UNIVERSITÉ DE GENÈVE
FACULTÉ DES SCIENCES

Institut national de la recherche scientifique

Addressing the lack of ecotoxicological data for technology-critical metals using QICAR

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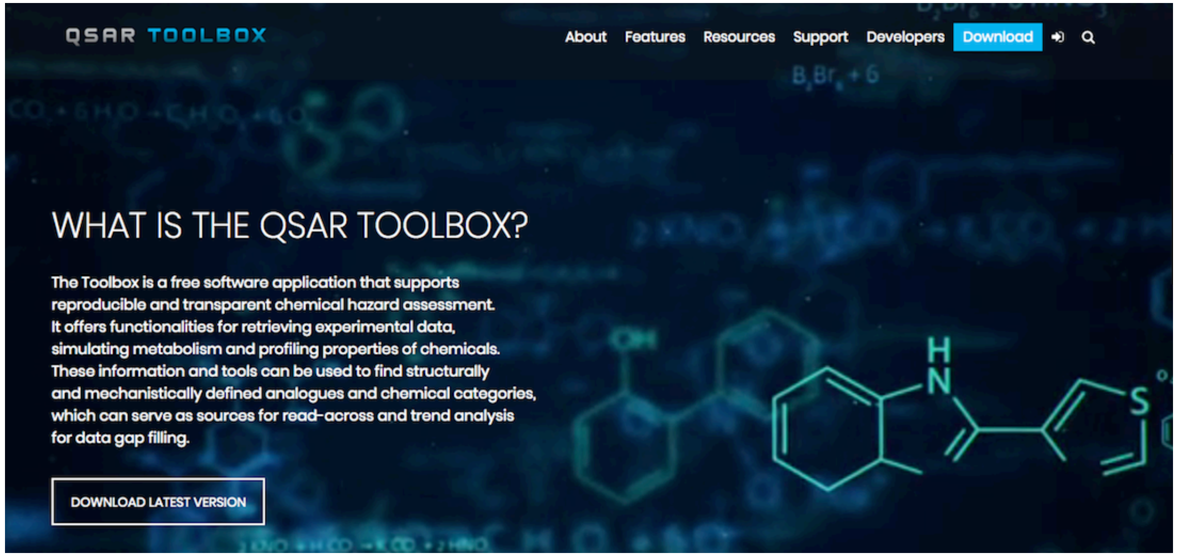
What is QICAR?

- QICAR stands for **Quantitative Ion Character-Activity Relationships**

- QICAR = QSAR (organic molecules)



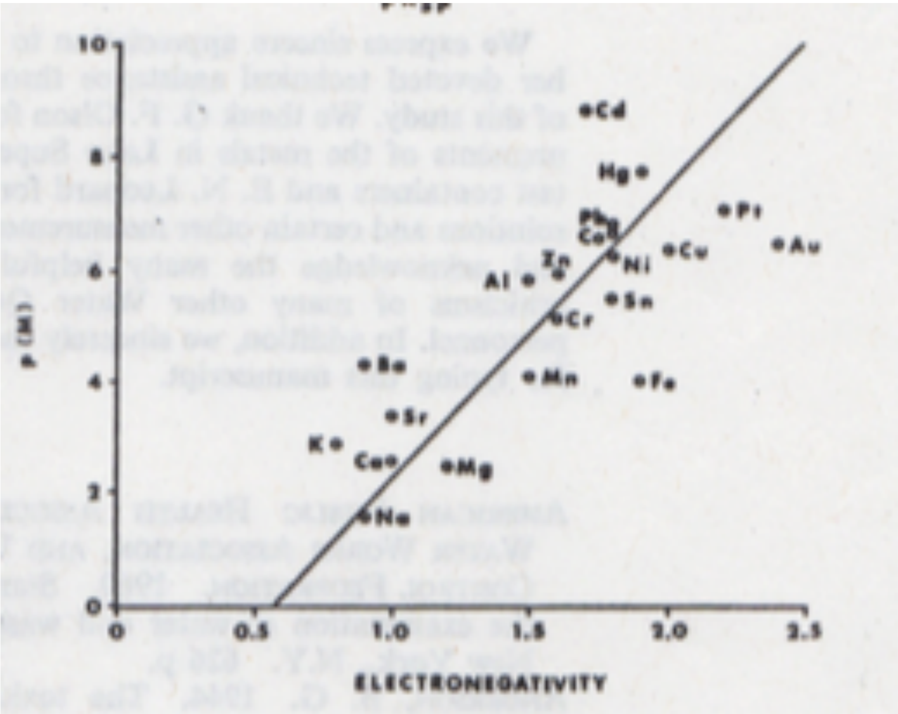
https://qsartoolbox.org/

- Predict metal toxicity based on metal intrinsic characteristics

What is QICAR?

- Example: Biesinger and Christensen model (1972)

<u>Endpoint</u>: 16% reproductive impairment concentration for *Daphnia magna* of metals



Electronegativity (χ_m)

Biesinger and Christensen, *J. Fish. Res. Board Can*., 1972

What is QICAR?

- Example: Wolterbeek and Verburg model (2001)

$$pT = a_0 + a_1\,\Delta E^0 + a_2\,logIP + a_3\,\chi_m + a_4\,log\frac{AR}{AW}$$

pT: - log [IC_{20}, EC_{50}, LC_{50}…]

Enzymes, bacteria, microalgae, invertebrates, fish….

ΔE^0: Electrochemical potential

Redox capacity

$logIP$: Ionization potential

Electron affinity

χ_m: Electronegativity

Electron attracting capability

$\frac{AR}{AW}$: $\frac{\text{Atomic radius}}{\text{Atomic weight}}$

Charge density

Wolterbeek and Verburg, *Sci. Total. Environ.*, 2001

What is QICAR?

- Several recent papers authored by Chinese researchers

Objectives of the project

- Develop QICARs for *data-poor* metals (Au, Ge, In, Ir, Pd, Pt, Re, Rh, Ru) to relate their acute aquatic toxicity (algae, daphnids, fish) to their ionic properties

- Refine the QICAR approach to include a metal speciation component

Approach

1. Choice of the metal characteristics

- Compilation
- PCA construction to highlight redundancy

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2. Compilation of the ecotoxicological data (algae, daphnids and fish)

- Ag, Ca, Co, Cu, K, Na, Mg, Mn, Na, Ni, Pb, Zn
- Measured acute EC_{50} values
- Composition of the exposure media
- Boxplots to highlight outliers

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3. Modeling (total dissolved concentrations)

- Simple linear regressions
- Multiple linear regressions (stepwise approach)
- All species and species specific models
- Test with measured EC_{50} values of *data-poor* metals

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5. Modeling (free metal ion activity)

- Speciation calculation with WHAM and VMINTEQ

Results – Metal characteristics database

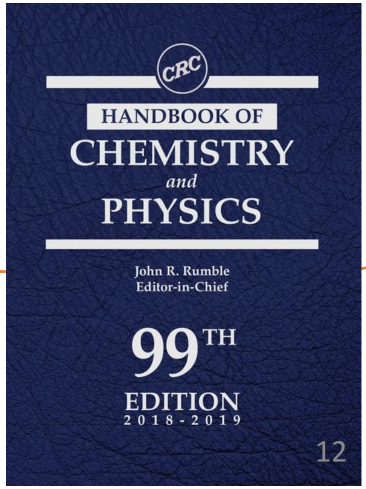
- Atomic weight (AW)
- Atomic volume (V)
- Density (ρ)
- Melting point (MP)
- Polarizability (α)
- Molar refractivity (MR)
- Atom size (AR/AW)
- Atomic number (AN)
- ~~Ionization energy (IP), Ionization potential (ΔIP~~)
- ~~Electron affinity~~ (E*)

- Oxidation number (OX)
- ~~Standard electrode potential~~ (E^0)
- ~~Electrochemical potential (ΔE^0)~~
- Ionic radius (r)
- Atomic radius (AR), Covalent radius (CR)
- Van der Waals radius (Vdw)
- Electronegativity (χ_m)
- Cation polarizing power (z/r, z/r^2, z^2/r)
- Covalent index ($\chi_m{}^2 r$)

- ~~Covalent bond stability ($\Delta\beta$)~~
- ~~Log of the first hydrolysis constant (log~~ K_{OH})
- ~~Hard and soft acids and bases (HSAB~~) theory (σp)

