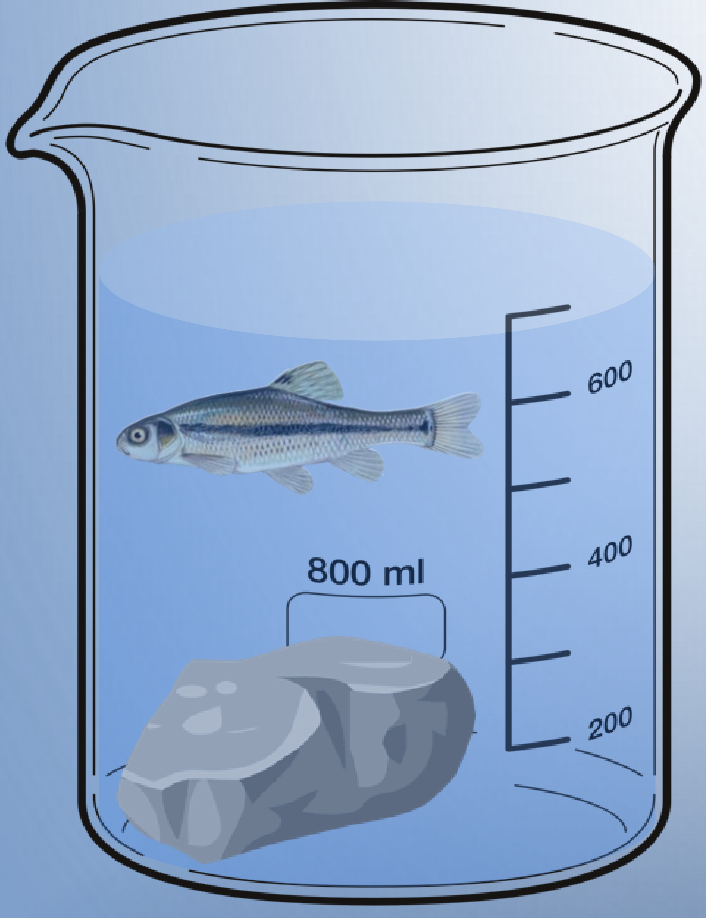


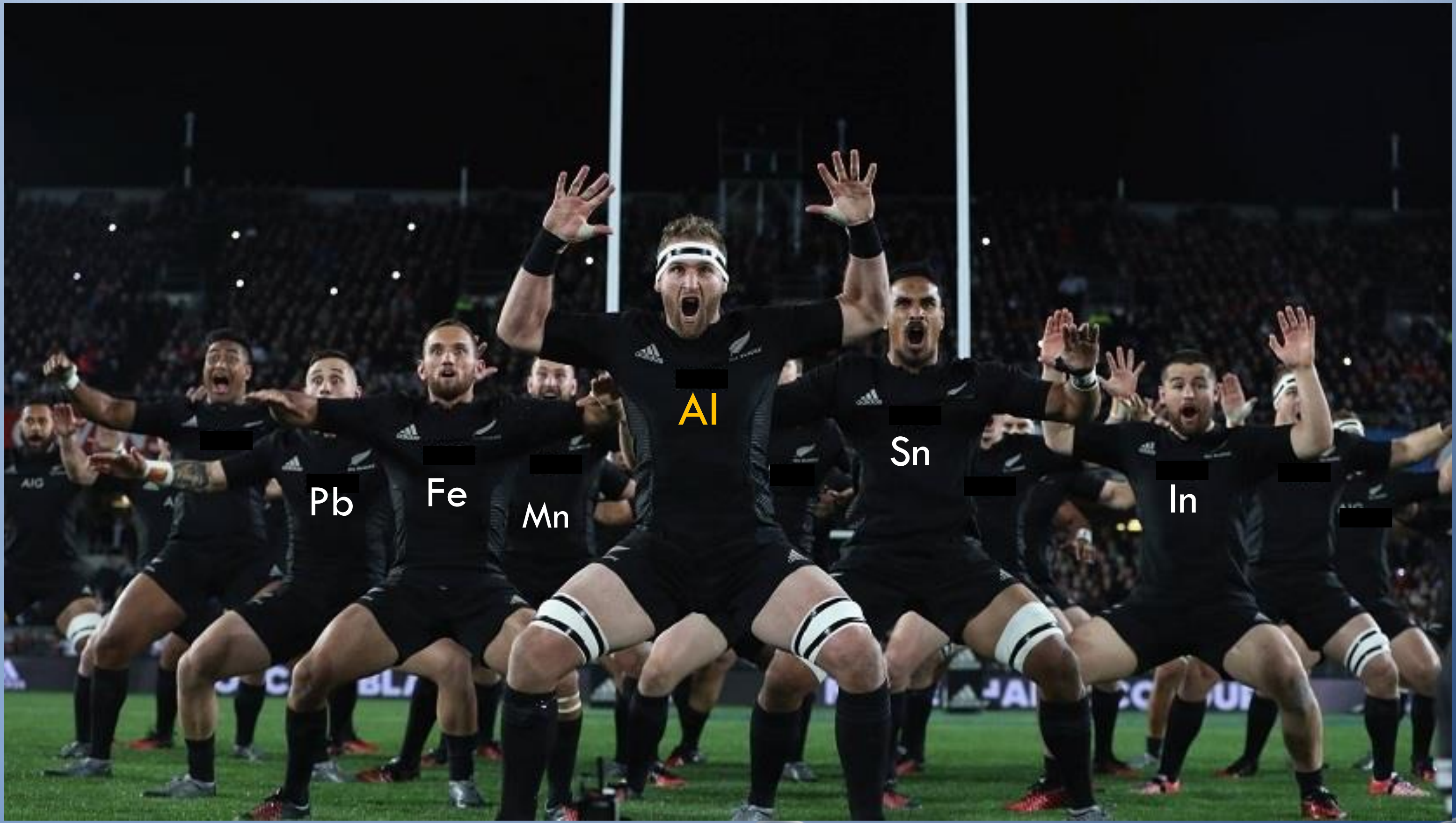
TESTING DIFFICULT SUBSTANCES

W STUBBLEFIELD, E NORDHEIM,

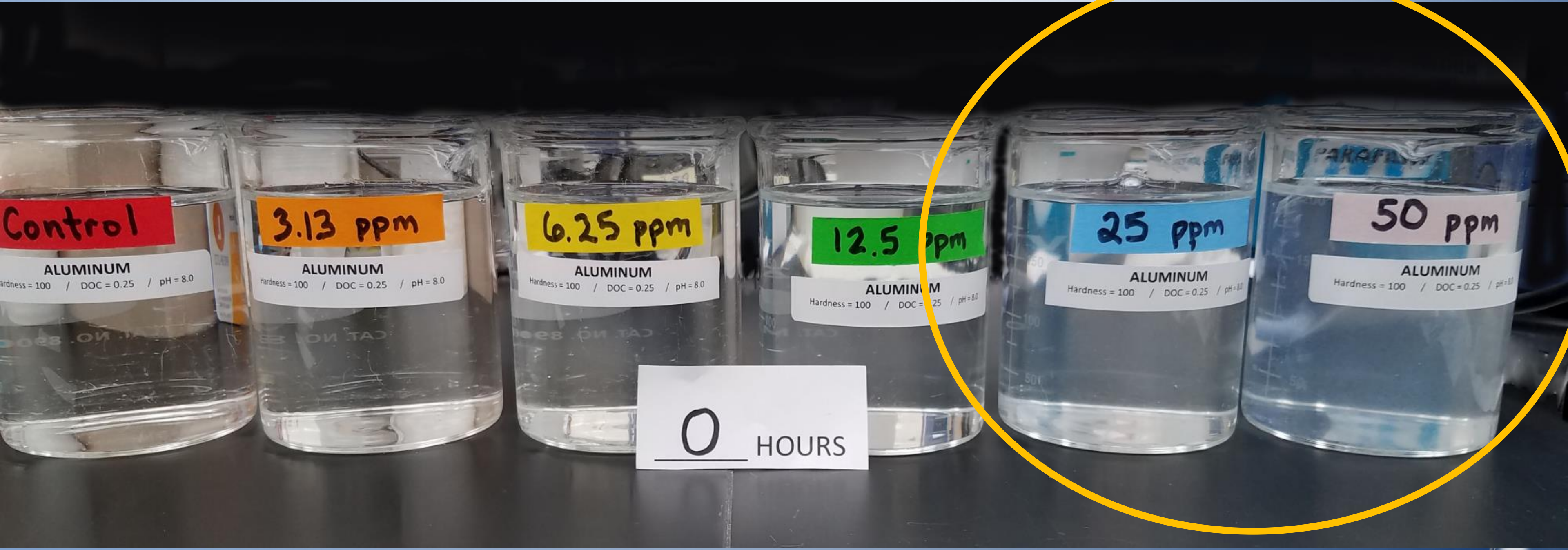
AND W ADAMS

THE EASY ONES….

THE BAD BOYS

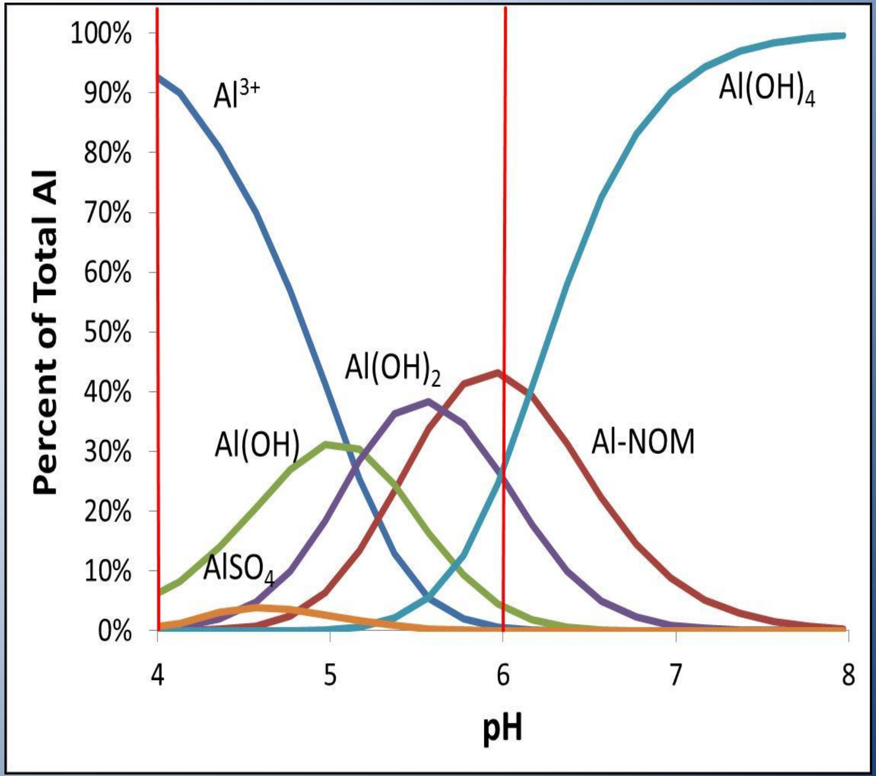


PRECIPITATE FORMATION



WHAT'S THE ISSUE?

- PRESENCE OF ALL THREE ALUMINUM HYDROXIDE SPECIES: $Al(OH)^{2+}$, $Al(OH)_2^{+}$, $Al(OH)_4^{-1}$ FAVORED AT pH >5.5.
  - ACID WATERS: Al^{3+} ION IS THE DOMINANT SPECIES PRESENT
  - HIGHER pH WATERS (pH >7), $Al(OH)_4^{-1}$ IS THE DOMINANT SPECIES



Example: Al Speciation diagram as a function of pH

WHY IS IT IMPORTANT?

