Topical Scientific Workshop on Risk Assessment for the Sediment Compartment

7-8 May 2013, Helsinki, Finland

CASE STUDY – SUMMARY FORM

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(Number to be filled by the organisers)

The case studies covering concrete examples of sediment risk assessments for particular chemicals and/or conditions are intended to support the breakout group discussions. All submitted case studies will be distributed to the participants as supporting background material for the workshop and will be included in the workshop proceedings. The Scientific Committee will select some case studies or selected areas of the case studies and will invite the authors to present these cases during the workshop, either at the plenary session or during the break-out groups.

NOTE: By submitting this form, the authors confirm that they have the ownership of the information presented in the case study and that they authorise ECHA to distribute the submitted information to the workshop participants and to publish it in paper and/or electronic format as part of the workshop proceedings.

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EUROPEAN CHEMICALS AGENCY

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Case study details

Case study is particularly relevant for the subthemes:
Note: the case study should cover all three areas, but please indicate if it is particularly relevant/informative for one or more subthemes

☒ Problem definition and conceptual model for sediment risk assessment
☒ Exposure assessment
☒ Effect assessment

Authors: Christian E. Schlekat[#], Henrik Tyle[◇], Emily Rogevich Garman[#], Marnix L.U. Vangheluwe§, Frederik A.M. Verdonck§, John M. Besser†, William G. Brumbaugh†, Christopher G. Ingersoll†, G. Allen Burton††, David Costello††, and Chad Hammerschmidt‡.

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Title: Bioavailability-based approach for assessing risk of Ni to sediment organisms: Laboratory and field evidence

Keywords: Nickel, sediments, bioavailability, species sensitivity distribution, field effects, AVS

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Summary:

To assess nickel 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 nickel in sediments and to develop an integrated equilibrium-partitioning based bioavailability model for assessing risks of nickel to benthic ecosystems.

The sediment testing program was a multi-institutional collaboration that involved extensive laboratory testing, field validation of laboratory findings, characterization of nickel behavior in natural and laboratory conditions, and examination of solid phase nickel speciation in sediments. The laboratory testing initiative was conducted in three phases to satisfy the following objectives:1) to evaluate various methods for spiking sediments with nickel to optimize the relevance of sediment nickel exposures; 2) to generate reliable ecotoxicity data by conducting standardized chronic ecotoxicity tests using nine benthic species in two sediments types with low and high nickel binding capacity; and, 3) to examine sediment bioavailability relationships by conducting chronic ecotoxicity testing using four benthic species in eight different sediment types. A subset of six nickel-spiked sediments was deployed in the field to examine benthic colonization and community effects.

The sediment testing program yielded a broad, high quality dataset which was used to develop a Species Sensitivity Distribution for benthic organisms in various sediment types, a reasonable worst case Predicted No-Effect Concentration for nickel in sediment (PNECsediment), and predictive model for bioavailability and toxicity of nickel in freshwater sediments.

A provisional risk characterization (RC) was performed using emissions from Ni producing and downstream user industry sectors. The RC highlighted the importance of the uncertainty analysis component of the EU risk assessment process, which along with various effect data related issues is included in the considerations related to the decision of the appropriate magnitude of the Assessment Factor (AF) used to calculate the Predicted No Effects Concentration for sediment (PNECsed). The analysis also included how the size of the selected assessment factor (AF= 1,1,5, 2 & 3) for calculating PNECsed from HCs of the SSD would affect the number of sites with an initial RCR >1 (i.e. PECsed local > PNECsed) at various AVS sediment concentrations (between the 10th and the 90th percentile for EU sediments). RC showed the importance of practical refinements that are possible in the risk assessment process. Refinements include

- thorough collection of factors used to calculate Predicted Environmental Concentrations (PEC), including concentrations of Ni in emissions and physico-chemical/hydrological parameters of the receiving waters (e.g., water flow, which determines dilution rates);
- bioavailability normalization; and,

CASE STUDY – SUMMARY FORM

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(Number to be filled by the organisers)

- measurement of site-specific sediment chemistry in lieu of modelling approaches for determining site-specific PECs.

Poster exhibition

The case study will be presented also as a poster

☒ Yes ☐ No

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SUGGESTED CONTENT FOR THE CASE STUDY: please try to limit the case study to 5 pages (or a maximum of 10 pages for complex case studies) focussing on the elements relevant for a broad general discussion on concepts, methods and approaches applicable to all chemicals or to specific chemical groups.

1. BACKGROUND AND PROBLEM DEFINITION

a. Please include a brief introduction to the assessment aims and goals, the legal and regulatory context if appropriate, the problem definition, and other elements relevant for understanding the assessment

Risk assessment of 5 nickel high production volume substances (nickel (metal) and four water soluble nickel salts: nickel dinitrate, nickel chloride, nickel sulphate & nickel (hydroxy)carbonate) were concluded under the former ESR programme (Council Reg. 793/EEC), with the exception of the risk assessment of nickel for freshwater sediment dwelling organisms. To fill this gap, further information (sediment toxicity testing to establish a PNEC for sediment organisms) was requested in COM Reg. 466/2008 ("Sediment toxicity testing").

