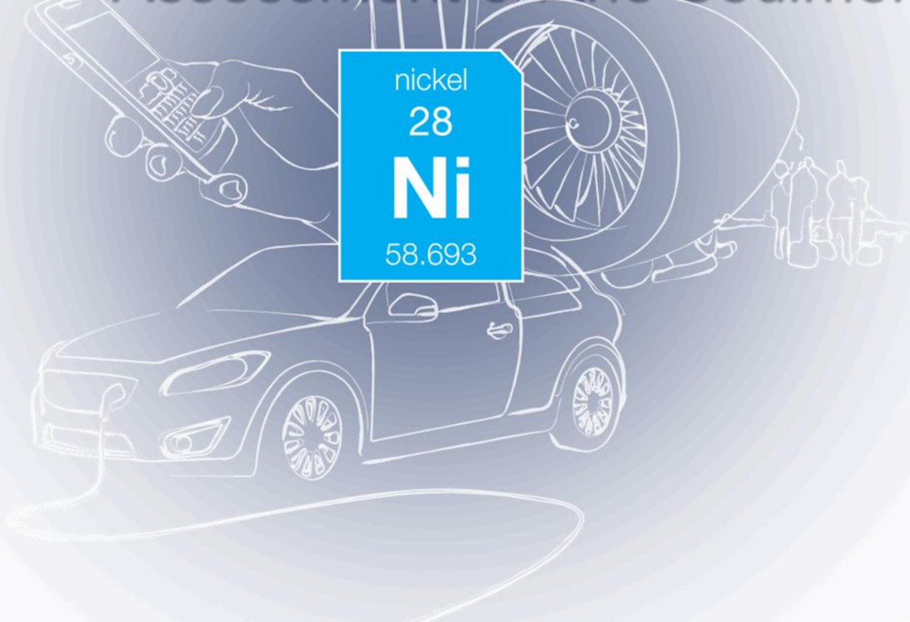
NiPERA Inc. Nickel Producers Environmental Research Association

Case Study: Bioavailability-based effects assessment for Ni in sediments

Topical Scientific Workshop on Risk Assessment on the Sediment Compartment



7-8 May 2013

Helsinki

Case Study: Bioavailability-based effects assessment for Ni in sediments

Chris Schlekat and Emily Rogevich-Garman

Nickel Producers Environmental Research Association (NiPERA)

Durham, NC USA

Henrik Tyle (supported by two reviewers: Henning Clausen DKEPA & Janneck Scotts-Fordesmand (Aarhus University))

Danish Environmental Protection Agency

Copenhagen, Denmark

Marnix Vangheluwe and Frederik Verdonk

Arche Consultants

Gent, Belgium

Jens Tørslev

DHI Consultants

Copenhagen, Denmark

Case Study: Bioavailability-based effects assessment for Ni in sediments

Chris Ingersoll, John Besser, and Bill Brumbaugh
US Geological Survey
Columbia, MO USA

G. Allen Burton and Dave Costello
University of Michigan
Anne Arbor, MI USA

Chad Hammerschmidt
Wright State University
Dayton, OH USA

Introduction to Ni sediment research program

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- Sediment effects assessment under EU Existing Substances Risk Assessment
  - Toxicity data rejected
  - Ni in overlying water explained toxicity
- Conclusion i) recommended by EU Member States
  - Conclusion i): More data required before conclusions concerning risk can be made
- Sediment ecotoxicity data:
  - Relevant for EU ESR program
  - Also for REACH, EU Water Framework Directive
- A “Technical Conclusion i) - Group” was formed to:
  - Review proposed work plan;
  - Meet regularly to review results and to make consensus decisions when different alternatives were available in terms of testing approaches;
  - Make recommendations on additional work

Questions addressed by Technical Conclusion i) Reseach Program

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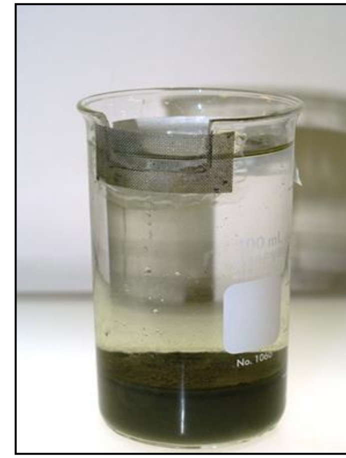
- How do we optimize spiking methodology to limit Ni loss from the sediments?
- How can we produce a high quality, reliable sediment toxicity dataset?
- How can we get a better understanding of Ni behavior in sediments?
- Can we develop bioavailability models to predict Ni toxicity in sediment?
- How well do laboratory-based toxicity data predict field-level effects?



Approach

- Multi-institutional collaborative effort to produce
  - Laboratory generated sediment toxicity data and extensive chemical characterization for nickel-spiked sediments
  - Supporting field-based toxicity data and chemical characterization
  - Solid-phase speciation data for laboratory spiked sediments
  - Predictive bioavailability models for Ni toxicity in sediment
  - Preliminary risk characterization for Ni emitting industries in Europe

USGS science for a changing world · MICHIGAN · WRIGHT STATE UNIVERSITY · NORTHWESTERN UNIVERSITY · ARCHE ASSESSING RISKS OF CHEMICALS · DHI

- Technical oversight by TC i) Group, which was comprised of:
  - Scientists involved in research
  - MS representatives from DK, NL, D, and UK
  - Ni IND representatives
  - An independent chair (C. Janssen, Ghent University)

Step 1
Optimize Spiking Methodology (USGS)