- 95% OF EUROPEAN SURFACE WATERS HAVE A pH OF >6.0 (FOREGS 2005), THUS pH OF >6.0 IS MORE REPRESENTATIVE OF TYPICAL “NON-ACIDIC” EUROPEAN WATERS.
- AND, AT pH >6.0, Al^{3+} IS PRESENT ONLY AT VANISHINGLY LOW CONCENTRATIONS

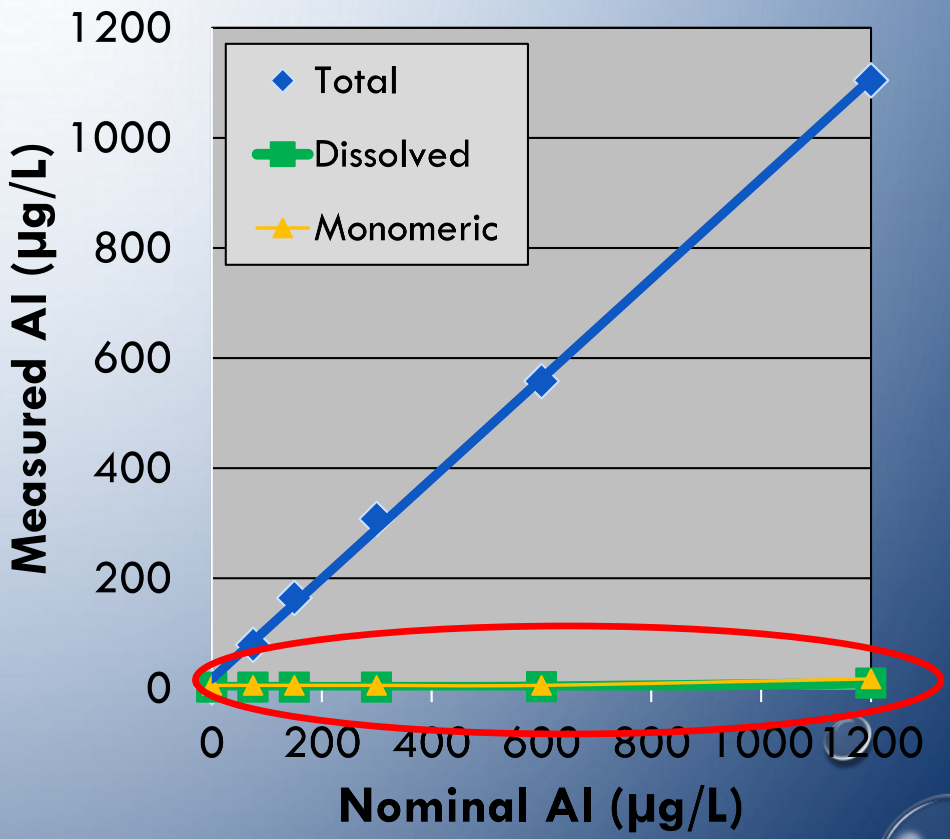
OUR APPROACH…

WHY “AGE” AI STOCKS?

- FRESHLY PREPARED AI SOLUTIONS ARE NOT AT CHEMICAL EQUILIBRIUM
    - NEWLY FORMED AI HYDROXIDES AND UNREACTED FREE-ION ARE MORE TOXIC AND LESS ENVIRONMENTALLY RELEVANT IN MOST CASES
- KINETICS OF PRECIPITATION REACTIONS AND STABILITY OF THE REACTION PRODUCTS ARE KEY TO UNDERSTANDING ENVIRONMENTAL EXPOSURES
- AGING OF STOCK SOLUTION BASED ON PPT KINETICS (e.g., 3 HOURS FOR AI) MUST BE INCORPORATED TO REDUCE TRANSIENT EFFECTS CAUSED BY DISEQUILIBRIUM AMONG AI SPECIES