In response to the requirements of COM Reg. 466/2008, NiPERA, on behalf of the Nickel industry, sponsored a laboratory and field testing program. The broad goal of this program was to develop a bioavailability-based approach for assessing risks of Ni to sediment organisms, which would yield Predicted No Effects Concentrations (PNECs) for Ni appropriate for site/region-specific sediment chemical properties. Sediment PNECs are necessary for determining Generic Exposure Scenarios within Chemical Safety Reports for nickel and nickel substances under the REACH regulation. Additionally, the underlying ecotoxicity data should be relevant for other global regulatory purposes, including the determination of bioavailability-based Environmental Quality Standards for Ni.

Ni is a priority substance (PS) under the EU Water Framework Directive (Dir. 2000/60/EC). A single EU-wide EQS is required for PS. A bioavailability-based tiered approach was proposed by the European Commission for Ni in the pelagic compartment. Recently, the Danish Environmental Protection Agency (DEPA) recommended that a sediment EQS be established for Ni under the WFD. DEPA also recommended that the Ni EQS for sediment under the WFD should consider the incorporation of bioavailability via a tiered approach.

Bioavailability-based approaches are needed because default approaches (e.g., applying the EU standard assessment factors for industrial chemicals regulated under REACH to EC10s/NOECs from sediment toxicity tests) result in many cases in values that are within or below ambient Ni sediment concentrations. Sediment

Quality Guidelines based on empirical approaches like TEL/PEL[1] and ERL/ERM are also in many cases within the range of ambient sediment concentrations for nickel. Bioavailability-based approaches are based on the principle that sediment chemistry affects the availability and toxicity of substances within sediment phases to infaunal sediment organisms.

In order to accommodate current regulatory approaches that require the use of a single Predicted No Effect Concentration (PNEC)/Environmental Quality Standard (EQS), a tiered approach was developed. The first tier in this approach is a PNEC based on a reasonable worst case (RWC), which in the EU is defined as conditions matching the 10th percentile concentration for factors that affect the bioavailability of a chemical substance. If the calculated nickel concentration for a local site exceed the RWC PNEC then bioavailability normalization based on site-specific sediment parameters and / or refinement of emission/ exposure assessment is performed. The latter case may include measuring representative nickel concentrations in the sediment at the local site. If such representative measured concentrations for the nickel concentration in sediment for a specific site exceed the RWC PNEC, then bioavailability normalization based on site-specific sediment parameters is performed. If measured concentrations exceed the bioavailability-normalized PNEC, then risk management measures lowering the nickel emission are appropriate. The principles behind bioavailability-based tiered approaches are supported by existing EU documents (e.g., the EQS TGD, EC 2011, c.f. also DEPA 2012). However, specific guidance is not provided in these documents; discussions on this approach at the ECHA workshop will therefore be valuable in refining / accepting the approach used in the Ni Case Study.

This research program sought to deliver data that could be used to develop bioavailability-based PNECsed values following the basic guidance set forth in the TG EQS document. The program included laboratory and field-based measurements of effects, and an identification of the exposure parameters required for implementation. All available standardized laboratory toxicity testing approaches were utilized (nine species were tested in a total of eight sediments), and a comprehensive field study was performed to test the validity of laboratory-based results.

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[1] TEL: Threshold effects level; PEL: Probable effects level; ERL: Effects range low; ERM: Effects range median

The outcome of this work yielded:

- a sediment database including chronic ecotoxicity data for four sediment toxicity test species obtained by use of slightly adapted standard test methods for these species;
- bioavailability models based on observed relationships between toxicity endpoints and sediment concentrations of Acid Volatile Sulfides (AVS);
- field data validating the relative sensitivity observed in laboratory tests as well as the bioavailability relationships established in laboratory exposures; and,
- a bioavailability-based tiered approach for Ni based on the use of bioavailability-normalized Species Sensitivity Distributions (SSDs), which will allow for site- and region-specific assessments of Ni toxicity to the sediment compartment while maintaining an uniform level of ecological protection.

Parameterizing the bioavailability models with the full range of AVS measured in EU sediments, normalizing the ecotoxicity data, and developing an SSD based on these data resulted in a range of HC5(50%) values from 94 mg Ni/kg dw to 300 mg Ni/kg dw depending on sediment characteristics.

These elements are summarized in later sections of this Case Study, and details are provided in the referenced literature.

Besides this extensive research program related to the HC5- and PNECsed-derivation, DEPA in addition conducted an initial EU generic sediment exposure assessment and risk characterisation in close collaboration with Ni IND. Due to lack of data for all industry sectors the exposure and risk assessment part of the analysis can only be considered as initial because it was restricted to selected industry sectors where at least some updated nickel emission/ exposure data were available. Another reason for the provisional nature of the exposure and risk assessment was that the assessment was in no case based on measure representative nickel concentrations in sediments at the local site.