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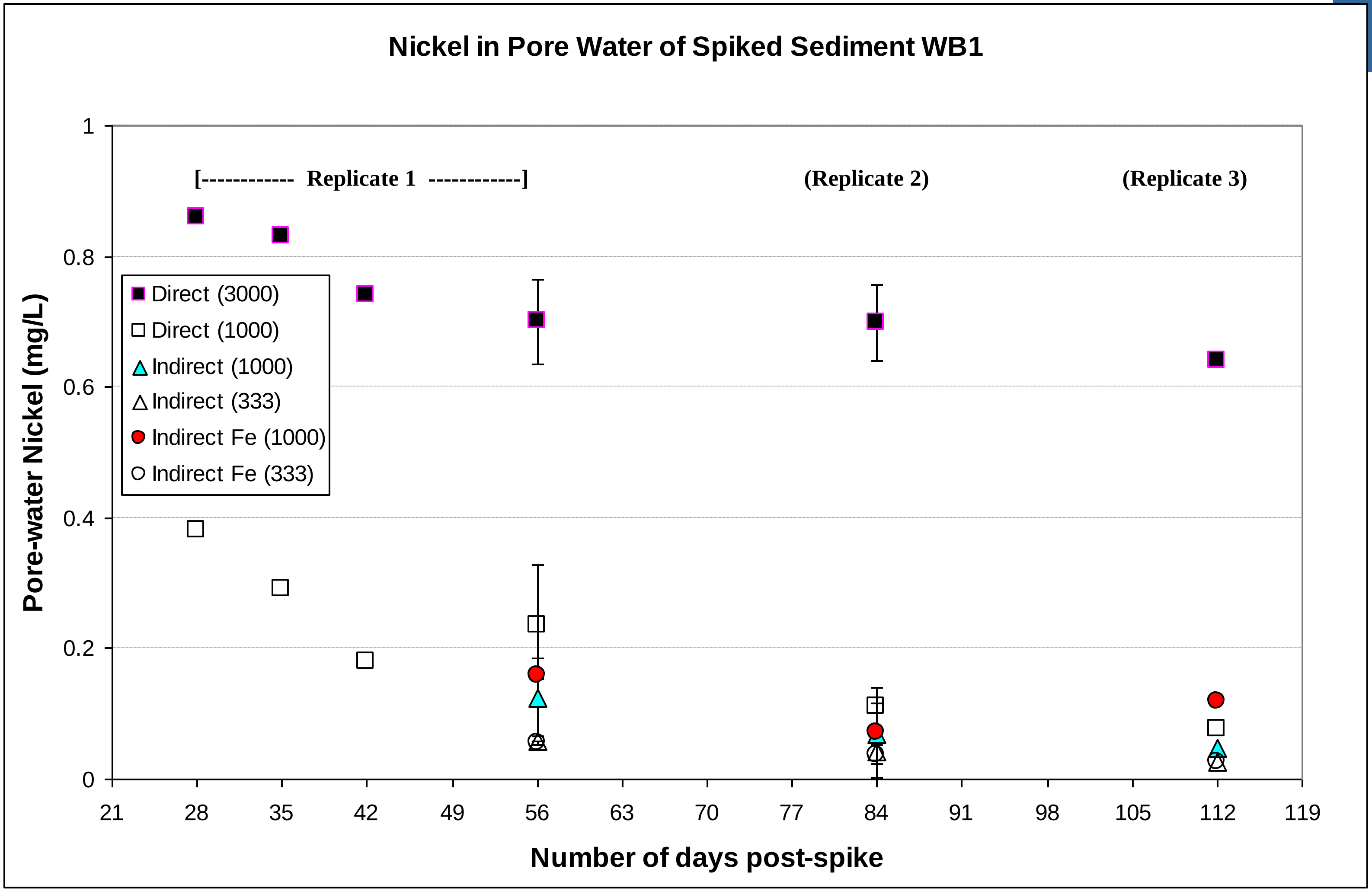
Key issues:

- Environmentally realistic sediment/pore water partitioning
- Sufficient equilibration time
- Stable pH
- Minimize disruption to major drivers controlling sediment binding, e.g., AVS, Oxidation-Reduction Potential, pore-water iron, REDOX gradients
- Determine appropriate overlying water replacement to minimize loss of Ni but maintain low OW Ni concentrations

Spiking Methods

- Two base sediments- Represent approximate range of nickel-binding capacity in EU freshwater sediments (10P & 90P)
  - **Low binding sediment –**sub-oxic river sediment; low AVS, low TOC
  - **High binding sediment –** anoxic/sulfidic lake sediment; high AVS, high TOC
- Three spiking methods (low and high nickel levels):
  - **Direct Spiking with pH adjustment–** $NiCl_2$ added directly to sediments at target levels
  - **Indirect Spiking with pH adjustment–** Higher level of $NiCl_2$ level added to portion of sediment to create "super spike" and after 4 weeks, SS diluted w/ base sediment
  - **Indirect Spiking + Iron with pH adjustment–** Same as Indirect, plus equal moles Fe(III) or FeS added w/ Ni
- Extensive chemical characterization – 8, 12, & 16 w
  - Sediment: pH, Oxidation-reduction potential (ORP), TR-Ni, AVS, 1M HCl extractable Nickel (SEM-Ni)
  - Pore water: Dissolved Ni, Fe, Mn, DOC, ammonia, hardness, alkalinity, pH, major cations, anions
- Toxicity tests
  - Confirmatory *H. azteca* 28 day sediment tests

Results: Pore-water Nickel in WB1 spiked sediment: Day 28 to Day 112



Day 56 & Day 84 are means of peeper and centrifuged samples (1 each). Error bars indicate ranges.

Development of novel spiking approach (Task 1 of USGS work)

Recommendations of Technical Conclusion i) Group:

- Spiking approach: Indirect
  - Stable sediment and PW parameters
  - Fewer manipulations required than other approaches
- Equilibration period:
  - 10 weeks prior to introduction of sediment to test chambers
  - 1 week in test chambers prior to introduction of test organisms
- Water replacement:
  - 8 volume additions per day
  - Maintained overlying Ni concentrations below critical dissolved concentrations

Step 2: Sediment Toxicity Data (USGS)

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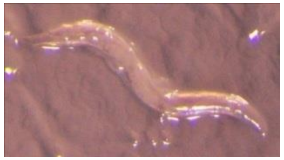
- Objective: Evaluate interspecies sensitivity of sediment-dwelling organisms to nickel-spiked sediments
  - Two sediments x 6 Ni concentrations x 9 species
  - Standard toxicity test methods
- Species:
  1. *Hyalella azteca*
  2. *Gammarus pseudolimnaeus*
  3. *Chironomus dilutus*
  4. *Chironomus riparius*
  5. *Lumbriculus variegatus*
  6. *Tubifex tubifex*
  7. *Lampsilis siliquoidea*
  8. *Hexagenia* sp.
  9. *Caenorhabditis elegans*