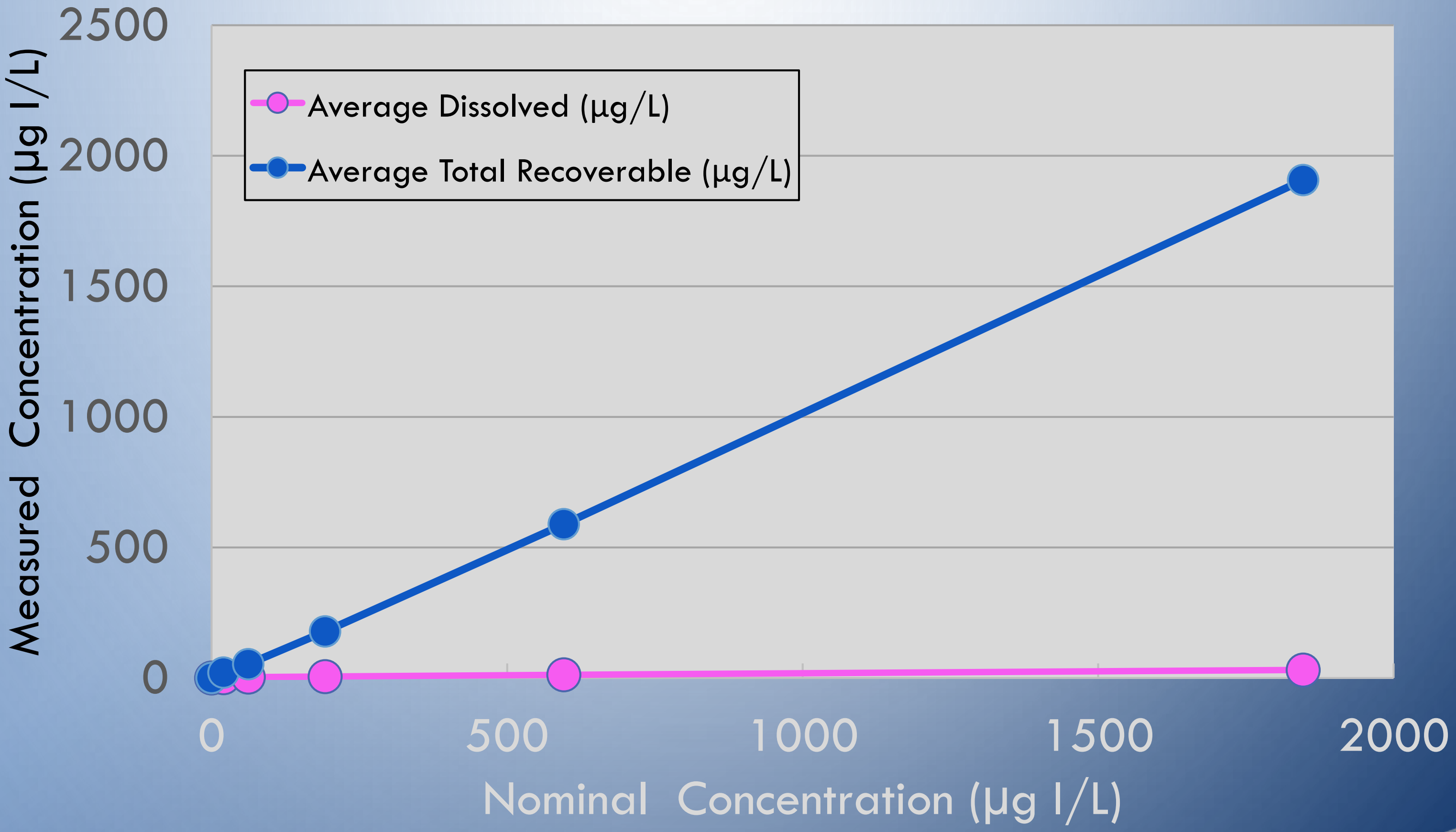
RESULTS

- TOTAL Al CORRELATES WELL WITH NOMINAL EXPOSURE CONCENTRATIONS AND TOXIC RESPONSES.
- DISSOLVED AND MONOMERIC Al : SIGNIFICANTLY LOW ACROSS ALL CONCENTRATIONS (DUE TO PRECIPITATION OF INSOLUBLE Al SPECIES)



Example: Fathead minnow Early-Life Stage Test pH 6

INDIUM SHOWS THE SAME RELATIONSHIP



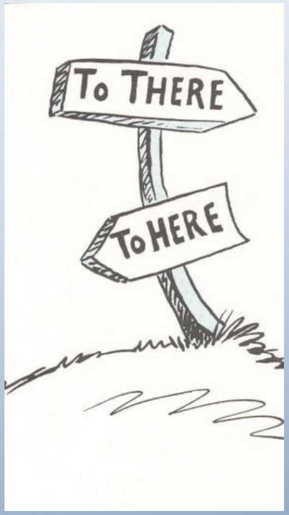
TEST PROCEDURES FLOW-THROUGH SYSTEM

- CONTINUOUS-FLOW PROPORTIONAL DILUTER (BENOIT et al. 1982)
- FISH TESTED IN BENOIT CHAMBER
- MIDGE AND AMPHIPOD TESTED IN WATER BATH

ANALYTICAL

- TOTAL, DISSOLVED, AND MONOMERIC Al SAMPLED THROUGHOUT TESTING
- TOTAL AND DISSOLVED Al ANALYZED BY ICP-OES / ICP-MS
- MONOMERIC Al ANALYSIS ACCORDING TO BARNES (1975) AND MCAVOY ET AL. (1992) BY EXTRACTION WITH 8-HYDROXYQUINOLINE IN METHYL-ISOBUTYL KETONE (MIBK)
- NATURAL WATERS TESTING INCLUDED pH 4 EXTRACTION METHOD (RODRIGUEZ ET AL. 2019), TO MEASURE POTENTIALLY BIOAVAILABLE Al.

THE DILEMMA…



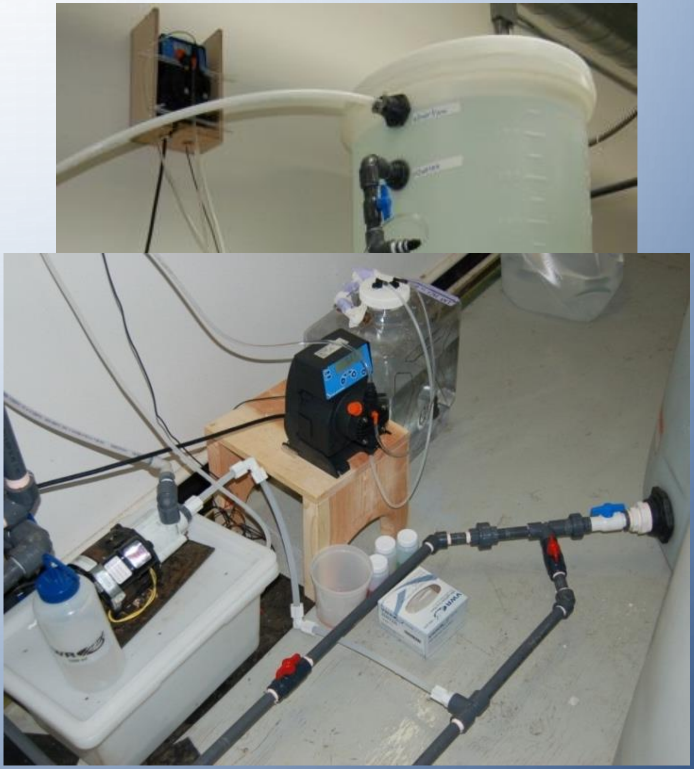
TEST PROCEDURES FLOW-THROUGH SYSTEM

DILUTION WATER

- pH ADJUSTED BY ADDITION OF DILUTE ACID (HCL) AND MAINTAINED USING A pH-CONTROL PUMP WITH PROPORTIONAL OUTPUT.