Several challenges were identified when attempting to incorporate data from this research into risk assessment using existing sediment guidance, such as guidance available for REACH and the TG for EQS. These challenges included:

- <u>Discrepancies between EU /REACH guidance for the use of SSDs for pelagic organisms and the number of standardized sediment toxicity tests that are available</u>: The EQ TGD and the REACH endpoint specific GD recommends that data be available for 10 to 15 species that are comprised of at least eight taxonomic groups before the SSD can be employed for the pelagic compartment. This was not achieved for the Ni sediment program, nor is it possible to do so with currently available standard test methods on sediment species. It is noted that currently there is no EU guidance for employing the SSD approach for sediment species
- <u>Incorporation of bioavailability into sediment risk assessment</u>: While the existing guidances recognizes the importance of factors that affect the bioavailability and toxicity of sediment-associated contaminants, guidance is still needed on how bioavailability correction should take place within tiered risk assessment frameworks.
- <u>Implementation of bioavailability-based approaches in compliance checking</u>: A common challenge encountered after developing bioavailability-based approaches is the absence of sufficient monitoring data required to implement the approach at site- or region-specific scales. For example, the bioavailability models developed in the Ni Case Study are

based on Acid Volatile Sulfide (AVS) concentrations in sediments. Few EU Member States measure AVS, making it currently difficult to perform the bioavailability normalizations in practice.

The Ni sediment research program also identified several areas where additional data would decrease the uncertainty surrounding the approach. These limitations, which are currently being addressed through additional research, include:

- The number of species in the database[2]. Nine species were tested, but reliable toxicity endpoints were generated for only four species, which limits the statistical power of an SSD. Data are currently being generated for an additional four species, which increase the total number of species to eight.
- The role of dietborne exposure in Ni toxicity to sediment organisms: As many benthic organisms ingest sediment for nutritional purposes, dietborne exposure becomes a plausible explanation for the observed toxicity. Studies to quantify the relative importance of dietborne versus pore water exposure are underway, results of which will reduce the uncertainty surrounding the mechanistic basis of the Ni bioavailability models.
- The potential influence of species specific microhabitat conditions influencing the available nickel concentration surrounding the organism. Some of the data could indicate that this hypothesis may explain the result observed (i.e. that creation of a ventilation current in the burrow of one of the species may create less sediment AVS dominated exposure conditions than for the other species)
- The role of ageing for metals in sediments. Results of the long-term field study indicated that toxicity of Ni in sediment phases decreased over time, which could be a function of changes in chemical speciation from exchangeable phases to more recalcitrant phases. Research is underway to quantify this effect, which could increase the field relevance of laboratory ecotoxicity data through an adjustment factor vis-à-vis metal risk assessment for soil.[3]

2. MAIN CASE STUDY DESCRIPTORS

a. Please describe with key words or short sentences the main characteristics of the risk assessment, e.g. generic or site-specific, local/regional/continental, freshwater/estuarine/marine; the chemical(s) or pollution source addressed, targeted to particular areas/concerns, etc.

Scope: Generic risk assessment focused on chemicals management of freshwater sediments in the European Union.
Approach: Bioavailability-based tiered approach
Habitat domain: Freshwater sediments
Chemical substances: Ni and Ni compounds. The principles behind the bioavailability-based tiered approach will be applicable to other cationic metals like Ag, Co, Cr, Cu, Pb, and Zn.

3. CONCEPTUAL MODEL

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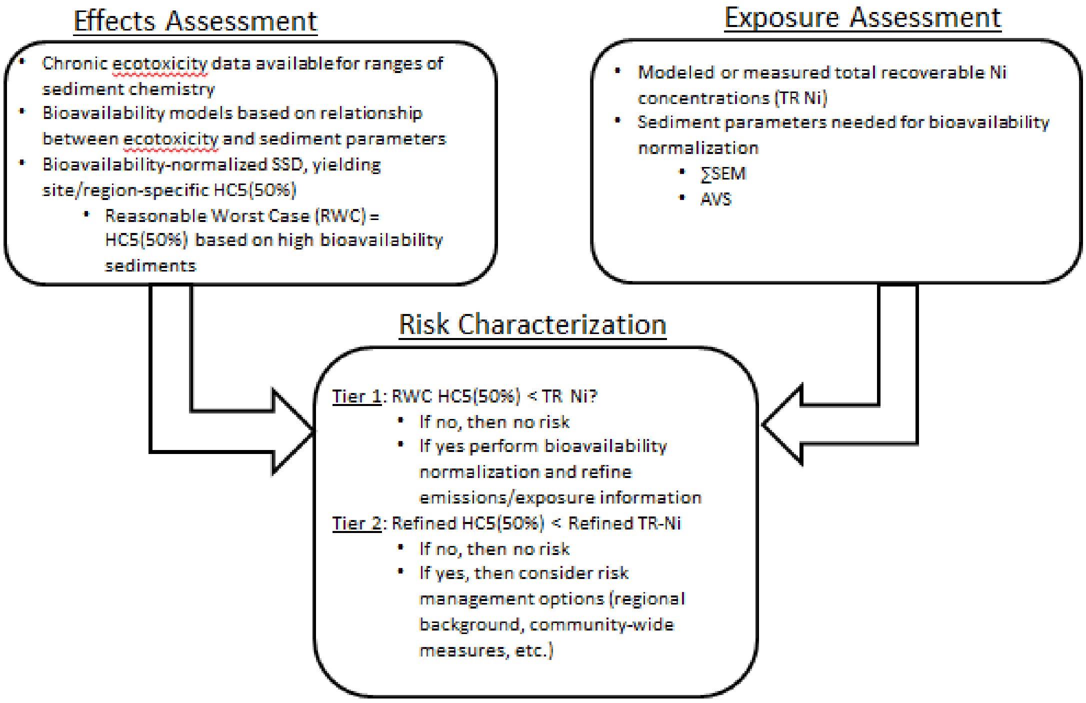
[2] Please see the following poster for more information: Nguyen et al.: Advanced research on nickel toxicity in sediments: species, bioavailability and toxicity.