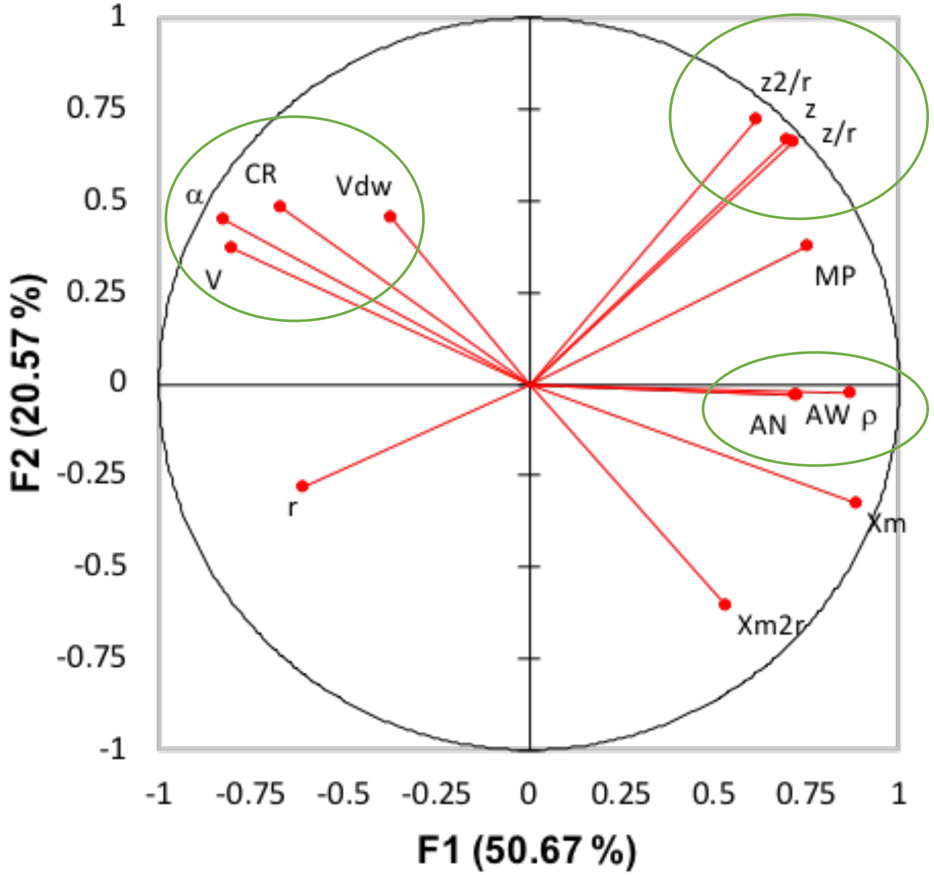
15

~~23~~ metal characteristics



Results – Metal characteristics database

- Construction of PCA to highlight redundancy



Remaining parameters: V, AN, z^2/r, χ_m or $\chi_m{}^2r$, MP, r

Results – EC_{50} values database for QICAR building

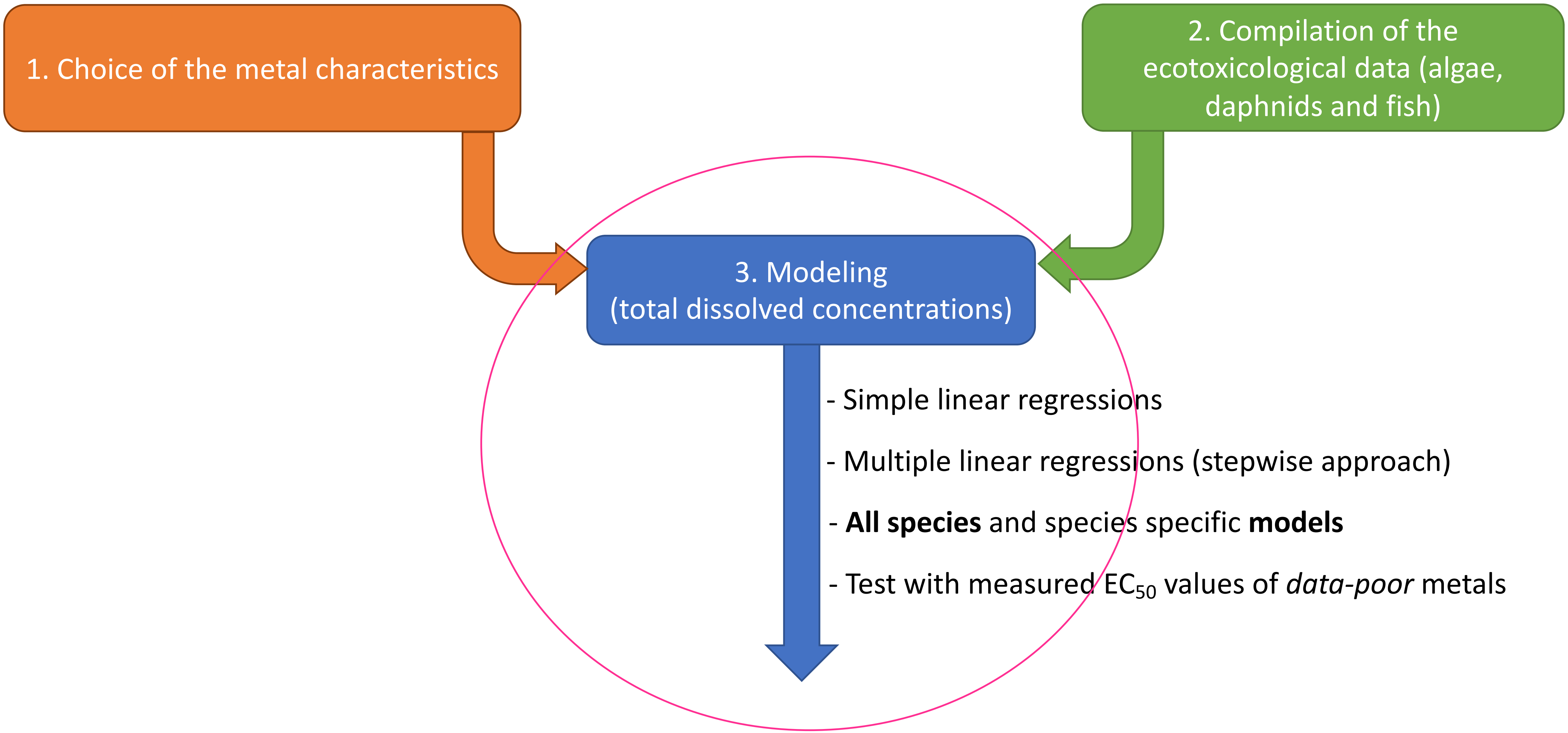
Number of tests	Algae	Daphnids	Fish
Ag	9	10	8
Ca	1	10	1
Cd	4	90	100
Co	31	41	2
Cu	61	239	201
K	2	27	2
Mg	2	45	2
Mn	2	14	4
Na	2	72	3
Ni	27	172	77
Pb	17	61	56
Zn	46	94	18

- Individual EC_{50} values database for *P. subcapitata*, *D. magna*, *C. dubia*, *P. promelas* and *O. mykiss*

Results – EC_{50} values database for QICAR testing

Number of tests	Algae	Daphnids	Fish
Al(III)*	2	11	-
Au(I)	1	1	1
Au(III)	2	4	1
In(III)	1	-	-
Ir(III)	-	1	-
Ge(IV)	2	1	1
Pd(II)	5	6	3
Pd(IV)	1	-	1
Re(VII)	2	-	-
Rh(III)	2	4	2
Ru(III)	1	1	-
Ru(IV)	1	-	-
Pt(II)	2	2	-
Pt(IV)	4	6	1