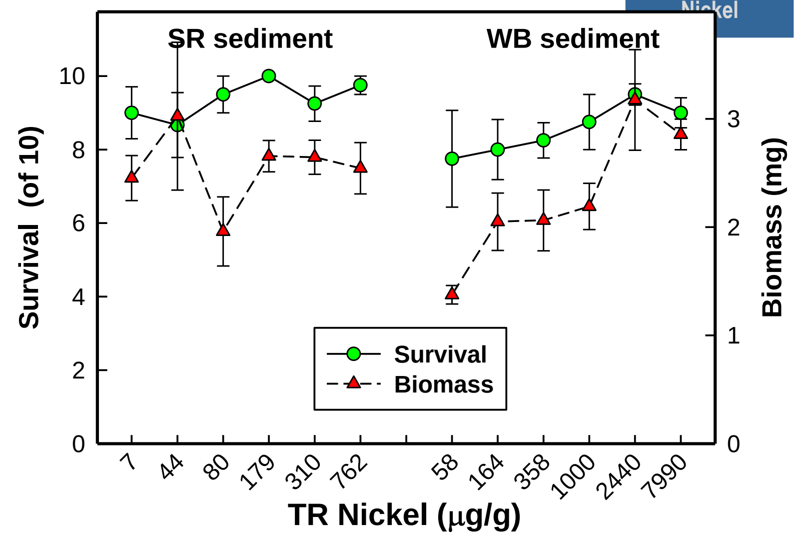


- Model concentration-response curves (estimate EC10s)
- Characterize species-sensitivity distributions (estimate HC_5)
- Examine differences in nickel bioavailability

Step 2
Sediment Toxicity Data (USGS)

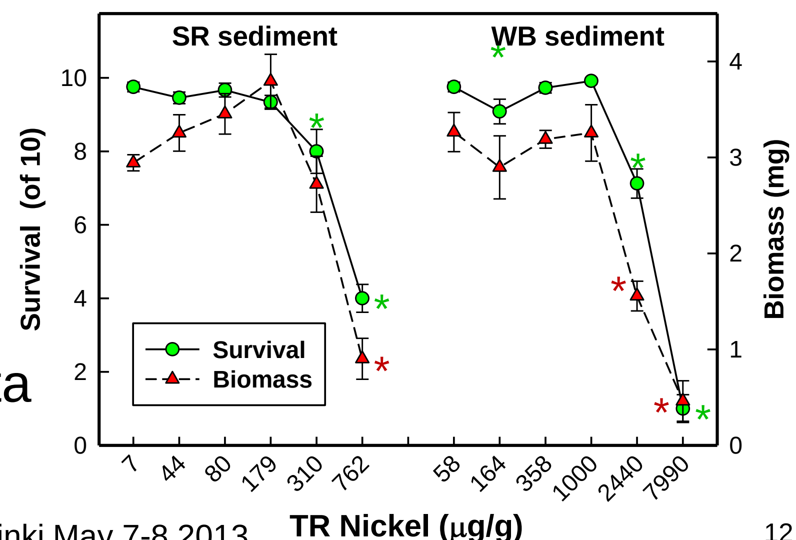
- Four species:
  No concentration response
  - *C.d., C.r., L.v., L.s.*
  - Test failed for C.e.

Mussel *(Lampsilis)*



- Four species:
  Concentration response
  - *H.a., G.p., H. sp., T.t.*

Hyalella test 2



- Obstacles:
  - Difficult to incorporate No Effects data into Species Sensitivity Distribution

Step 3: Bioavailability Modelling (USGS)

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- Objectives:
  - Evaluate influence of sediment characteristics on nickel toxicity
- Approach:
  - Eight sediments covering ranges of sediment factors known to control metal bioavailability and chemistry
    - Acid volatile sulfides (AVS)
    - Organic carbon
    - Fe and Mn oxyhydroxides
  - Chronic toxicity tests with responsive species from Step 2
    - *H. azteca, G. pseudolimnaeus, Hexagenia* sp., and *T. tubifex*

Step 3: Bioavailability Modelling (USGS)

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- Test sediments:

Task	ID	Site	Location	TOC (%)	AVS (umol/g)
2	SR	Spring River	Missouri	0.40	1.1
3	DOW	Dow Creek	Michigan	1.2	1.0
3	STJ	St. Joseph River	Michigan	1.9	4.0
3	RR2	Raisin River #2	Michigan	4.1	6.2
3	RR3	Raisin River #3	Michigan	8.1	8.5
3	P30	CERC Pond 30	Missouri	1.8	13
3	STM	S. Trib. Mill Creek	Michigan	8.1	26
2	WB	W. Bearskin Lake	Minnesota	10.5	36

Step 3: Bioavailability Modelling (USGS)

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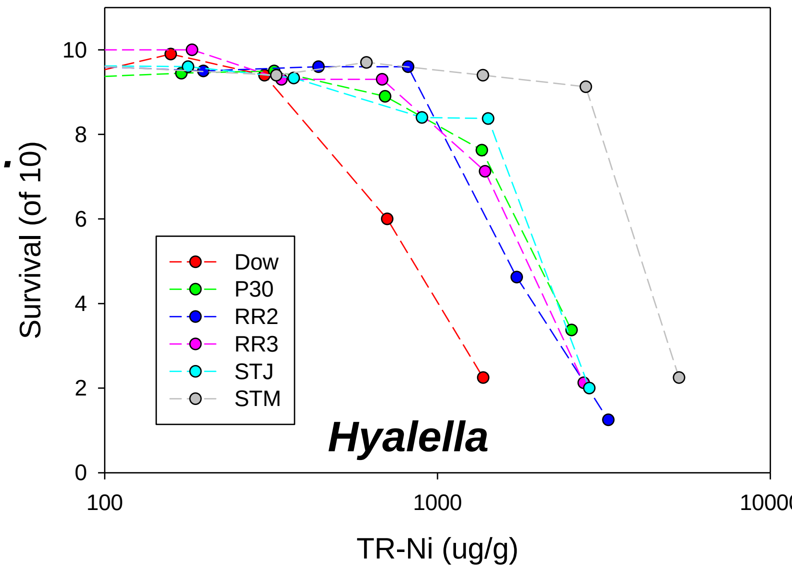
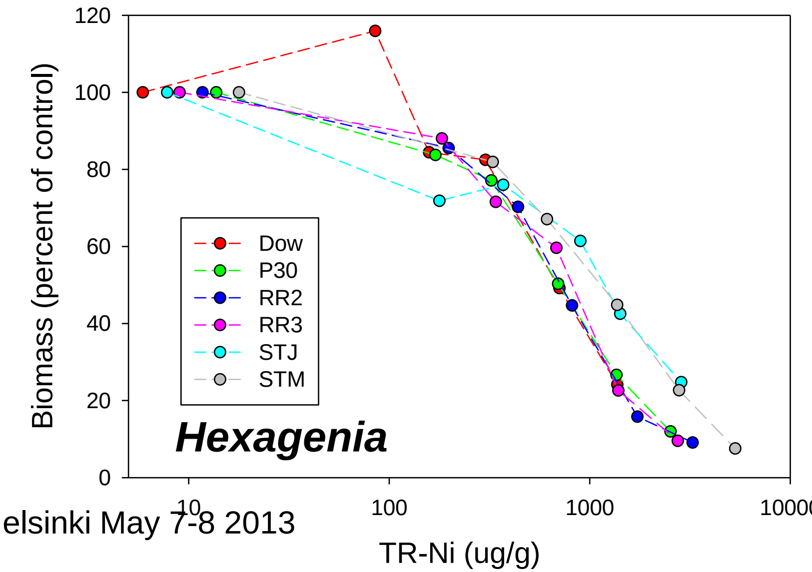
- Clear bioavailability relationships:
  - Amphipod species (*H. azteca, G. pseudolimnaeus*)
  - Toxicity thresholds differ among sediments