[3] Please see the following poster for more information: Costello et al.: Experiments measuring bioavailability in oxic and spiked sediments.

a. Please describe the links between the problem formulation (the risk to be assessed), the exposure and effect assessments and its comparisons in the risk characterisation (how the endpoints/receptors were selected and the risk estimated). Include graphical conceptual models, lines of evidence or risk lines (linking the source and/or stressor with the receptors/endpoints for which the risk is estimated).

The conceptual model behind the Ni Case Study is a bioavailability-based tiered approach. The approach is described in the figure below.



Effects Assessment

- Chronic ecotoxicity data available for ranges of sediment chemistry
- Bioavailability models based on relationship between ecotoxicity and sediment parameters
- Bioavailability-normalized SSD, yielding site/region-specific HC5(50%)
    - Reasonable Worst Case (RWC) = HC5(50%) based on high bioavailability sediments

Exposure Assessment

- Modeled or measured total recoverable Ni concentrations (TR Ni)
- Sediment parameters needed for bioavailability normalization
    - ∑SEM
    - AVS

Risk Characterization

Tier 1: RWC HC5(50%) < TR Ni?
- If no, then no risk
- If yes perform bioavailability normalization and refine emissions/exposure information

Tier 2: Refined HC5(50%) < Refined TR-Ni
- If no, then no risk
- If yes, then consider risk management options (regional background, community-wide measures, etc.)

b. Please indicate if the assessment has followed a particular guidance or recommendation and include the reference and/or link.

4. EXPOSURE ASSESSMENT

a. **METHODOLOGY:** Please describe briefly the main elements of the exposure assessment (e.g. release estimation, environmental processes considered, assumptions, use of monitoring data, …)

Two independent concepts are covered in this section. The first concept describes the approaches used to measure Ni exposure in laboratory and field toxicity tests in order to identify relevant sediment phases to measure in refined effects assessments. The second concept describes methods used to estimate Predicted Environmental Concentrations (PEC) from Ni emitting facilities in a provisional risk characterization.

I) Determination of relevant sediment phases to measure in sediment effects assessments of Ni

Details of the Exposure Assessment methodology and results are described in Chapter 1 of Besser et al. 2011 (http://pubs.usgs.gov/sir/2011/5225/). These will be briefly summarized here.

Goal: The main goal of the exposure assessment effort was to provide analytical data that would assist in the determination of the most appropriate sediment phase (e.g., total sediment Ni or Ni associated with specific sediment phases such as pore water, sulphides, organic carbon, etc.) that should be used in risk characterization.

Approach: The first step in this process was to determine appropriate methods for spiking soluble Ni salts into sediments that achieved the following criteria:

1. Minimal Ni lost from sediment phases to overlying water during toxicity testing;
2. Distribution of Ni between sediment and pore water phases similar to those of natural sediments; and,
3. Practical to perform and repeatable.

An indirect spiking method was used, which incorporated the following steps:

1. Adding $NiCl_2$ to a relatively small volume of sediment to create a highly enriched "super spike" (SS);
2. After four weeks, dilution of the SS with a larger volume of uncontaminated sediment from the same source to create a dilution series;
3. Neutralization with NaOH; and,
4. Equilibration for ten weeks, after which time the sediments were ready for toxicity testing.

The following parameters were measured for sediments used in both laboratory and field testing: Total recoverable Ni; Ni in Simultaneously Extracted Metals (SEM) fraction; pore water Ni (using peepers and DGT); Acid Volatile Sulfides (AVS); total organic carbon; total iron and manganese; particle size distribution; cation exchange capacity (CEC); oxidation-reduction potential, and pH. Pore water analyses included pH, major ions, conductivity, alkalinity, hardness, and DOC.