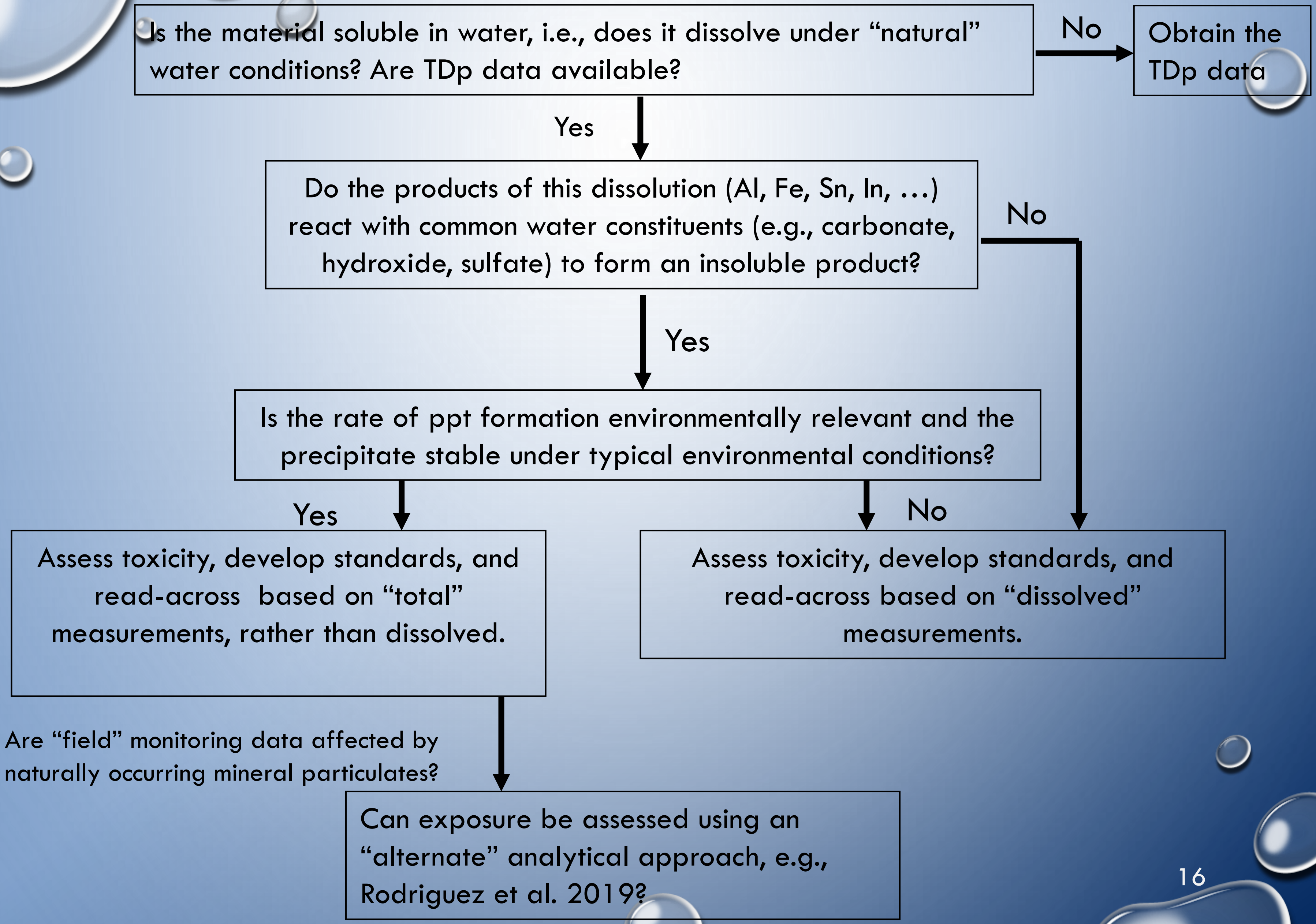
Al STOCK SOLUTION

- HIGHEST EXPOSURE SOLUTION WAS PREPARED BY ADDITION OF ACID AND CONCENTRATED AL STOCK IN LARGE TANKS
- MIXED FOR 3-HOUR EQUILIBRIUM PERIOD AT pH 6 USING A pH-PUMP CONTROLLER INJECTING DILUTE ACID (HCl)



REAL-WORLD COMPLICATIONS

- FOR METALS REMAINING IN SUSPENSION PRIMARILY AS METAL HYDROXIDES, TOXICITY CORRELATES WITH ”TOTAL” METAL
- LABORATORY DILUTION WATERS DO NOT CONTAIN SUSPENDED SOLIDS, CLAYS, OR PARTICULATE MATTER TO WHICH PARTICLE-REACTIVE METALS SUCH AS AL (AND FE, PB, ETC.) CAN BIND, REDUCING THEIR POTENTIAL BIOAVAILABILITY.
- A DISTINCTION MUST BE MADE IN HOW MEASUREMENTS OF AL IN WATER ARE MADE, SO THAT EXTRAPOLATING LABORATORY DATA TO NATURAL WATERS IS BETTER CONSTRAINED.



Is the material soluble in water, i.e., does it dissolve under “natural” water conditions? Are TDp data available?

No

Obtain the TDp data

Yes

Do the products of this dissolution (Al, Fe, Sn, In, …) react with common water constituents (e.g., carbonate, hydroxide, sulfate) to form an insoluble product?

No

Yes

Is the rate of ppt formation environmentally relevant and the precipitate stable under typical environmental conditions?

Yes

No

Assess toxicity, develop standards, and read-across based on “total” measurements, rather than dissolved.

Assess toxicity, develop standards, and read-across based on “dissolved” measurements.

Are “field” monitoring data affected by naturally occurring mineral particulates?

Can exposure be assessed using an “alternate” analytical approach, e.g., Rodriguez et al. 2019?

SUMMARY FOR DIFFICULT TO TEST METAL SUBSTANCES

- SEVERAL METALS (E.G., AL, FE, MN, PB, SN) FORM INSOLUBLE METAL SPECIES IN STANDARD OECD TOXICITY TEST MEDIA (METAL HYDROXIDES OR CARBONATES)
- TO OBTAIN USEFUL DATA FROM TOXICITY TESTS:
  - PH AND TOXICITY NEED TO BE STABLE
  - METAL SPECIES IN SOLUTION AS A FUNCTION OF PH MUST BE KNOWN
  - MEASUREMENTS OF METAL CONCENTRATION MUST BE RELATED TO EFFECT (THE EXACT TYPE OF MEASURE, I.E. TOTAL, DISSOLVED, OTHER, MAY VARY BY METAL)
- INTERACTIONS WITH DOC, HARDNESS, AND PH ARE IMPORTANT FOR AL, FE, PB. OTHERS?
- ALL TESTS TO DATE USED SOLUBLE METAL SUBSTANCES, I.E., METAL CHLORIDE, NITRATE, OR SULFATE, ETC. – OTHER LESS SOLUBLE FORMS SHOWN TO BE NON-TOXIC