- Weak bioavailability relationships:
  - *Hexagenia* sp.

- No concentration response
  - *T. tubifex*



Step 4: Bioavailability Modeling (Arche)

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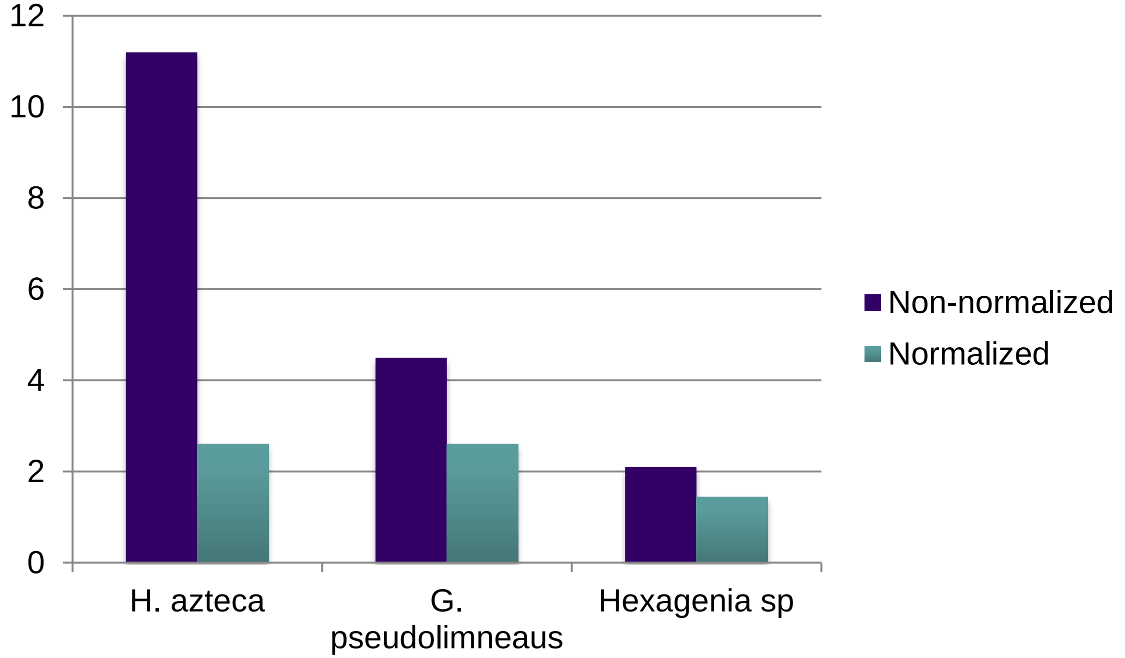
- Identification of key sediment parameters driving nickel toxicity in sediments
- Development of bioavailability models for three sediment species:
  - *Hyalella azteca*
  - *Gammarus pseudolimneaus*
  - *Hexagenia* sp.
- Correlations and simple linear regressions
- Sediment parameters examined were:
  - AVS, TOC, pH
  - Fetot, Mntot , FeSEM , MnSEM
  - CEC, sand, silt, clay

Step 4: Bioavailability Modeling (Arche)

- Statistically significant relationships:

Species	Model	R^2	Slope
H. azteca	Log EC_{20} TR Ni = 2.65 + 0.492log AVS	0.74	0.492
G. pseudolimnaeus	Log EC_{20} TR Ni = 2.8 + 0.3584log AVS	0.62	0.358
Hexagenia sp.	Log EC_{20} TR Ni = 2.35 + 0.1745log AVS	0.59	0.174

- Reduction in intra-species variability:



Bioavailability Normalization Approach

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Chronic Ni Database

↓

Bioavailability Models

↓

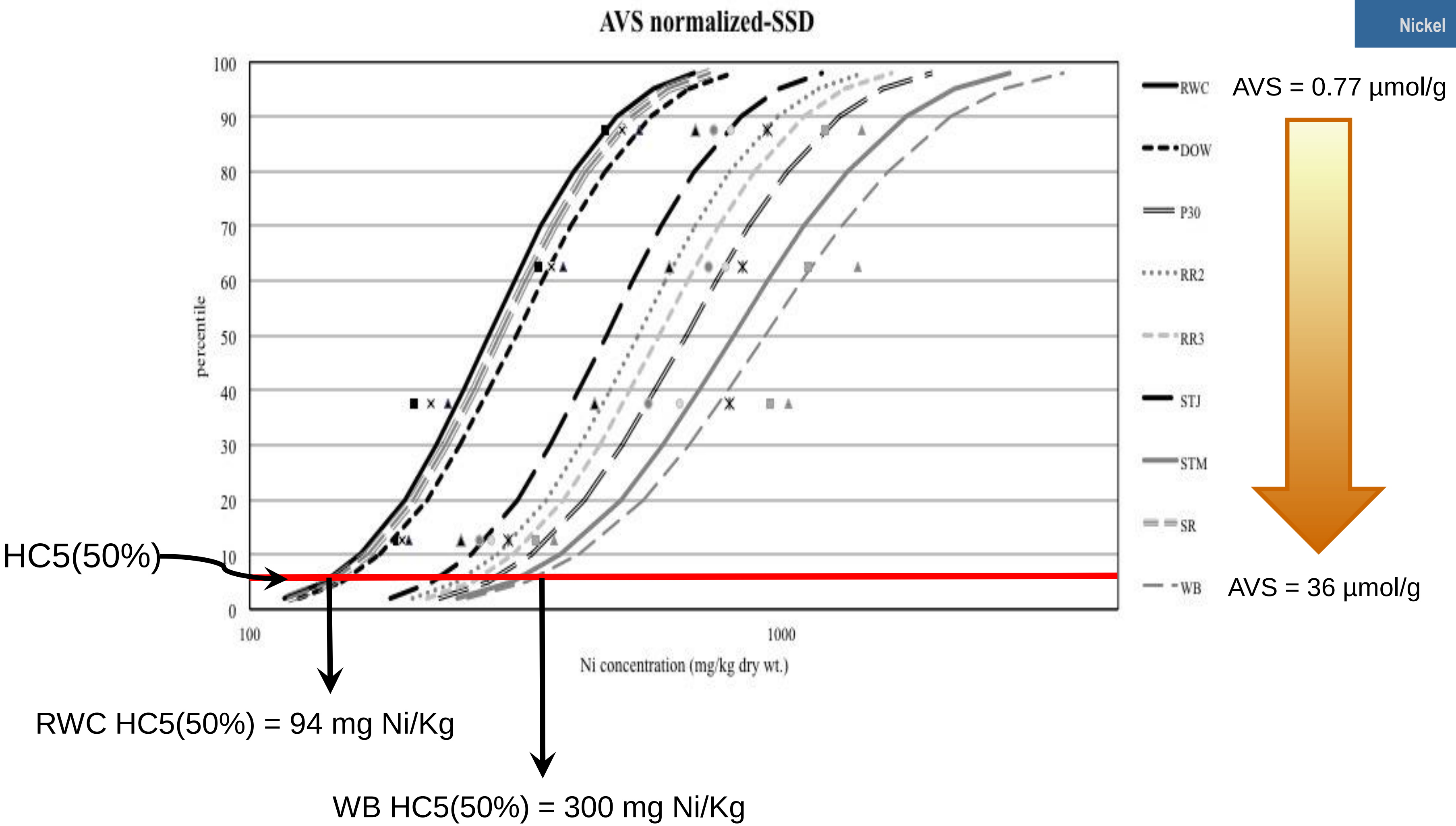
SSD Calculation

- **Toxicity data available for 4 species**
- **No response from 4 additional species (i.e., unbounded NOEC of ≥ 760 mg Ni/kg)**

- **AVS model used**
- **Use AVS in test sediments to illustrate range of effects concentrations likely for EU systems (10P to 90P)**

- **Outcome: HC5(50%) value**

Outcome: Influence of AVS on HC5(50%)



Alternatives to direct sediment testing: EqP

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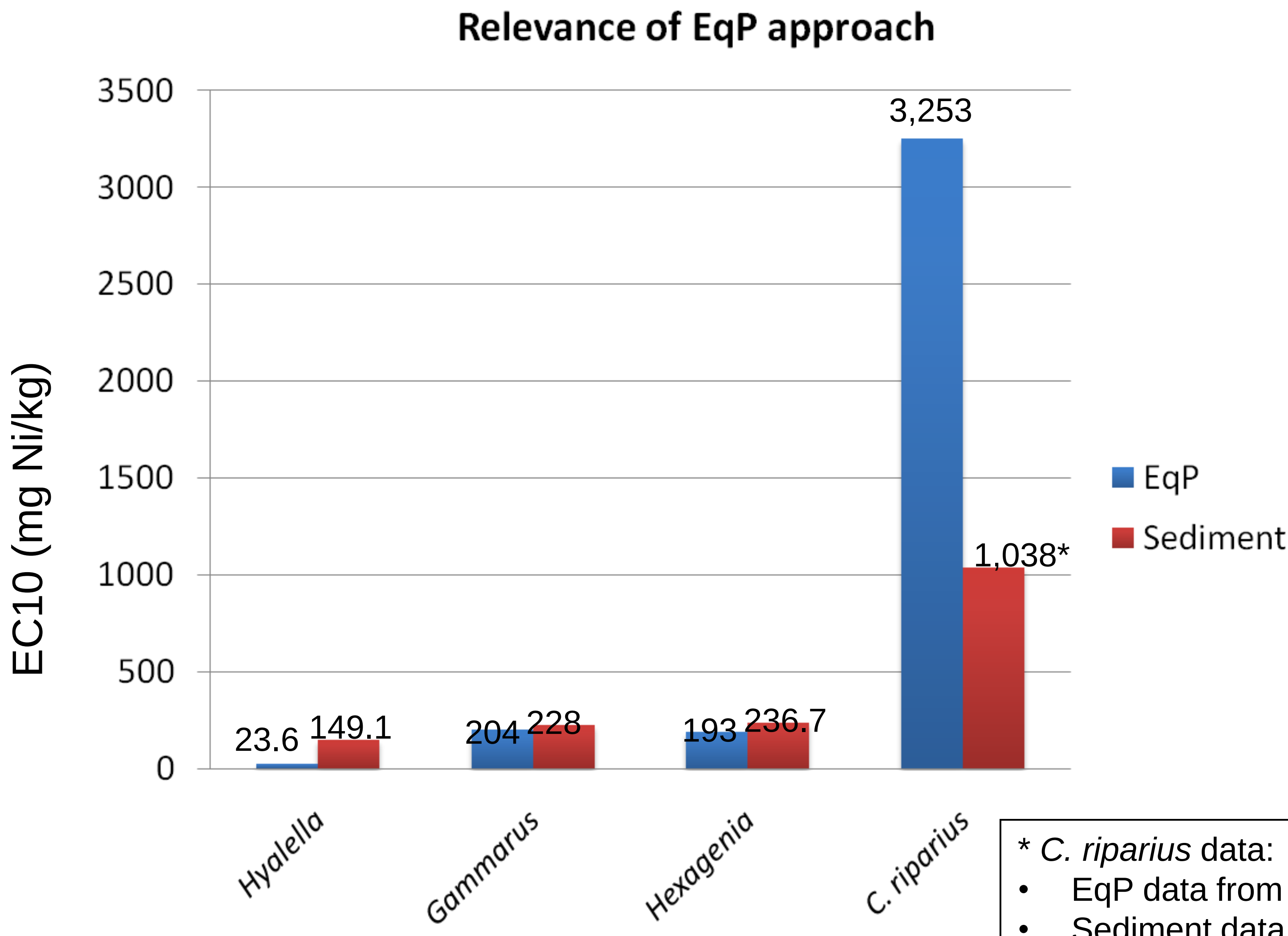

* *C. riparius* data:
- EqP data from USGS
- Sediment data from Gent U.