II. Estimation of PEC for risk characterization

Approaches for PEC estimation can be found in DEPA (2012). Briefly, emissions data from local sites of Ni producing and downstream user industry sectors were collected. Major industry sectors included manufacturers of stainless steel, FeNi alloys, batteries, and catalysts, as well as surface finishers (plating). Emissions data and information on receiving waters (e.g. flow or dilution) were used to calculate local sediment nickel concentrations following standard EU guidance. To evaluate the impact of bioavailability normalization, distributions of AVS in EU sediments were determined.

b. **RESULTS:** Please describe briefly the outcome of the exposure estimation

I) Determination of relevant sediment phases to measure in sediment effects assessments of Ni

Results of the indirect spiking method indicated the following positive attributes:

- Consistent and stable pore water pH and sediment AVS concentrations;
- Overlying water levels maintained below concentrations of concern to test organisms; and,
- Distribution coefficients (Kd) ranging from log 2.6 in low binding sediments (AVS = 1.0 umol AVS/g dry wet.; TOC = 0.4%) to log 4.4 for high binding sediments (AVS = 36 umol AVS/g dry wt.; TOC = 10.4%),

which is within the range of log Kds reported for field collected sediments (50^{th} percentile reported in Ni EU RAR[4] = log 3.85)

Based on this evaluation, the indirect spiking method was used to spike sediments used for subsequent laboratory and field experiments.

Implications for Risk Assessment

Results of the program highlight the monitoring data required for implementing the approach in regulatory frameworks like REACH, the WFD, and other compliance-based regulations. In order to implement the bioavailability-based tiered approach, it is recommended that the following sediment parameters be monitored:

- Total recoverable Ni;
- ∑SEM (simultaneously extractable metals); and,
- AVS (acid volatile sulphides)

II. Estimation of PEC for risk characterization

Roughly 75% of Ni use in the EU was covered by the industry sectors examined. Sediment Ni concentrations ranged widely within and among the Ni industry sectors. The analysis also included how the size of the selected assessment factor (AF= 1,1,5, 2 & 3) for calculating $PNEC_{sed}$ from HCs of the SSD would affect the number of sites with an initial RCR >1 (i.e. $PEC_{sed\ local} > PNEC_{sed}$) at various AVS sediment concentrations (between the 10th and the 90th percentile for EU sediments). Results of the risk characterization are covered in Section 6.

5. EFFECT ASSESSMENT

a. **METHODOLOGY:** Please describe briefly the main elements of the effect assessment (e.g. ecological receptors and endpoints, data and assessment principles; PNEC or quality criteria derivation, use of full concentration-response curve, etc. …)

Laboratory testing

Full descriptions of laboratory testing can be found in Chapters 2 and 3 of Besser et al. 2011 (http://pubs.usgs.gov/sir/2011/5225/). Interpretation of toxicity data and the incorporation into a bioavailability-based approach is described by Vangheluwe and Verdonk (2012). These will be briefly summarized here.

Sediment toxicity tests were conducted with 9 sediment species, including amphipods (*Hyalella azteca, Gammarus pseudolimnaeus*), mayflies (*Hexagenia* sp.), oligochaetes (*Tubifex tubifex, Lumbriculus variegatus*), mussels (*Lampsilis siliquoidea*) midges (*Chironomus dilutus, Chironomus riparius*), and nematodes (*Caenorhabditis elegans*). Standard chronic ecotoxicity test protocols were used to the greatest extent possible (e.g., ASTM and/or US EPA protocols were followed for all species except *C. elegans*, for which a modified ISO method was followed).

Laboratory testing was performed under flow-through conditions to maintain acceptable water quality parameters and to decrease concentrations of Ni in the overlying water.

Tests were performed on eight sediments that exhibited broad ranges of sediment parameters known to affect metal bioavailability. These parameters included (ranges shown in parentheses):

- AVS (1.0 – 36 µmol/g dry wt.);

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[4] Existing Substances Risk Assessment of Ni: http://esis.jrc.ec.europa.eu/doc/risk_assessment/REPORT/nickelreport311.pdf

- TOC (0.4 – 10.5%);
- Fe (7,750 – 51,300 mg/kg dry wt.); and,
- CEC (5.6 – 41 meq/100 g).

Two of the sediments (SR and Dow) collected satisfied the definition of RWC, i.e., sediments reflecting conditions that represent the 10th percentile of parameters for EU sediments which are controlling nickel bioavailability (see Table 1 of Vangheluwe and Verdonk (2012)). AVS and TOC concentrations from all eight sediments covered the 10th to 90th percentile distributions of these parameters observed in EU surface waters.

Field testing

Full descriptions of field testing can be found in Costello et al. (2011).

Briefly, subsamples of sediments used in laboratory testing were deployed to four freshwater systems for periods of up to six months. The following ecological information was collected after four and eight weeks of deployment: Invertebrate abundance, taxa richness (family level), Shannon diversity, and abundance of common and sensitive taxa.

b. **RESULTS:** Please describe briefly the outcome of the effect assessment

Laboratory Testing

Results of the **first set** of tests, which were performed on sediments reflecting 10th (SR sediment) and 90th (WB sediment) percentile of AVS and TOC, showed widely different toxicities to the test organisms (Table 1). These results highlight the influence of sediment chemistry on Ni toxicity.