SUMMARY FOR DIFFICULT TO TEST SUBSTANCES

- APPLICATION OF THESE DATA TO OTHER SPARINGLY SOLUBLE SUBSTANCES, i.e., OXIDES OR SULPHIDES OR METAL POWDERS **MUST** BE DONE IN CONJUNCTION WITH TRANSFORMATION – DISSOLUTION STUDIES FOR THOSE SUBSTANCES
- EACH OF THESE SUBSTANCES MUST BE EVALUATED AS A SPECIFIC CASE, WHICH DOES NOT FOLLOW GENERAL GUIDANCE, AND THEY SHOULD BE RECOGNIZED AS DIFFERENT FROM OTHER METALS.
- ALUMINIUM AND IRON ARE THE TWO MOST COMMON METALS IN THE EARTH'S CRUST AND ANY CONCENTRATION FOUND IN THE AQUATIC ENVIRONMENT WILL BE DOMINATED BY GEOGENIC SOURCES.

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Metals that are difficult to test

CASE STUDY: EXPOSURE BASED WAIVING IRON AND ALUMINIUM ECOTOXICITY TESTING FOR SOILS AND SEDIMENTS

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Ecotoxicity testing iron and aluminium

Iron and aluminum are not classified as dangerous for the environment but two examples of metals where natural background concentrations outweigh the anthropogenic contributions in soils and sediments.

Necessity to test?: Depends on two main factors:

- Relative contribution of anthropogenic iron and aluminium oxide to the natural iron and aluminium oxide baseline
- Fate and reactivity/toxicity of freshly formed iron oxides vs natural aged natural background

Relative contribution anthropogenic iron and aluminum

Exposure model EUSES was used to calculate the relative contribution of anthropogenic iron and aluminium oxide to the natural iron and aluminium oxide baseline concentrations found in soils and sediments.

Media	Parameter	Unit	Natural baseline	Anthropogenic contribution	Relative contribution (%)
Topsoil	Iron	g/kg dry wt.	18.5	0.0166	0.09
Stream sediment	Iron	g/kg dry wt.	18.2	0.1668	0.9
Topsoil	Aluminium oxide	%	10.5	0.022	0.2
Stream sediment	Aluminium oxide	%	9.8	0.0167	0.17

Anthropogenic iron and aluminium contribution less then 1 % of the natural geochemical iron and aluminium cycling.

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Fate/kinetics and ecotoxicity freshly formed anthropogenic iron and aluminum

- Freshly formed iron and aluminium oxides are less crystalline and therefore have an initial higher reactivity than older more crystalline iron and aluminium oxides.
- However, no scientific evidence that ageing and integration in the natural iron and aluminium cycle would be a slow process.

Conclusion: the relative contribution of anthropogenic iron and aluminium to the already present natural iron and aluminium pool in soils and sediments is not relevant in terms of added amounts and in terms of toxicity. Hence no need to perform ecotoxicity tests for iron and aluminium for the soil and sediment compartment.

CASE STUDY: TESTING METALS IN THE SOIL COMPARTMENT

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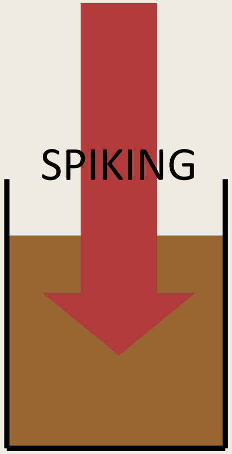
Soil testing: impact of spiking methods

Lab conditions



- Sudden disturbance
- No long-term equilibration
- Increased ionic strength and decreased pH

Field conditions

- Gradual accumulation
- Ageing reactions
- Excess ions leached out

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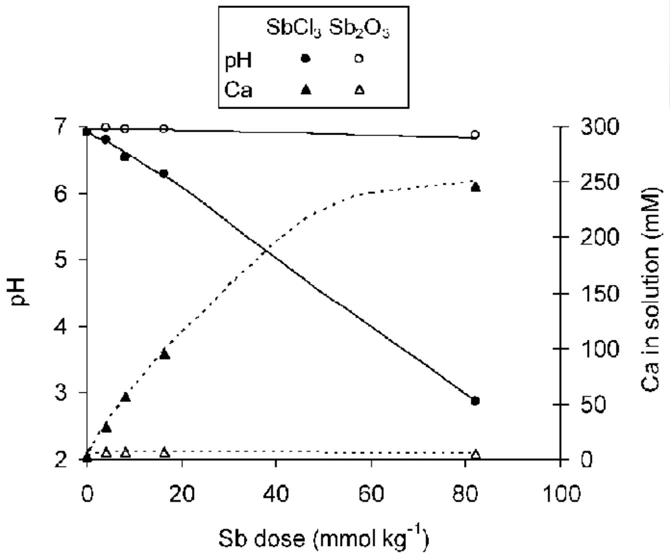
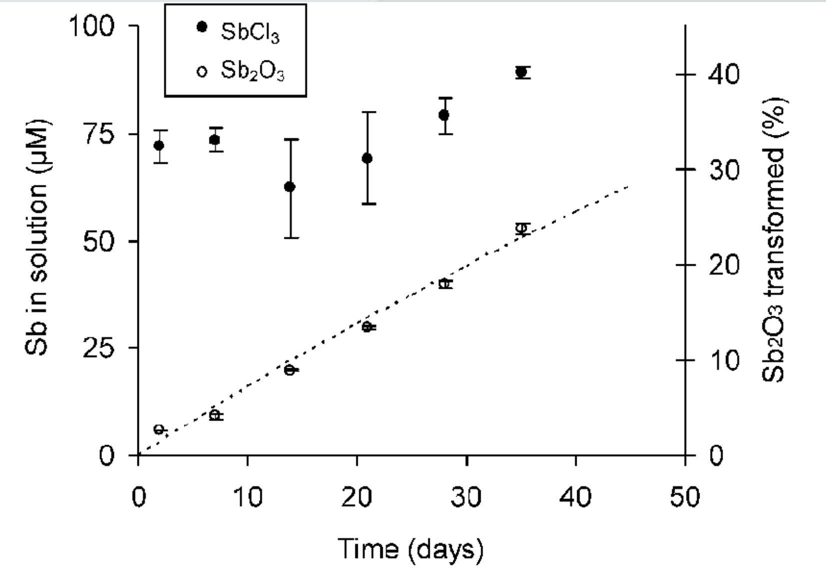
Sb toxicity testing in soil