Step 5: Field Validation (U. Michigan, WSU)

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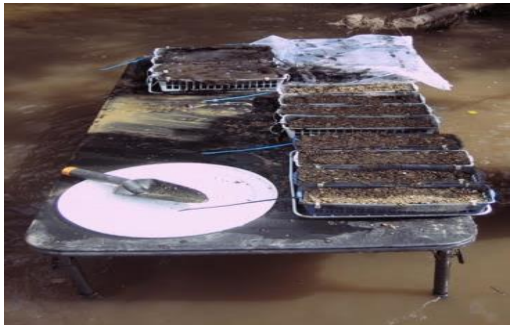
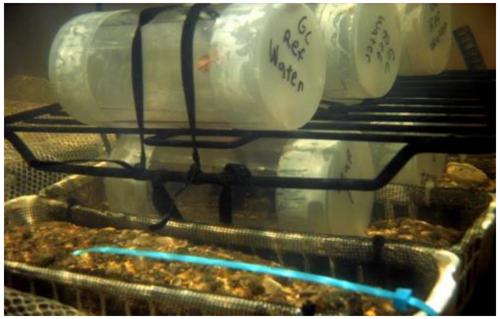
- Field experiments conducted to validate laboratory results
- Field study conducted with 5 of 8 sediments from Laboratory testing
  - Laboratory Ni spiked sediments at 3 Ni conc. (plus 1 ref)
- Endpoints:
  - Short-term *in-situ* caged studies with *H. azteca (acute toxicity)*
  - Long term colonization (6 months)
    - Invert. abundance, taxa richness (family level), Shannon diversity, abundance of common and sensitive taxa
  - Extensive chemical characterization
    - pH (surface/pore), hardness/alkalinity (surface), DOC, ammonia (pore), AVS/SE-Ni (sed), TOC, total recoverable Ni, Fe/Mn oxides, DGT labile Fe/Mn/Ni

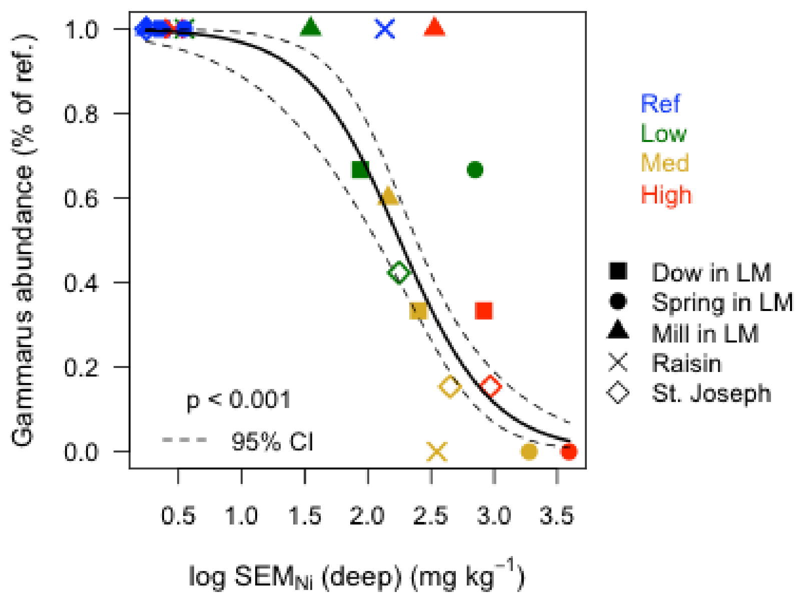




Step 5: Field Validation (U. Michigan, WSU)

- Behavior:
  - Partitioning changed over time, reflecting ageing process
- Toxicity:
  - <u>At 4 weeks</u>:
    - Effects on ecological communities observed
    - Relationships related to same factors observed in lab studies (AVS, TOC, Fe)
  - <u>At 8 weeks:</u>
    - No Ni-related effects
    - Concentrations remained as high as 3,000 mg Ni/kg
- Conclusions
  - Laboratory effects protective of recorded field effects

Gammarus abundance: 4 weeks



Weight of Evidence Evaluation

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1. Laboratory sediment toxicity data
   - HC5(50%) from RWS sediment = 94 mg Ni/kg
   - Below lowest measured EC10 (138 mg Ni/kg, for *H. azteca*)
2. Field effects data
   - Effects observed at 28 d, but not at 56 d ([Ni] as high as 3000 mg Ni/kg)
   - Suggests "ageing" process, which is not reflected in laboratory data
3. Bioavailability relationships
   - Both lab and field effects were affected by sediment parameters (AVS, OC, Fe)
   - Toxicity varies among sediments
   - Normalization approach greatly influenced by *Hexagenia* slope (i.e., the least "AVS-SEM- dependent" species)
4. Background Ni sediment concentrations
   - Good control performance in sediments with [Ni] as high as 51 mg/kg
   - P50 for some regions (Finland) as high as 41 mg Ni/kg

Distributions of Ni and AVS in EU sediments

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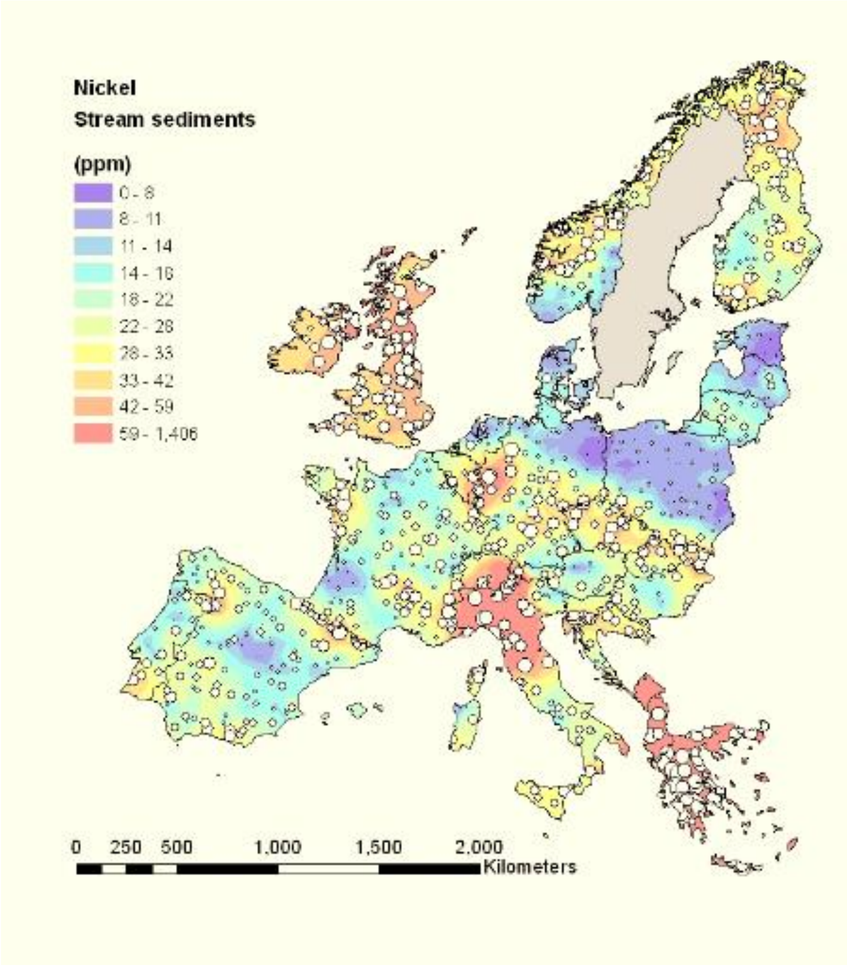