Four of the eight species yielded reliable EC10 values (*H. azteca*, *G. pseudolimnaeus*, *Hexagenia* and *L. variegatus*) for the SR sediment, which represented the RWC. Unfortunately, four species tested resulted in unbounded (censored) data (i.e. no effects were observed at the highest test concentration), which indicate the insensitivity of these important sediment dwelling species towards nickel. For three species of these four species no effect at all was observed at the highest tested concentration.

Table 1. Species EC10-NOEC values (total recoverable Ni, mg Ni/kg dry wt.) for the most sensitive endpoint for all sediment dwelling organisms for the Spring River (SR) and West Bear (WB) sediments.

		SR Sediment (AVS = 1.1 µmol/g)	**WB Sediment** (AVS = 34 µmol/g)
Organism	**Most sensitive endpoint**	**Species EC_{10}-NOEC (mg total Ni/kg dry wt)**	**Species EC_{10}-NOEC (mg total Ni/kg dry wt)**
Hyalella azteca	Biomass	160[a] (49-609)	855[b] (259-2816)
Gammarus pseudolimnaeus	Biomass	Test failed[c]	1132 (105-12200)
Hexagenia species	Biomass	371 (94-1,463)	1409 (571-3471)
Lumbriculus variegatus	Abundance	554 (169-1,816)	4865 (threshold model)

Chironomus dilutus	Emergence	> 762^{d}	1625 (388-6815)
Chironomus riparius	Eggs/case	> 762^{d}	3307 (267-40867)
Lampsilis siliquoidea		> 762^{d}	>7990
Tubifex tubifex		> 762^{d}	1904 (374-9709)
Caenorhabditis elegans		Test failed	Test failed

a mean of two tests: EC10 values and CL = 82 (95 % CL: 45-149) and 337 (95 % CL: 53-1,069) mg total Ni/kg dry wt.
b mean of two tests: EC10 values and CL = 1744 (95 % CL: 471-6451) and 1431 (95 % CL: 189-10800) mg total Ni/kg dry wt.
b unacceptable control mortality
c unbounded NOEC
/ test not conducted

The **second set** of experiments was performed with four species (*H. azteca, G. pseudolimnaeus, Hexagenia* sp.and *T. tubifex*) in six additional sediments. No dose response was observed for tests performed with *T. tubifex*. For tests with *H. azteca* and *G. pseudolimnaeus*, toxicity varied substantially as a function of AVS content of the sediments (Fig 2). Inter-sediment differences were observed for *Hexagenia* sp., but these differences were not as clear as for the amphipod species (Fig 2).

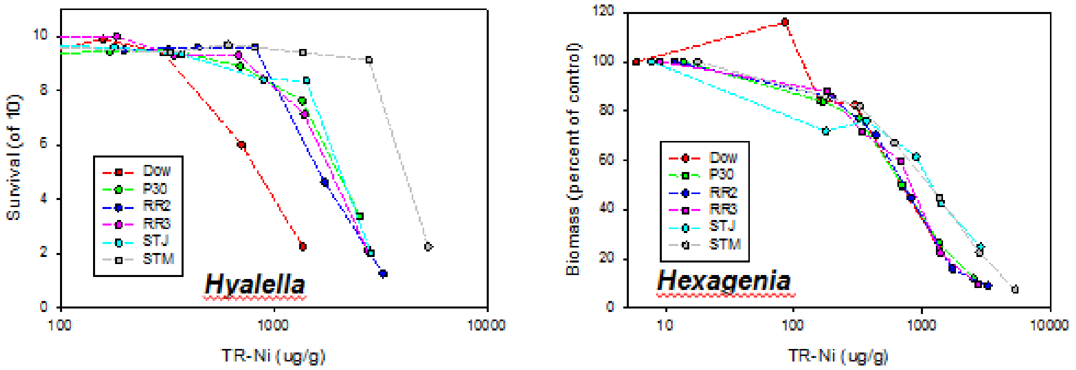

Figure 2. Results of toxicity tests with *H. azteca* and *Hexagenia* sp. performed in sediments with AVS ranging from 1.0 umol/g AVS (Dow) to 26 umol/g (STM).

<u>Bioavailability modelling based on laboratory results</u>
For details on the bioavailability modelling approach and results, see Vangheluwe and Verdonk (2012).

Briefly, bioavailability models were developed based on results of the second set of toxicity tests. Correlations and simple linear regressions between toxicity thresholds (EC20 values) and measured sediment properties were calculated to identify the sediment properties that explain the greatest proportion of variation in the toxicity thresholds.

Nickel toxicity thresholds were significantly correlated with AVS, Fe, TOC and CEC content of the sediment for all amphipod assays. For *Hexagenia* Fe and/or AVS were correlated with the toxicity values. None of the toxicity thresholds based on pore water were significantly correlated. Ultimately, models based on relationships between total recoverable Ni and sediment AVS were chosen (Table 2).