Approach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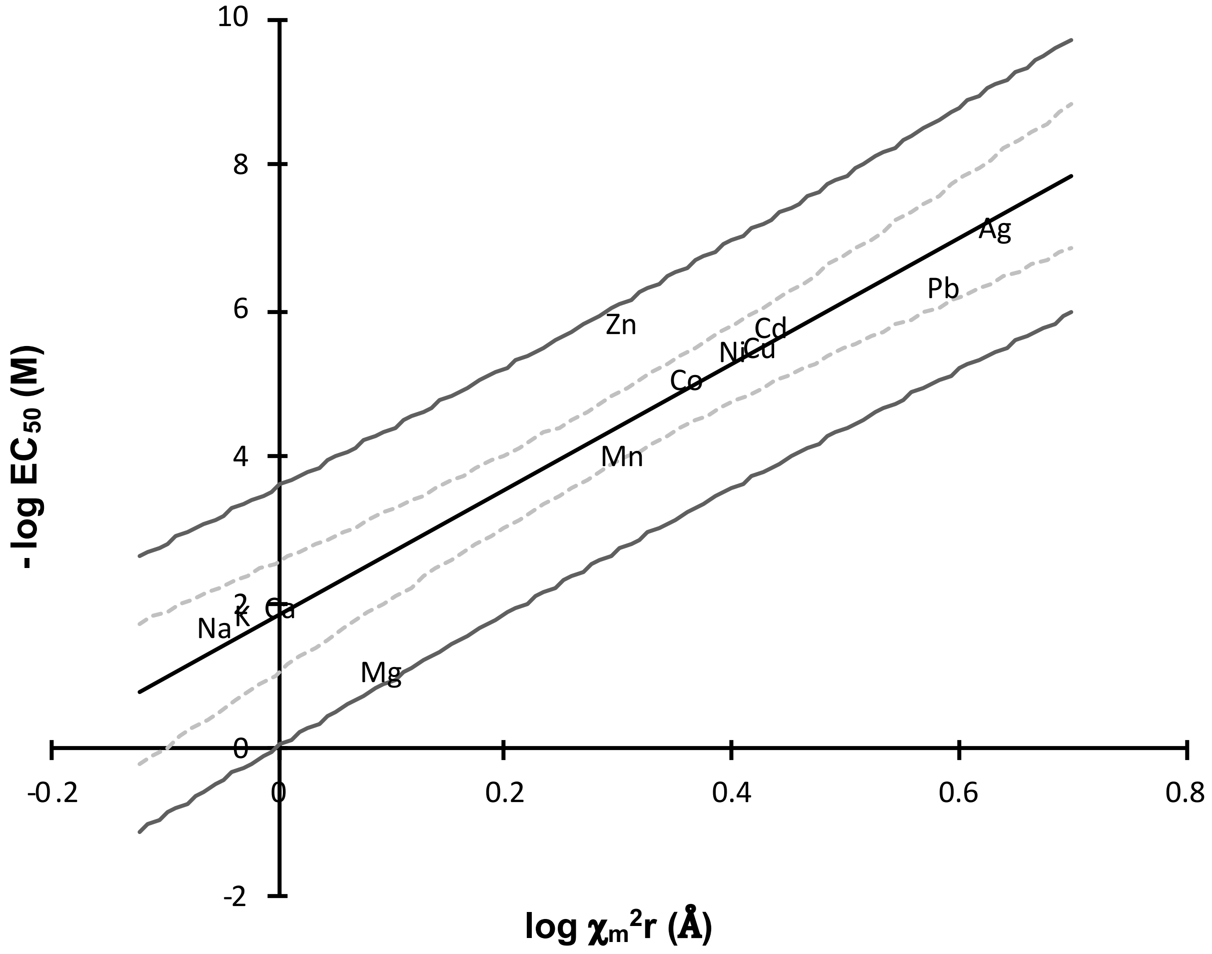
(total dissolved concentrations)
- Simple linear regressions
- Multiple linear regressions (stepwise approach)
- **All species** and species specific **models**
- Test with measured EC_{50} values of *data-poor* metals

Results – QICAR for algae – total dissolved concentration

$-\log EC_{50} = 1.816 + 8.607 \times \log \chi_m^2 r$

(r^2_{adj}=0.89)