- Problem: confounding effects from *acidification* and *increased salt concentration* caused by spiking with soluble Sb salts:

$$SbCl_3 + 3H_2O \rightarrow Sb(OH)_3 \underline{+ 3H^+ + 3Cl^-}$$

- Alternative: spiking with Sb_2O_3 ($Sb_2O_3 + 3H_2O \rightarrow 2Sb(OH)_3$)
- Issue: poor solubility of Sb_2O_3

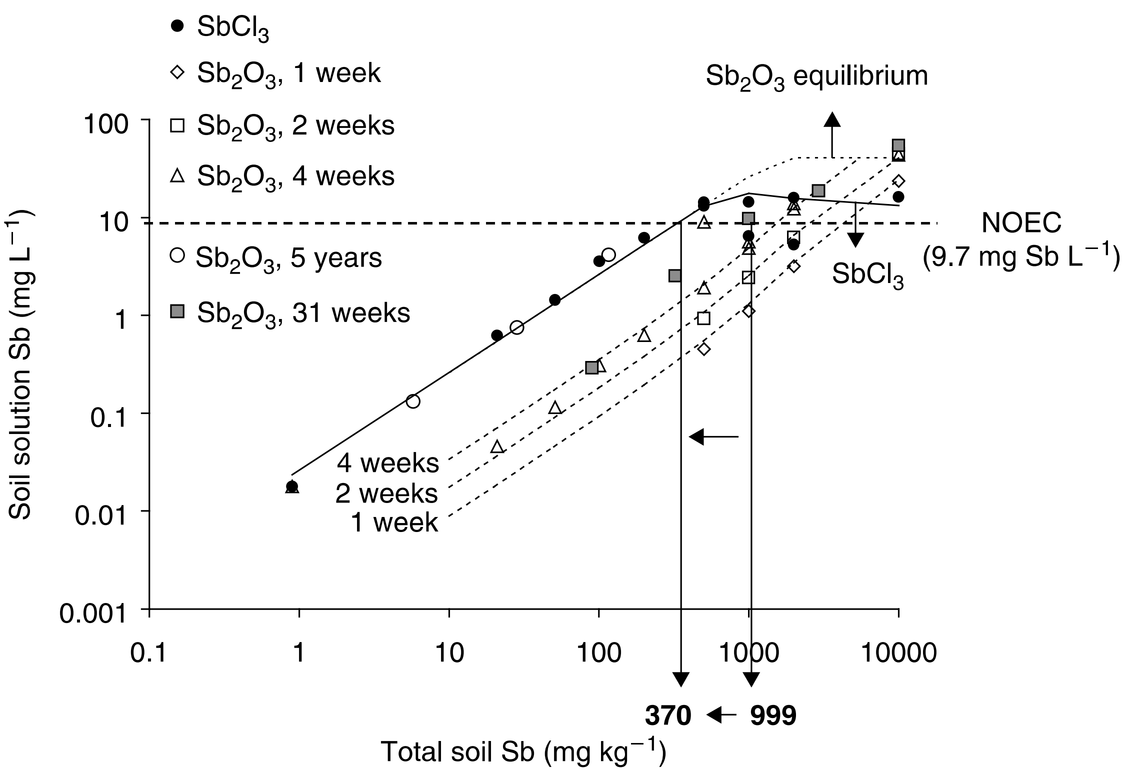




From: Oorts et al. 2008. Environ. Sci. Technol. 42, 4378–4383

Sb toxicity testing in soil

- Solution: correction for lower solubility of Sb_2O_3 via the pore water concentration at NOEC and information on fate of released ions in soil.



From: Oorts and Smolders. 2009. Environ. Chem. 6, 116-121

CASE STUDY: TESTING METALS IN THE SEDIMENT COMPARTMENT

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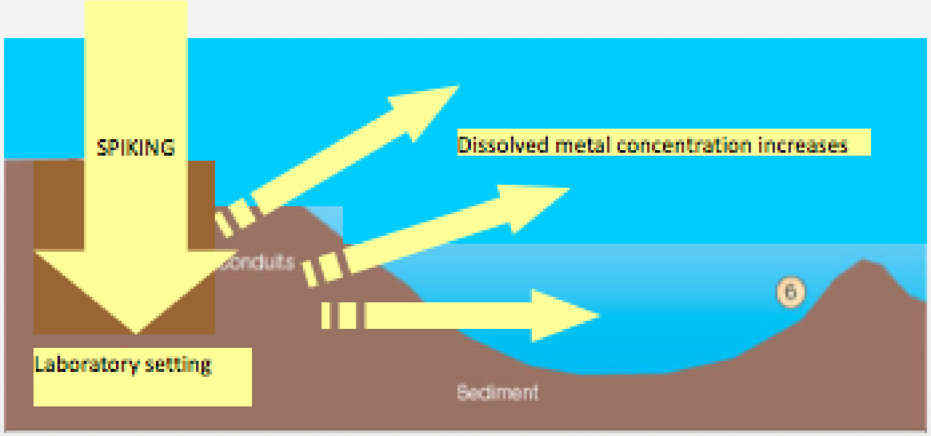
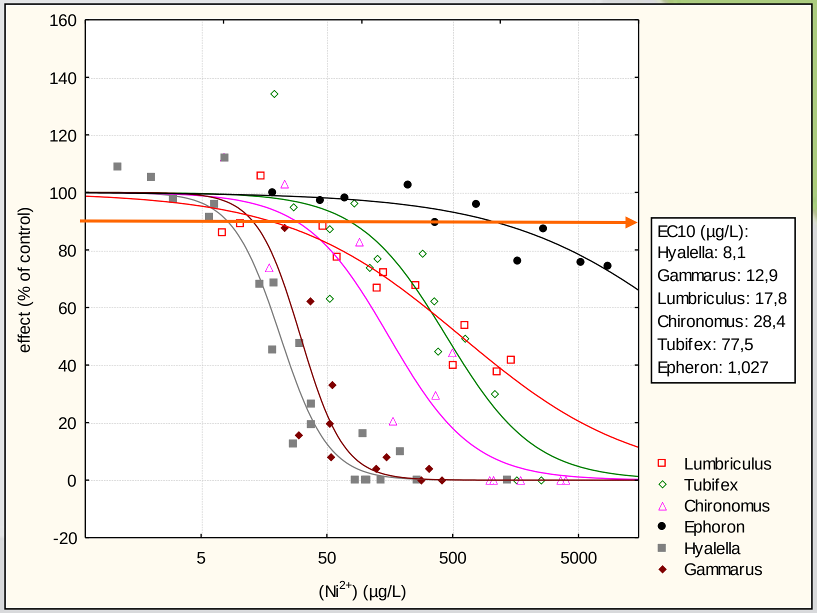
Sediment testing: impact spiking procedures (e.g. Ni)