Table 2. Overview of derived regression models relating the toxicity of nickel to AVS in sediment.

Species	**Model**	R^2	**Intercept**	**Slope**
	AVS based		(S.E.)	(S.E.)
H. Azteca	Log EC_{20} total Ni (mg/kg dry wt) = 2.65 + 0.492 Log AVS (µmol/g dry wt.)	0.74	2.65 (0.11)	0.492 (0.11)
G. pseudolimnaeus	Log EC_{20} total Ni (mg/kg dry wt) = 2.8 + 0.358 Log AVS (µmol/g dry wt.)	0.62	2.8 (0.13)	0.358 (0.13)
Hexagenia sp.	Log EC_{20} total Ni (mg/kg dry wt) = 2.35 + 0.175 Log AVS (µmol/g dry wt.)	0.59* ($p = 0.07$)	2.35 (0.06)	0.175 (0.07)*

* non-significant

Field testing

Details on results of the field test are described by Costello et al. (2011). Briefly, the following summary points are notable:

- Ni binding to sediment phases showed dynamic behavior over the deployment period, shifting from initial association with sulphides to organic carbon and ultimately to Fe/Mn oxides;
- After four weeks, colonizing macroinvertebrates showed a strong negative response to the Ni-treated sediments and SEM-AVS models of bioavailability differentiated between toxic and nontoxic conditions;
- After eight weeks, six out of the eight benthic indexes were no longer affected by exposure to Ni, despite Ni concentrations as high as 3,000 mg Ni/kg.
- The reduction in response of the benthic community over time suggests that Ni bioavailability decreases over time. This ageing phenomenon is not captured by current mechanistic approaches for metals that are based on labotory-based approaches using sediments spiked with soluble metal salts as the basis for performing sediment toxicity tests.

6. RISK CHARACTERISATION & CONCLUSIONS

a. **METHODOLOGY:** Please describe briefly the main elements of the risk characterisation (e.g. lower/higher tier, risk maps or other geo-referred approaches, deterministic/probabilistic), the metrics (risk quotients, quantitative likelihood estimations, qualitative likelihood estimations, risk expressions indicating the magnitude and likelihood of the expected impact, etc.), uncertainty and variability assessments, how ecological processes such as recovery, re-colonisation, resilience, redundancy, etc. were accounted for.

This section is divided between I) the development of the bioavailability normalization approach and II) the provisional risk characterization.

I) Development of the bioavailability-normalization approach

Laboratory toxicity test results and bioavailability modelling were integrated using a semi-probabilistic approach.

In terms of effects assessment, SSDs were developed to determine HC5(50%) values for reasonable worst case (RWC) sediments. The overall assessment incorporated probabilistic information on exposure by determining distributions of factors affecting Ni bioavailability, namely AVS concentrations, within EU sediments. Distributions of AVS (e.g., 10th, 50th, 90th) were used in the bioavailability models to normalize the ecotoxicity data and thereby produce expected ranges of HC5(50%) values for Ni in EU sediments.

II) Initial risk characterization

Approaches for risk characterization are more fully described in DEPA (2012) & DHI (2012). Briefly, risk characterization entails a comparison of PECs estimated from site emissions to PNECs. PNECs were developed by varying the Assessment Factor (AF) from 1 to 3 (where PNEC = HC5(50%)/AF). Both RWC and bioavailability-normalized PNECs were included in the analysis.

b. **RESULTS:** Please describe briefly the outcome of the risk assessment including the risk communication phase.

I) Development of the bioavailability-normalization approach

Bioavailability normalized HC5(50%) values ranged from 119 to 300 mg Ni/kg (Figure 3 – from Vangheluwe and Verdonk 2012).