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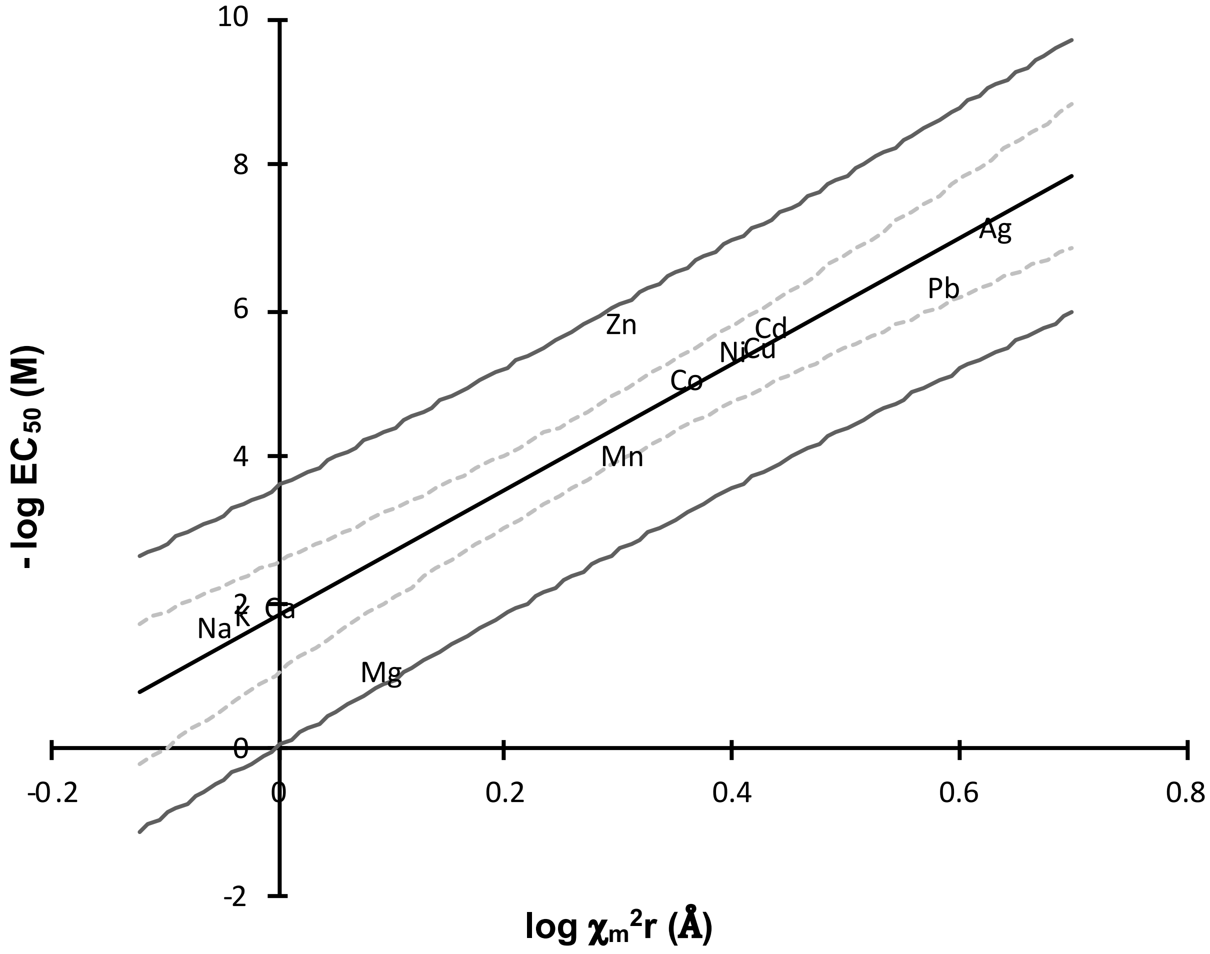
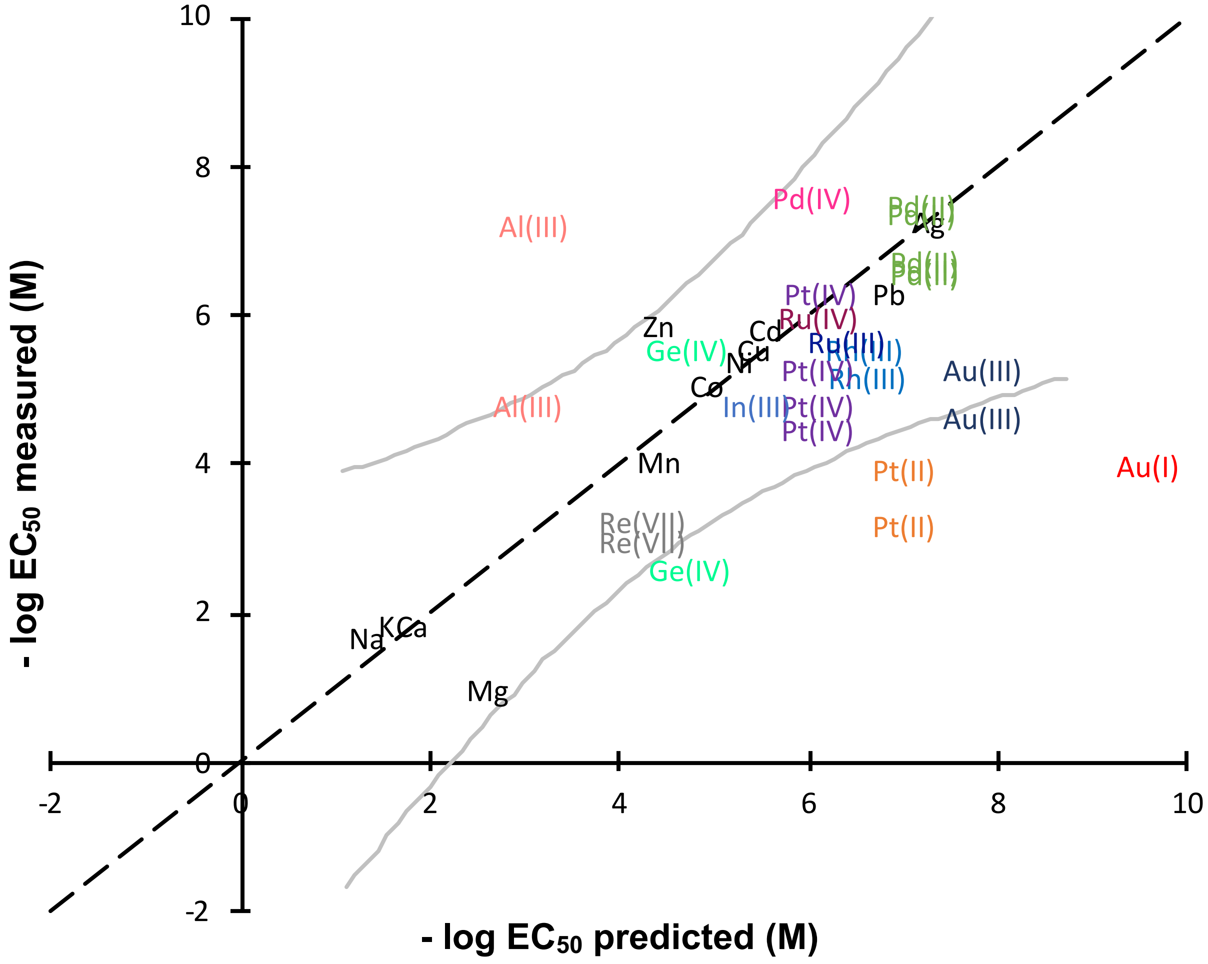
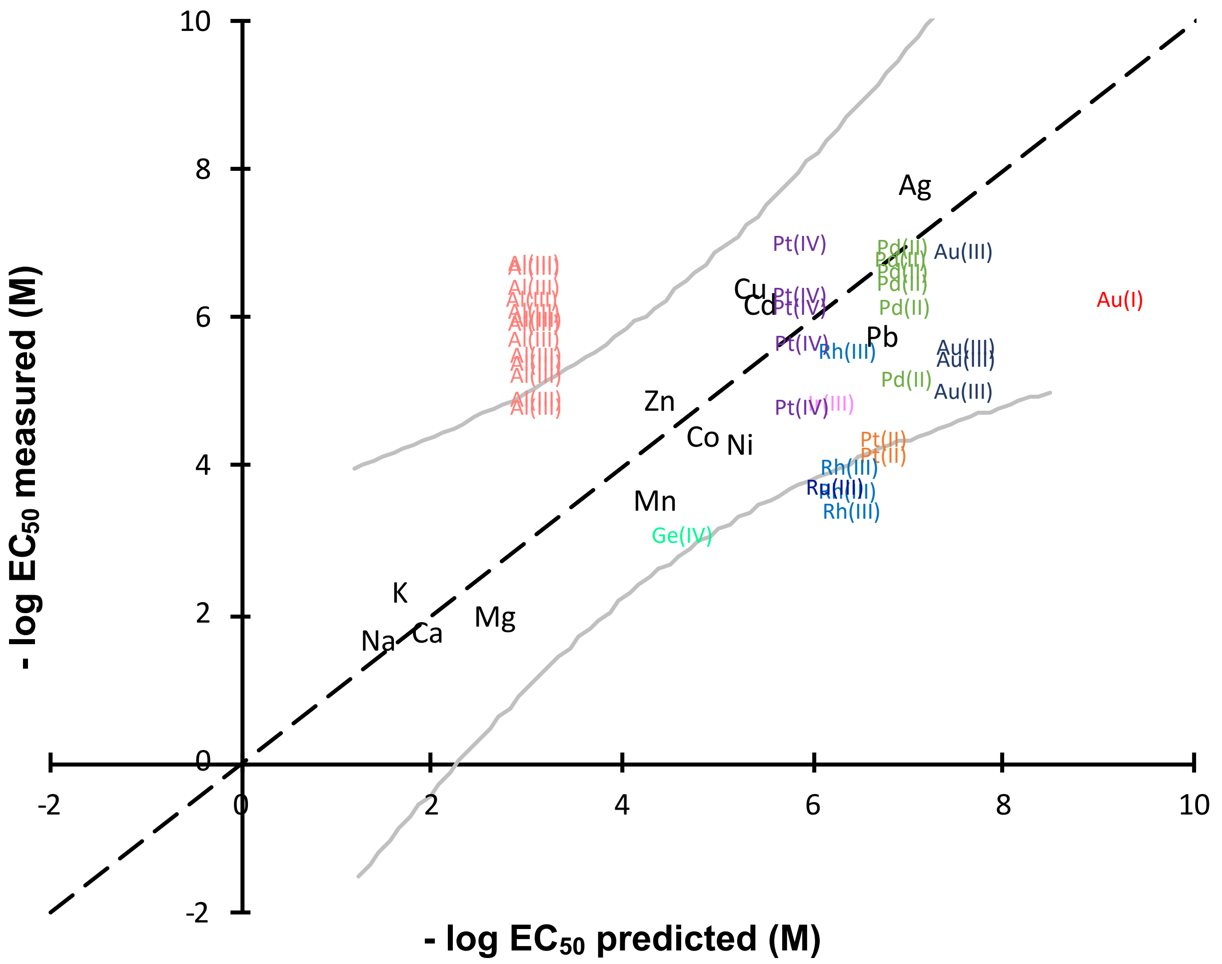