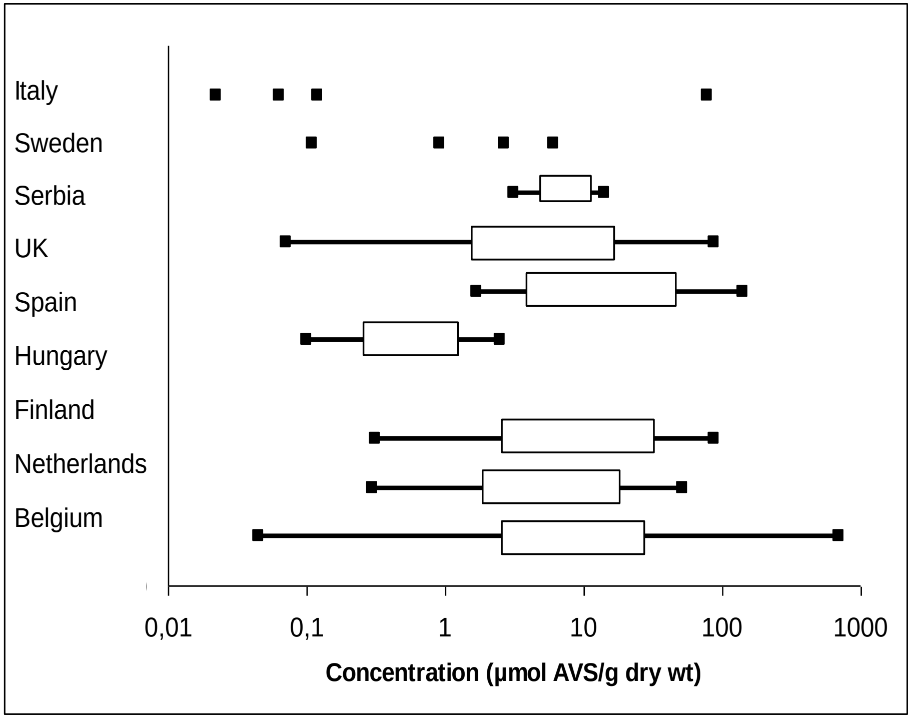

Provisional risk characterization

- Bioavailability-normalization approach used to assess risk for selected Ni producing and downstream-using industries
  - Industries assessed included stainless steel, FeNi, surface plating, chemicals, catalysts, batteries, and ceramics
- Site-specific Ni sediment concentrations (PEC) estimated from
  - Regional background Ni sediment concentrations (24 – 29 mg Ni/kg)
  - Estimated contributions from site-specific emissions calculated using EqP approach
- Site-specific PNECs as a function of
  - Applying range of Assessment Factors (1 to 3) to HC5(50%) of the SSD_{bioav}.
  - Using 10P to 90P range of AVS for species dependent bioavailability normalisation
- Risk characterization
  - RCR = PEC/PNEC

Initial Risk characterization: Effect of AF

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Industrial Sector	No. of sites with RCR > 1 / total no. of sites			
	AF = 1	AF = 1.5	AF = 2	AF = 3
Nickel metal producers	1/7	2/7	2/7	5/7
Stainless Steel production	9/23	9/23	9/23	23/23
Ferro-nickel producers	0/1	1/1	1/1	1/1
Chemicals production	1/11	2/11	2/11	9/11
Nickel plating	4/12	4/12	6/12	11/12
Catalyst producers	2/10	4/10	4/10	10/10
Battery production	0/ 3	0/ 3	0/3	3/3
Ceramics production	0/2	0/2	0/2	2/2
No. of sites RCR>1/ total no. of sites	17/69	22/69	24/69	64/69