Laboratory experiments

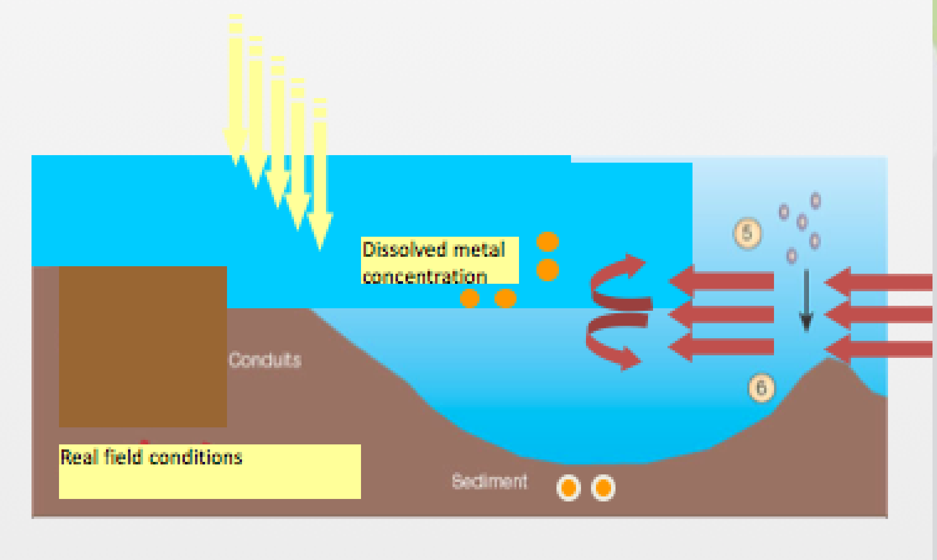
-Semi-static system: built-up of high overlying water concentrations

Overlying water Ni concentrations explained better observed effects then bulk sediment concentration



Important for metals with slow equilibration kinetics for certain sediment solid phases.

Sediment testing: impact spiking procedures (e.g. Ni)



SOLUTION

- Use of well equilibrated sediments (at least 10 weeks) is necessary to avoid bias by overlying water triggering toxicity.
- New spiking procedures were developed keeping Ni water concentrations well below chronic Ni water concentrations (Brumbaugh et al, 2013). Two-step spiking approach
- Flow-through test conditions are recommended (e.g. 8 volume additions/day)

Stable and environmentally realistic partitioning of Ni in spiked sediments was achieved following the above.

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Metals that are difficult to test for ENV

MISA Environment Workshop

07 February 2019

Marta Sobanska, Anne-Mari Karjalainen, Bram Versonnen, and Evita Luschutzky

Metals that are difficult to test for ENV

- For metals and poorly soluble metal compounds, aquatic tox information should be derived with test on a soluble metal salt in comparison with results from T/Dp test.
- For readily soluble metal compounds no T/Dp data need to be generated.
- Ready solubility is considered if water solubility (after 24 hours T/Dp) ≥ acute ERV of dissolved metal ion concentration

- WAF testing is not a reliable testing method for metals for the following reasons:
    - *WAF does not take into account the influence of pH*
    - *milling or making the material more massive could influence the outcome of test*
    - *precipitation or other reactions could hide the potential for toxicity*
    - *WAF provides results in nominal values*

Revised OECD GD 23:

7. STOCK AND TEST SOLUTION PREPARATION AND EXPOSURE SYSTEMS FOR DIFFICULT TEST CHEMICALS

30. It should be noted that **OECD GD 29** and **98** provide considerations regarding transformation/dissolution of metals and metal compounds in aqueous media and may assist to determine the test solution preparation procedure and hazard assessment of metals and metal compounds. In addition, it may be relevant to consider the same methodology for classification of poorly soluble test chemicals that are known to transform gradually (e.g. via hydrolysis) to substances of higher concern (e.g. as a supplement or alternative to tests based on water-accommodated fractions [WAFs]).

7.10. ALLOYS

156. In general, alloys can be considered separately from other preparations due to their unique physicochemical properties that differentiate them from simple mixtures of component elements. Due to the decreased solubility or lack of solubility of many alloys, the approaches identified for multi-component test chemicals are not appropriate [*e.g WAF*]. However, care should be taken due to the fact that some alloys such as powered brass show toxicity to aquatic organisms.

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OECD GD 29 (T/Dp) as referred to in OECD GD 23

- Determine the production of soluble available ionic and other metal-bearing species in aqueous media under standard laboratory conditions representative of those generally occurring in the environment.

- Applicable to all metals and sparingly soluble inorganic metal compounds, including UVCBs.

- Together with ecotox data for soluble metal ion, T/Dp can also be used to justify that aquatic toxicity is unlikely to occur due to high insolubility in water.