Results – QICAR for daphnids – total dissolved concentration

$$-\log EC_{50} = 1.912 + 8.154 \times \log \chi_m^2 r$$

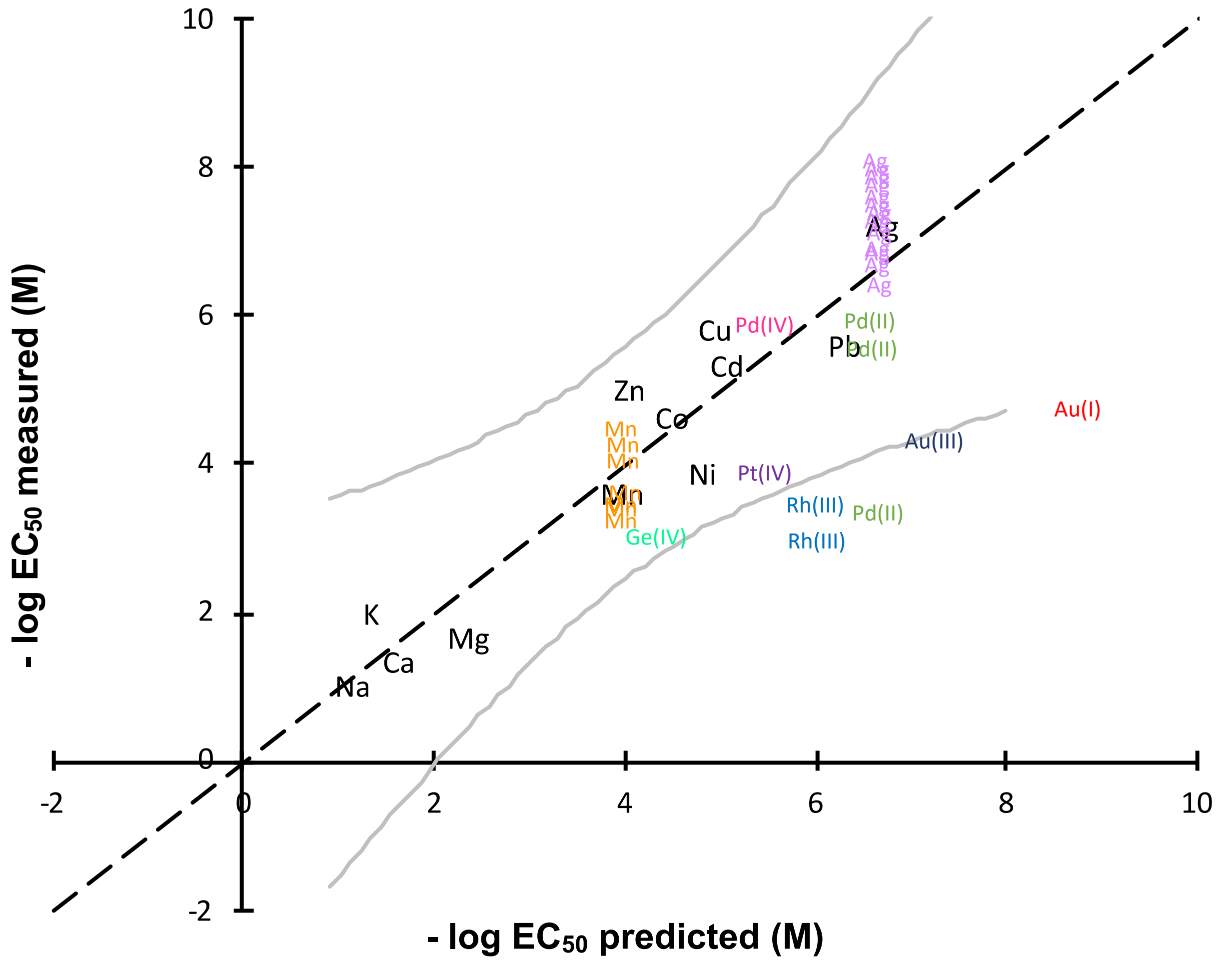
$(r^2_{adj}=0.86)$



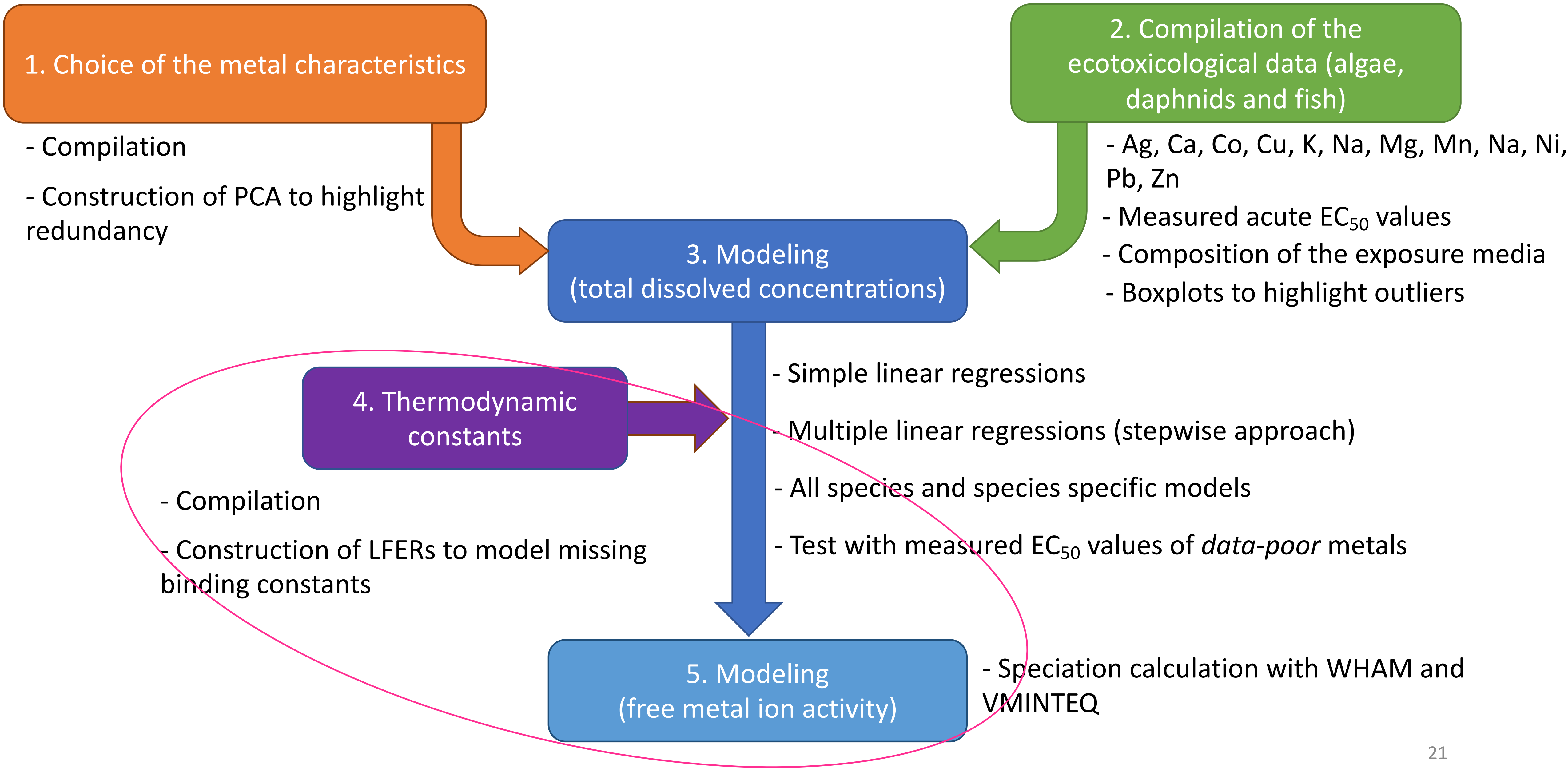
Results – QICAR for fish – total dissolved concentration

$$-\log EC_{50} = 1.582 + 8.050 \times \log \chi_m^2 r$$

$(r^2_{adj}=0.89)$



Approach



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2. Compilation of the ecotoxicological data (algae, daphnids and fish)
- Ag, Ca, Co, Cu, K, Na, Mg, Mn, Na, Ni, Pb, Zn
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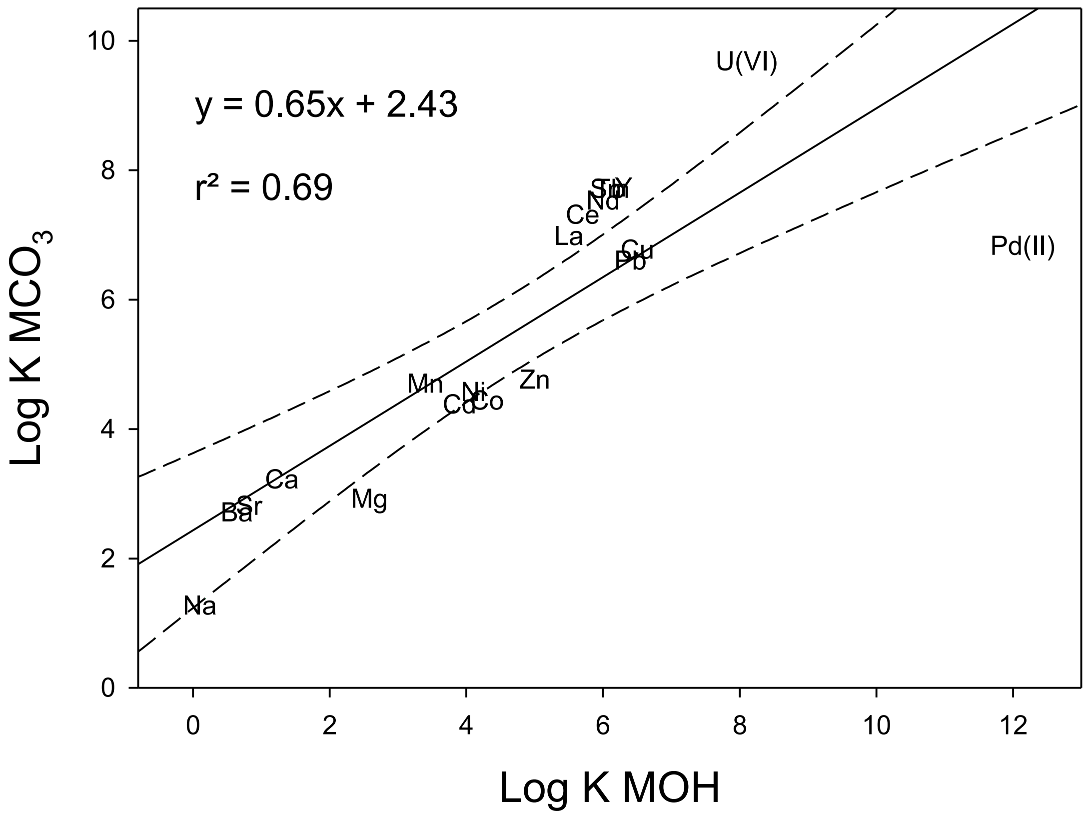
Results – Speciation calculation

- Compilation of thermodynamic constants with OH^-, CO_3^{2-}, Cl^-, $EDTA^{4-}$, CN^-
- When missing, construction of Linear Free Energy Relationships (LFERs)