Risk characterization: Impact of Bioavailability normalization

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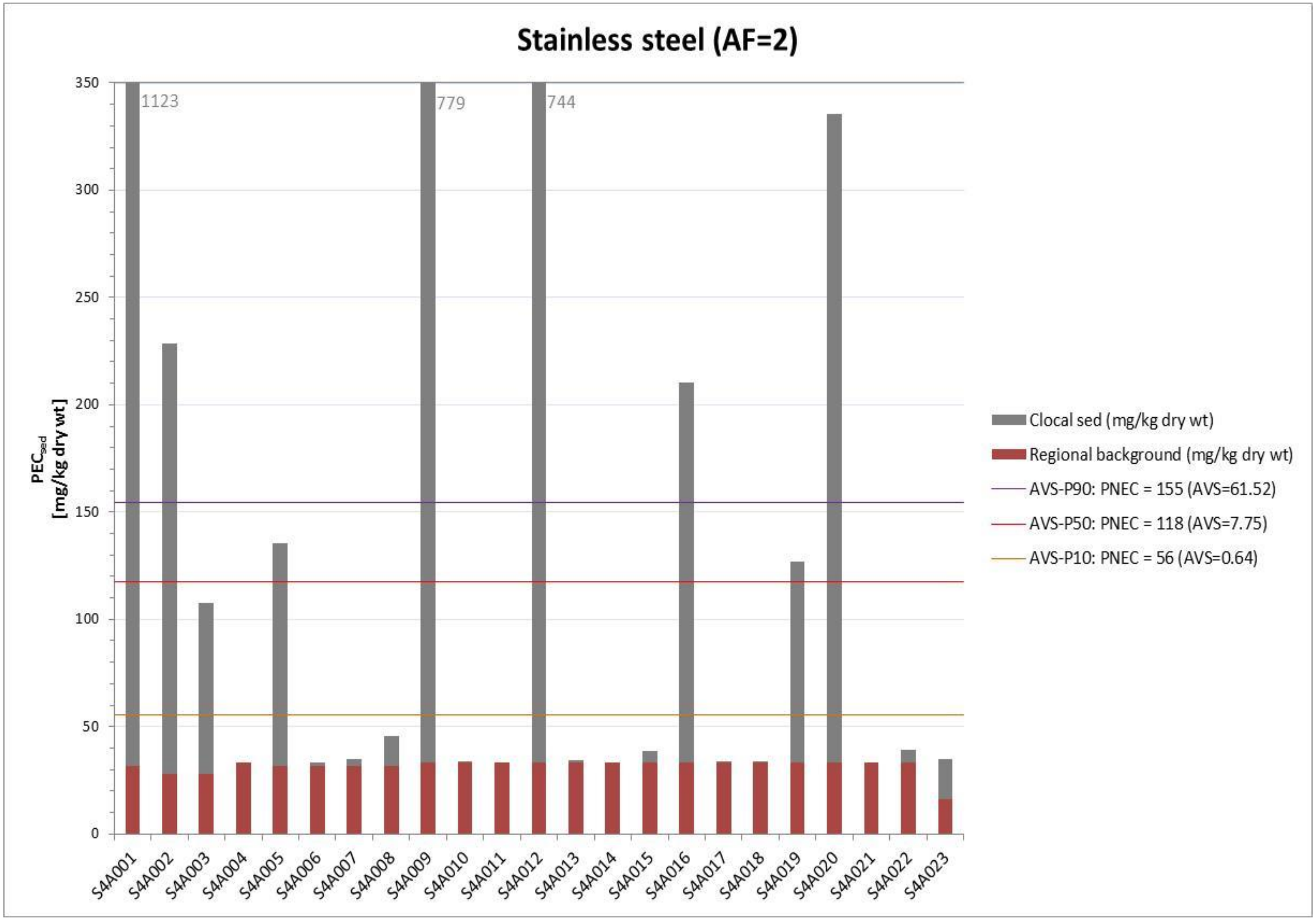

Implementation in Risk Assessment – refinements to consider in tiered approach

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- In a tiered approach, Tier 1 will include comparison of ambient sediment Ni concentrations with RWC HC5(50%)/PNEC
- If Tier 1 indicates potential risk, several types of refinements are possible

Reduce the uncertainty in deriving the PEC aquatic

•Measured Ni in effluent

•Measured daily wastewater emissions

• Dilution factor

Refinement options PEC

Collect exposure/emission data for the aquatic compartment

Collect exposure/emission data for the sediment compartment

Reduce the uncertainty in deriving the PEC sediment

•Measured value only avaliable for one site

Refinement options bioavailability

Screen out potential sites at risk using a generic PNEC reflecting high bioavailability

Use of historical AVS data and subsequently normalize PNEC local

Collect actual SEM-AVS data

SEM-AVS < 0 no risk
SEM-AVS > 0 potential risk

Allows to normalize the PNEC for bioavailability

- **Historical AVS data is limited**
- **AVS is not a routine measurement**

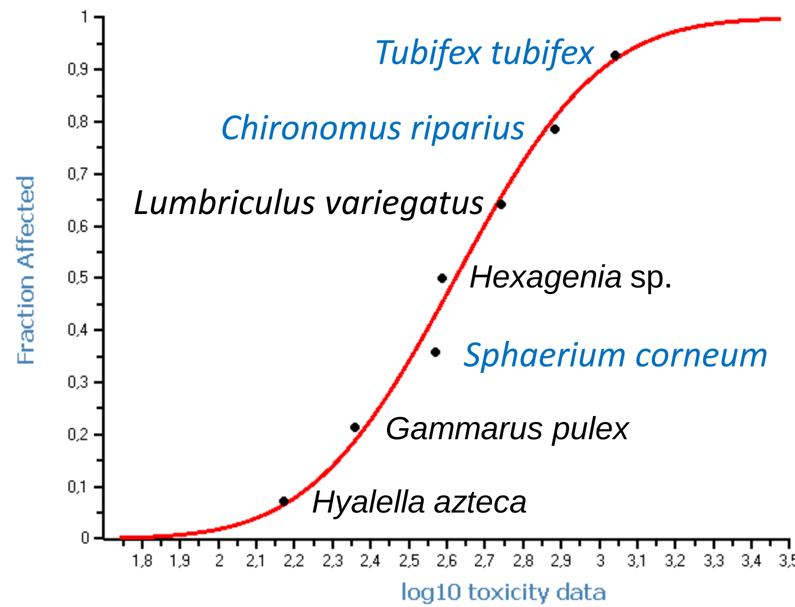
Generate Site-specific PNEC

- **SEM-AVS < 0 can be used as an indicator for absence of toxicity**

Data gaps

Areas of uncertainty and recommendations of the TC i) Group

1. Breadth of SSD
   - SSD comprised of four species (four additional species did not respond to highest Ni concentrations)
   - Not ideal for HC5(50%) determination
   - <u>Recommendation</u>: Test additional species
     - <u>New research</u>: Testing at U. Gent for oligochaetes (*Tubifex tubifex*), insects (*Chironomus riparius*, *Ephoron virgo*), and molluscs (*Sphaerium corneum*)
     - See poster by Nguyen et al. for more details
     - Impact on SSD?



$HC_{5\text{-}50}$ = 127 mg Ni/kg dry wt.

Data gaps

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Areas of uncertainty and recommendations of the TC i) Group

2. Role of dietborne exposure
   - Hypothesis for weaker bioavailability relationships with *Hexagenia* sp.
   - Legitimate source of uncertainty in sediment risk assessment
   - Recommendation of TC i) Group: Quantify relative importance of dietborne exposure for manifestation of Ni toxicity to sediment organisms
     - New research: Testing at U. Ghent on *Lumbriculus variegatus* and *Spaerium cornuem*
3. Validation of bioavailability models
   - Address alternative hypotheses for weaker bioavailability relationships with *Hexagenia* sp.
   - Recommendation of TC i) Group: Independent analysis with additional species, additional sediments
     - New research: Testing at U. Ghent to evaluate validity of existing models for new test species

Thank you!

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Please send comments/questions to

cschlekat@nipera.org