2.85 + 0.1798 Log AVS (μmol/g dry wt)	0.99

AVS ( $\mu\text{mol/g}$  dry wt)

( $p < 0.05$ )

<sup>a</sup>Nonsignificant.

**Table 3.** Overview slope and intercepts of the different bioavailability models

<b>Species</b>	<b>Life strategy</b>	<b>Intercept (SE)</b>	<b>Slope (SE)</b>
<i>Hyalella azteca</i>	Swimmer, sprawler, surface deposit feeder	2.65 (0.11)	0.492 (0.11)
<i>Sphaerium corneum</i>	Burrower, surface deposit feeder	2.73 (0.01)	0.478 (0.011)
<i>Gammarus pseudolimnaeus</i>	Swimmer, sprawler, surface deposit feeder	2.8 (0.13)	0.358 (0.13)
<i>Hexagenia</i> sp.	Burrower, surface and subsurface feeder	2.35 (0.06)	0.175 (0.07)
<i>Chironomus riparius</i>	Burrower, surface and subsurface feeder	2.85 (0.017)	0.180 (0.017)
<i>Tubifex tubifex</i>	Burrower, subsurface feeder	3.05 (0.006)	0.125 (0.006)

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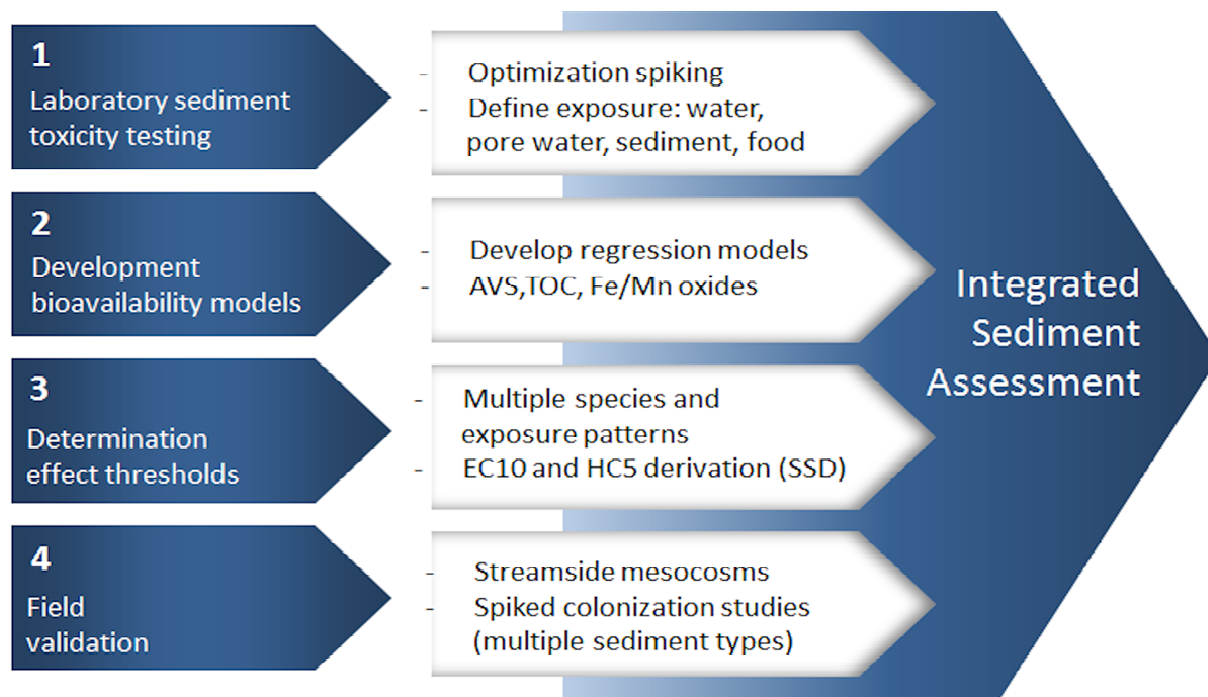