K MCO_3 for
- Ag
- Au(I)
- Au(III)*
- Ge(IV)*
- In(III)
- Pt(II)*
- Rh(III)*
- Ru(III)*

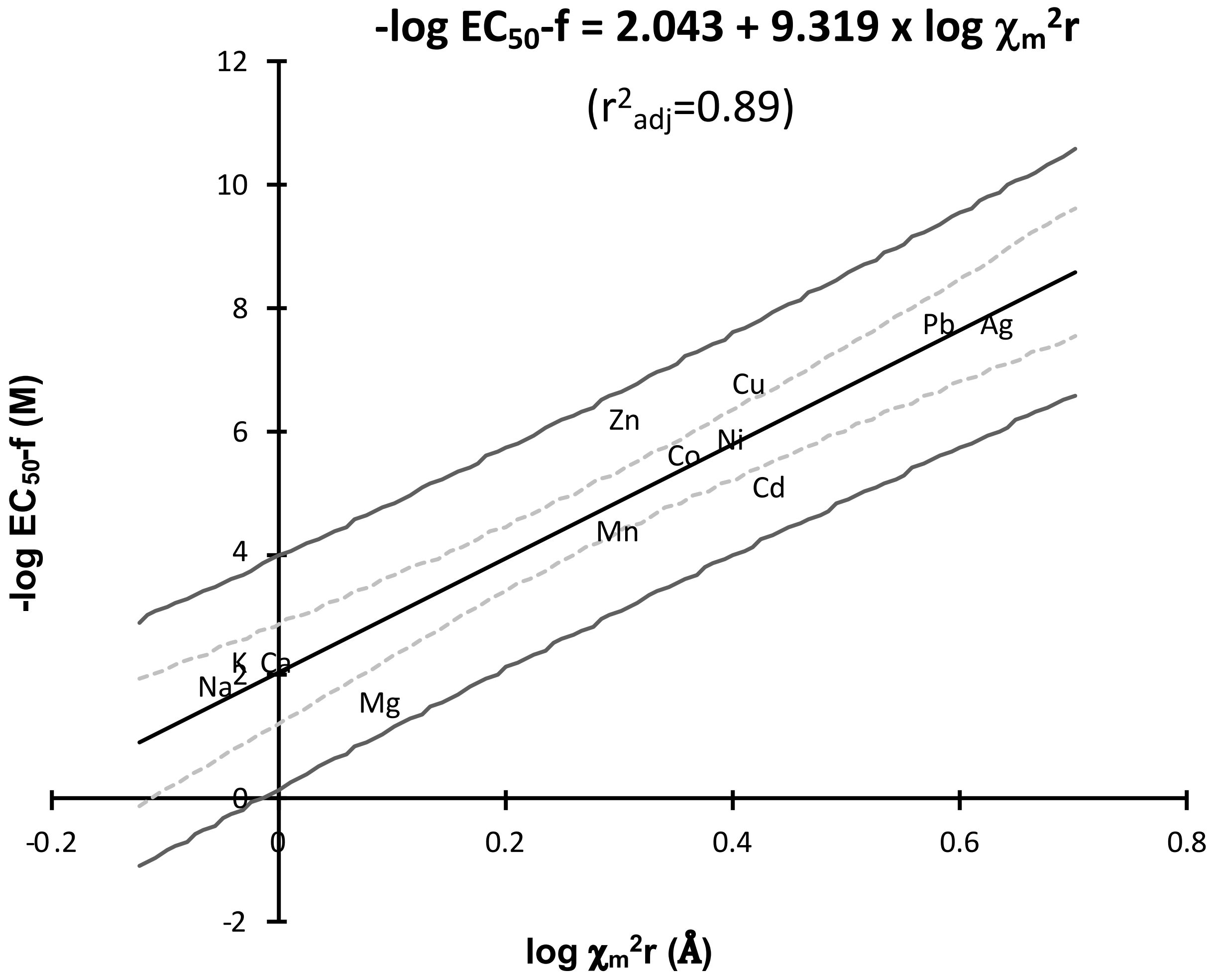
- No thermodynamic data available for Ir(III), Pd(IV), Pt(IV), Re(VII), Rh(I) and Ru(IV)

Results – Speciation calculation (algae exposure media)

	M^{z+}	$M(OH)_n$	$M(CO_3)_n$	$M(Cl)_n$	$M(SO_4)_n$	$M(X)_n$	M-DOM
Au(I)	<1%	<1%	<1%	<1%	<1%	100% [$Au(CN)_2^-$]	0
Ge(IV)	<1%	100% [$Ge(OH)_4^0$]	<1%	<1%	<1%	0	0
In(III)	<1%	100% [$In(OH)_3^0$]	<1%	<1%	<1%	0	0
Pd(II)	<1%	100% [$Pd(OH)_2^0$]	<1%	<1%	<1%	0	0
Pt(II)	<1%	100% [$Pt(OH)_2^0$]	<1%	<1%	<1%	0	0
Rh(III)	<1%	100% [$Rh(OH)_3^0$]	<1%	<1%	<1%	0	0
Ru(III)	<1%	100% [$Ru(OH)_3^0$]	<1%	<1%	<1%	0	0