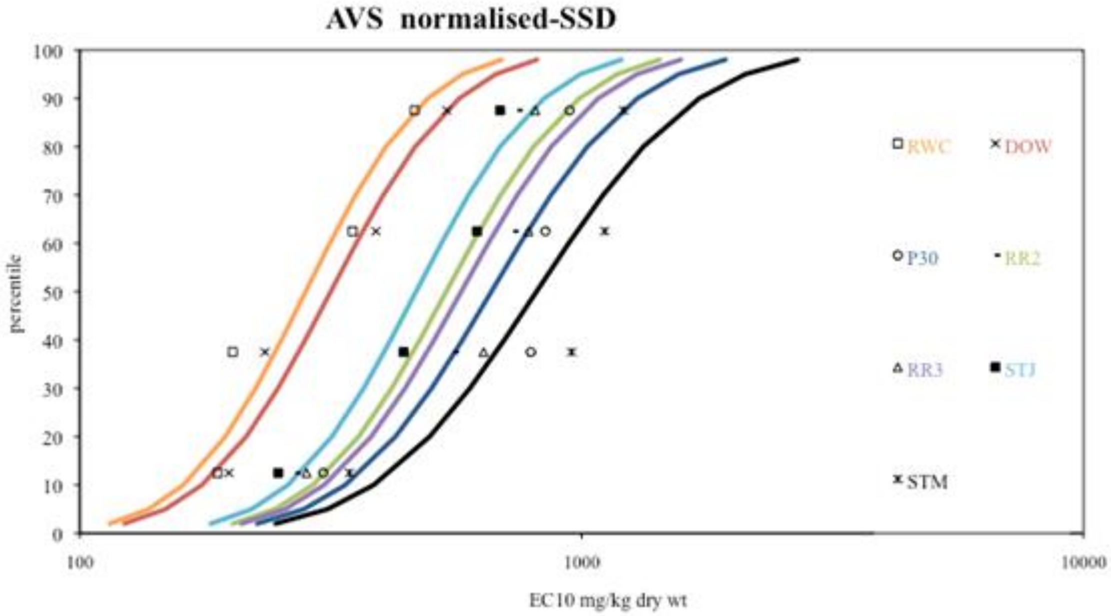

Figure 3. Bioavailability normalized Species Sensitivity Distributions using AVS concentrations from eight sediments (AVS range = 0.77 umol/g for Reasonable Worst Case [RWC] to 24.7 umol/g for STM [S. tributary of Mill Creek]). RWC represents the 10th percentile of AVS concentrations in EU sediments, whereas STM represents the 75th percentile. Using the 90th percentile (36 umo/g) yields an HC5(50%) of 300 mg Ni/kg.

II) Initial risk characterization

Depending of industry sector the number of sites with initial RCR > 1 increased significantly and in some cases by more than three-fold depending on whether the selected AF was set to either 1 or 3. The analysis also suggested that implementation of AVS based bioavailability normalization would often significantly decrease the number of local sites with RCRs > 1.

Uncertainties

Vangheluwe and Verdonk (2012) evaluated several sources of potential uncertainty within the process of calculating bioavailability normalized HC5(50%) values. These sources of uncertainty are recognized in the EQS TGD, and are used in the determination of Assessment Factors[5]. The following sources of uncertainty are relevant for discussion:

1. Overall quality of the ecotoxicity database: The quality of the Ni ecotoxicity data were considered to be high, given that ecotoxicologically relevant endpoints (e.g., growth and reproduction) were covered; sensitive lifestages (e.g., juvenile molluscs and oligochaetes, 4-7 d old chironomids); and, chronic exposures between 28 and 42 d were used.
2. Diversity of taxonomic groups: The database covers eight species of benthic invertebrate species, covering a range of feeding habits and ecological niches. The species tested represents the spectrum of currently available standardized sediment toxicity tests. Four of the eight species did not respond to Ni exposure in RWC sediments, despite concentrations as high as 761 mg Ni/kg. This presents a challenge in terms of justifying the use of the SSD, where some guidance documents recommend a minimum of 8-10 species before the SSD can be used.
3. Field studies: Higher tier ecological information (Costello et al. 2011, Nguyen et al. 2011) was evaluated by comparing laboratory-based bioavailability HC5(50%) values with effects observed in the field. Overall, laboratory-based HC5(50%) values were protective of effects observed under field conditions.
4. Validity of AVS-based normalized models: AVS-based models were highly significant for two amphipod species (Table 2), but the AVS relationship was not as strong for the insect *Hexagenia* sp. (the Fe relationship was also not significant for this species). The mechanism behind this species-specificty is unclear, and contributes to the overall uncertainty of the assessment approach.
5. Dietborne toxicity: Many of the test species used in this study ingest sediments, raising the possibility that the dietborne exposure route may participate in the observed toxicity. A critical review of the literature on dietborne nickel exposure and toxicity was performed by DeForest and Fairbrother (2010). Only a few studies were found in the literature for aquatic organisms, and most of them studied the effect of diet on bioaccumulation, which although it provides useful information on exposure it cannot be necessarily linked to toxicity. Additional studies are ongoing to elucidate the role of dietborne exposure (Please see poster by Nguyen et al.)
6. Natural nickel background concentrations: According to the FOREGS Geochemical Baseline Mapping Program, Ni-ambient concentrations in freshwater sediments from uncontaminated first order streams in the EU varied between 2 and 942 mg/kg dry wt (90th % = 46 mg Ni/kg dry wt; 50th % = 18 mg Ni/kg dry wt.). Depending on the magnitude of any Assessment Factor that is applied to an HC5(50%), background concentrations may overlap with PNECsed values.
7. Due to the provisional nature of the currently conducted exposure and risk assessment no firm conclusion can be made in relation to the actual RCR at most individual nickel industry producing or using sites. Nickel industry will however soon update the current REACH registrations of relevant

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[5] According to the EU EQS TGD, for data-rich chemical substances where SSDs are used, the PNEC is equal to the HC5(50%) divided by an Assessment Factor that can range from 1 to 5.

nickel substances and will provide RCRs for the relevant nickel industry sectors and for most sectors also for the individual sites.

7. ATTACHMENTS, REFERENCES AND BACKGROUND MATERIAL

a. Please, include if you wish relevant additional documents with detailed information, references or links to the case study.

References

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