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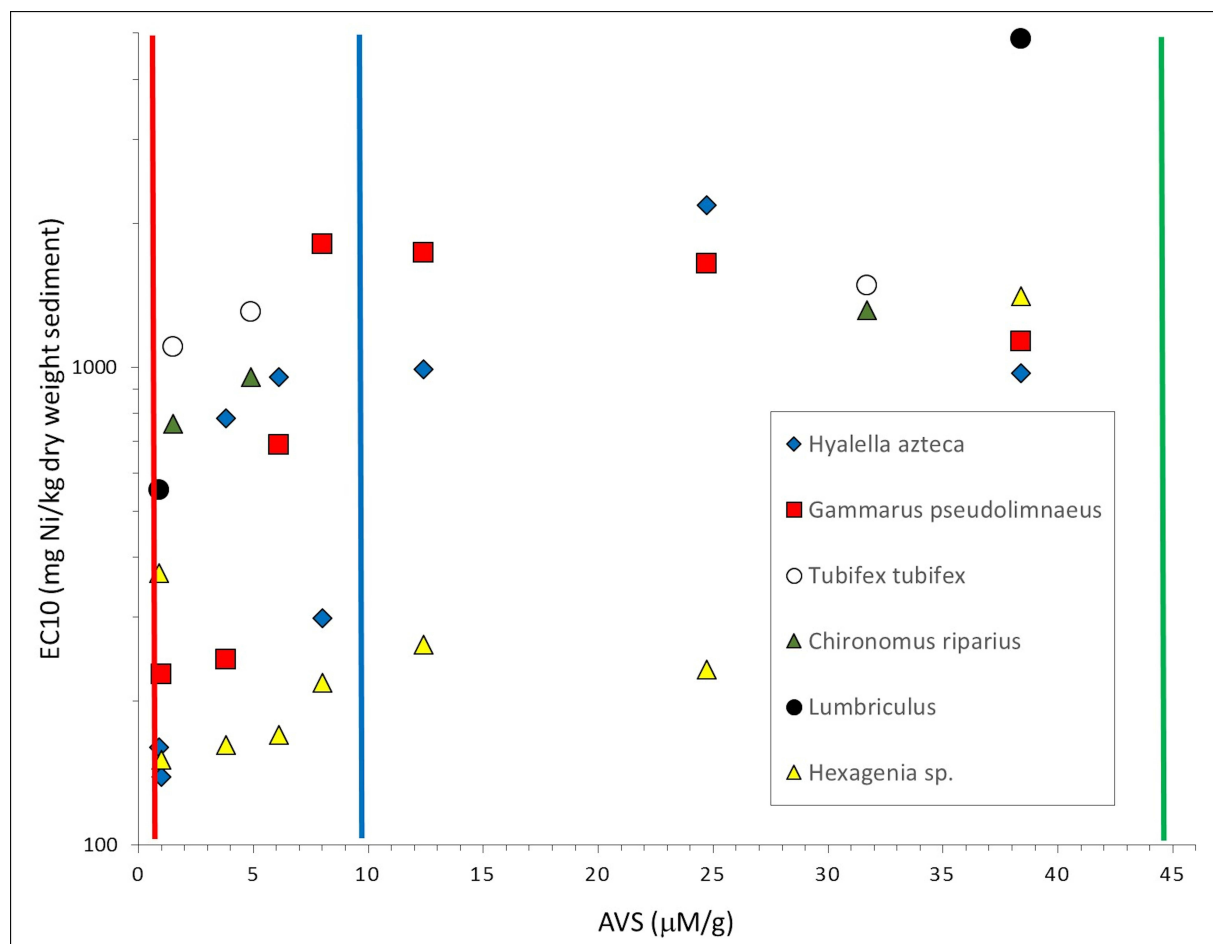


Figure 2 Schlekat et al IEAM version 20 .