Results – QICAR for algae – free metal ion activity

Free



Results – QICAR for algae – free metal ion activity

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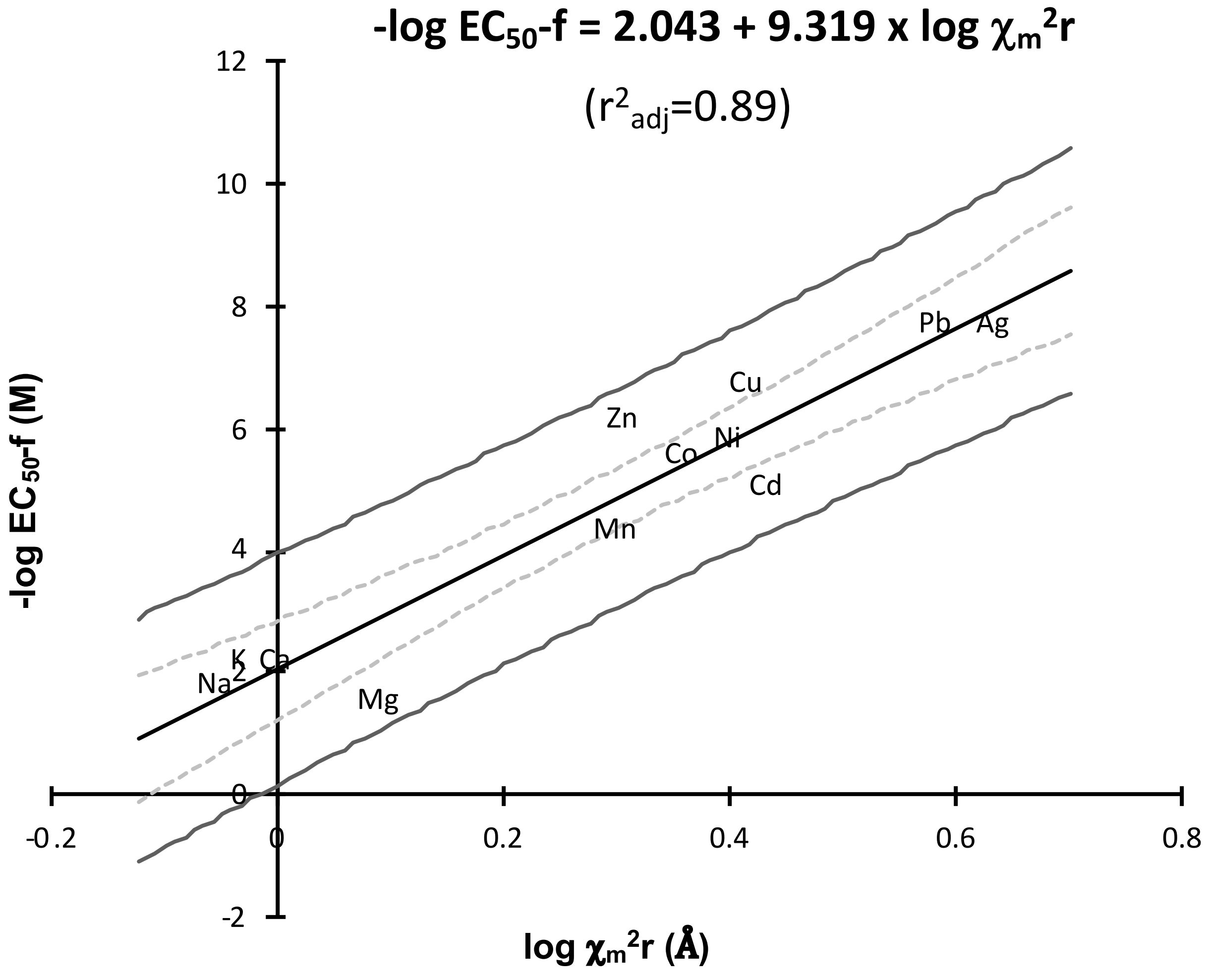
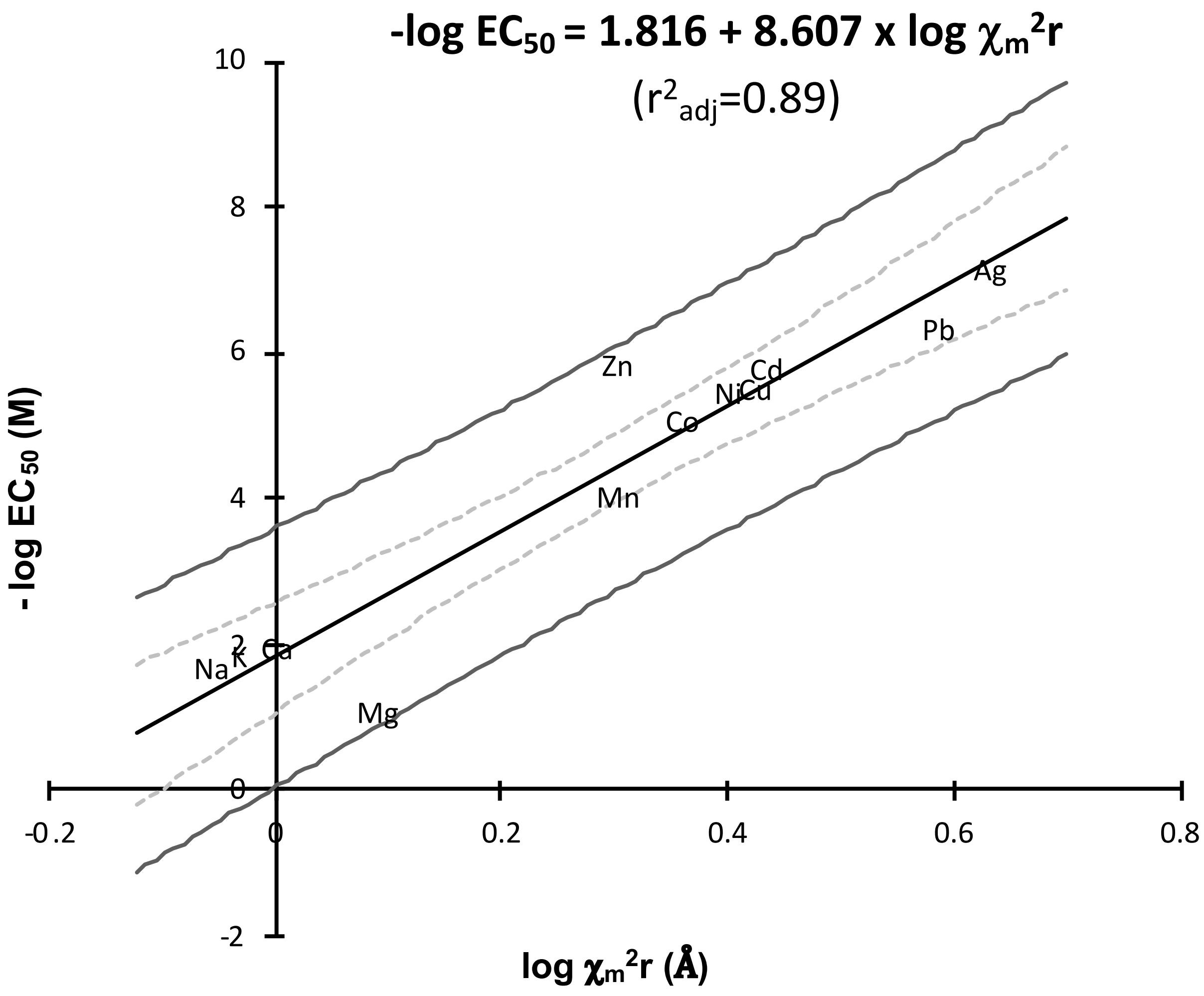