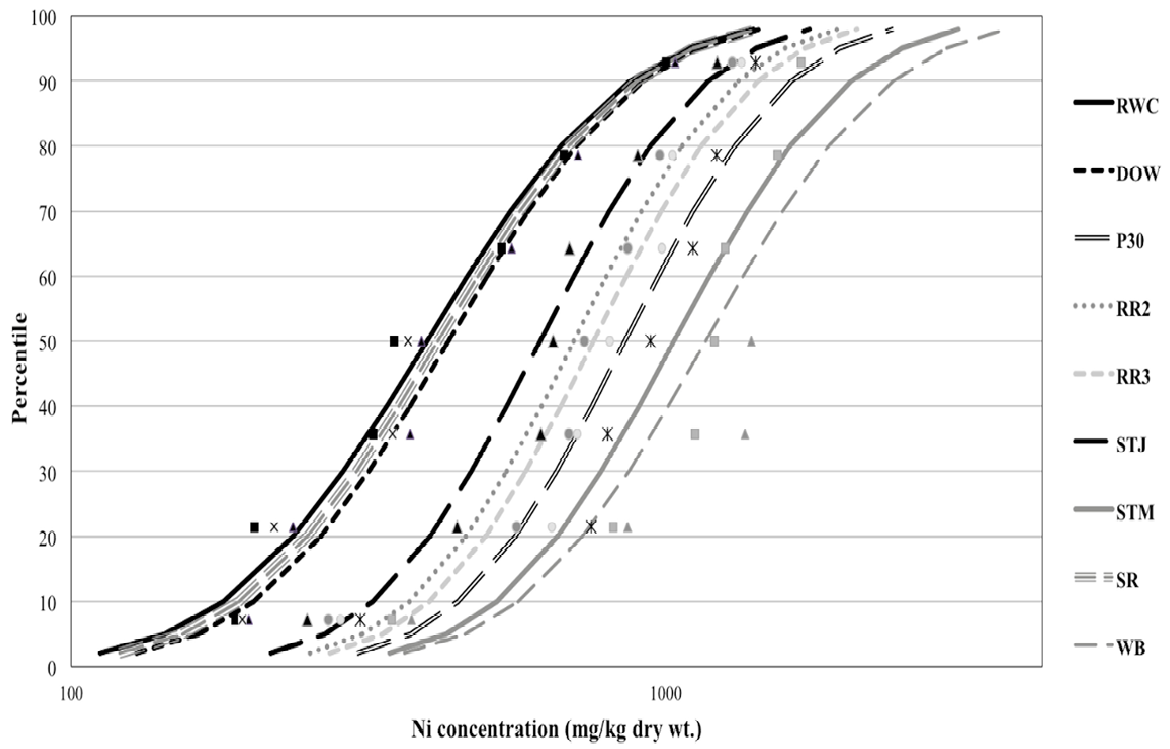


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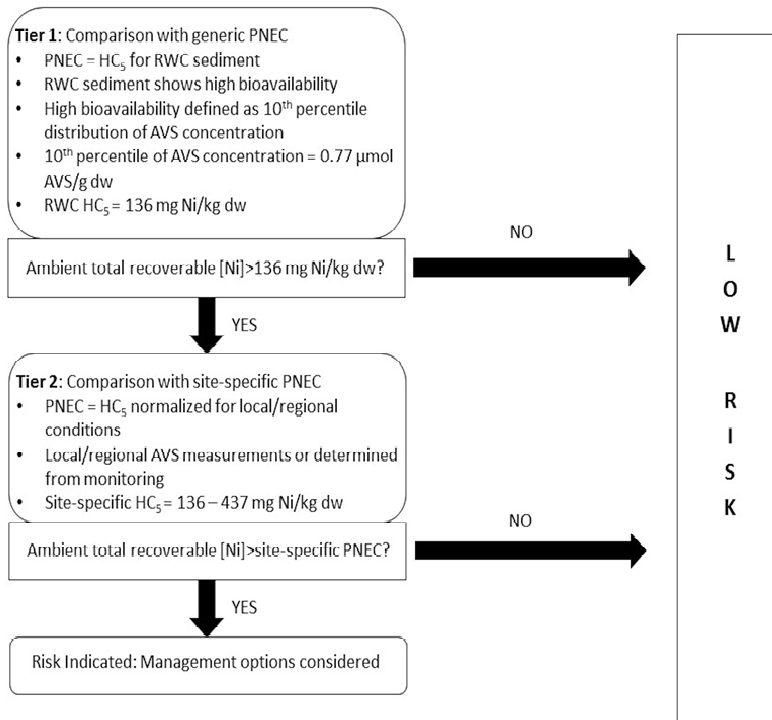


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