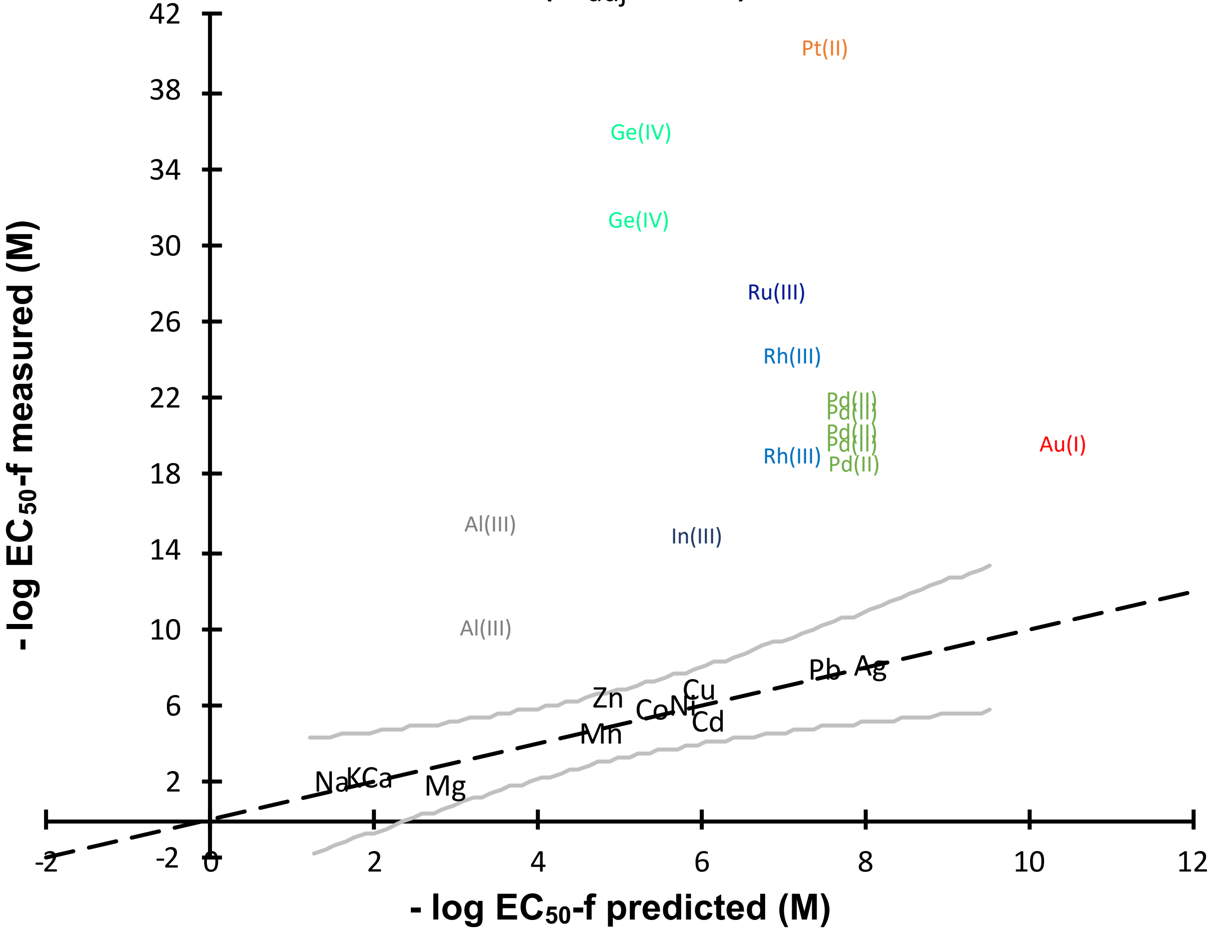
Total



Results – QICAR for algae – free metal ion activity

$$-\log EC_{50}\text{-f} = 2.043 + 9.319 \times \log \chi_m^2 r$$

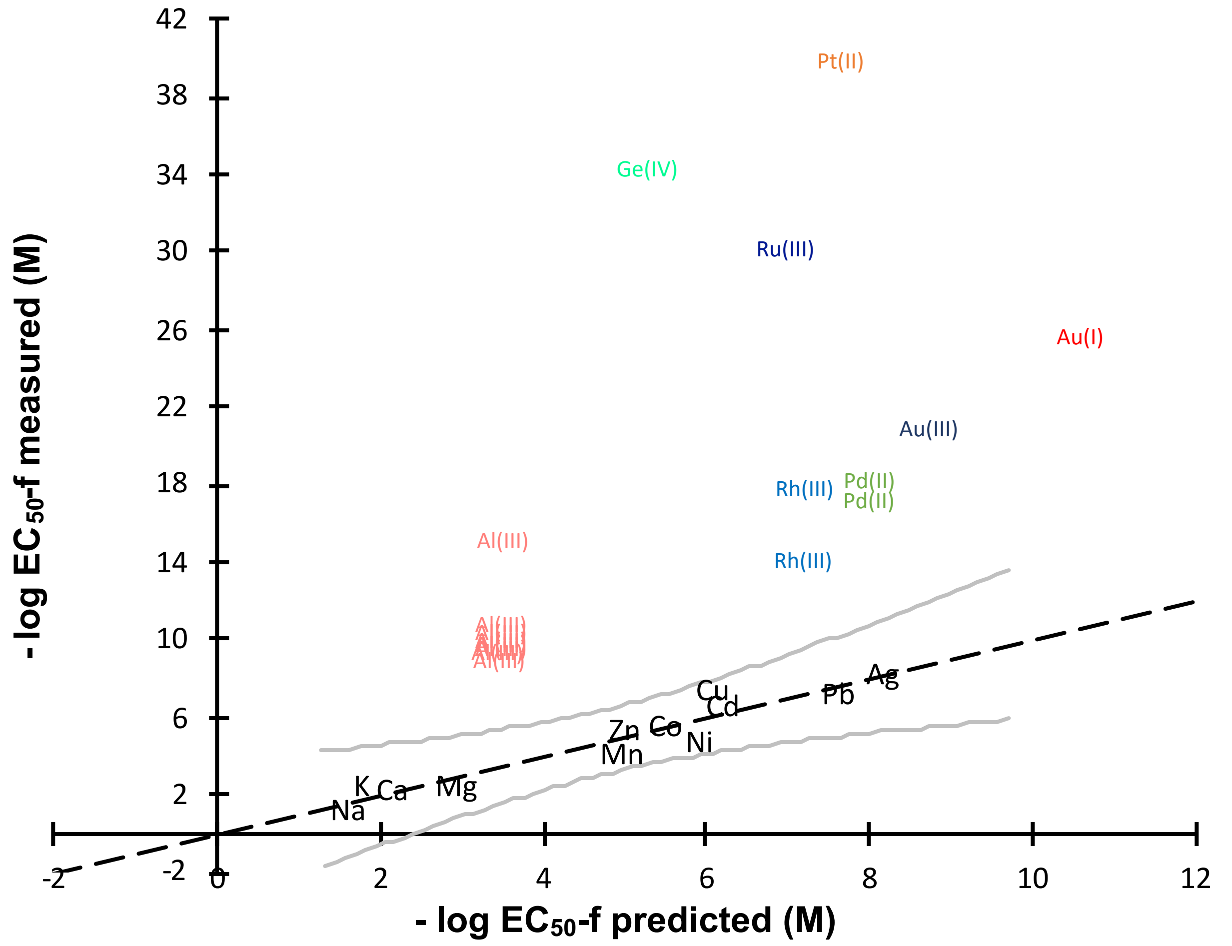
$(r^2_{adj}=0.89)$



Results – QICAR for daphnids – free metal ion activity

$$-\log EC_{50}\text{-f} = 2.099 + 9.464 \times \log \chi_m^2$$

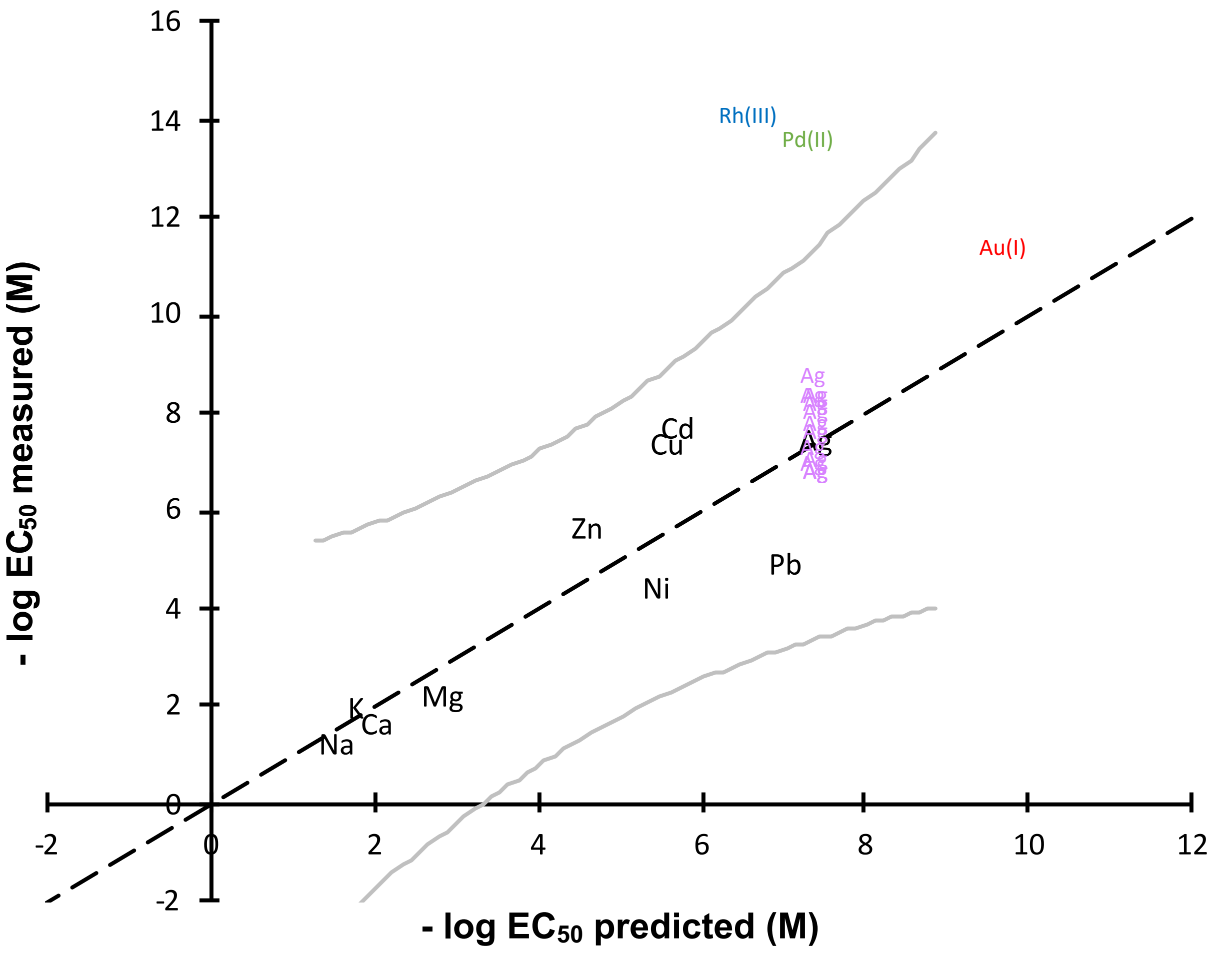
$$(r^2_{adj}=0.91)$$



Results – QICAR for fish – free metal ion activity

$$-\log EC_{50}\text{-f} = 2.048 + 8.469 \times \log \chi_m^2 r$$

$(r^2_{adj}=0.73)$



Conclusions and recommendations

- $\chi_m^2 r$ is the best predictor of metal toxicity

- QICAR - total concentration:

  - Very good correlations found between $\chi_m^2 r$ and EC_{50} values ($r^2_{adj} > 0.6$)

  - Poor predictions for Au (algae, daphnids, fish), Pd(II) (fish), Pt(II) (algae, daphnids), Rh and Ru (daphnids)

  - Limited number of tests available for the data-poor metals

Conclusions and recommendations

- Speciation calculation:

  - Data-rich metal speciation dominated by the free metal ion

  - Data-poor metal speciation dominated by polyhydroxo complexes in exposure media ($Au(OH)_3^0$, $Ge(OH)_4^0$, $In(OH)_3^0$, $Pd(OH)_2^0$, $Pt(OH)_2^0$, $Rh(OH)_3^0$ and $Ru(OH)_3^0$) or the anionic cyano-complex ($Au(CN)_2^-$)

Conclusions and recommendations

- QICAR - free metal ion :

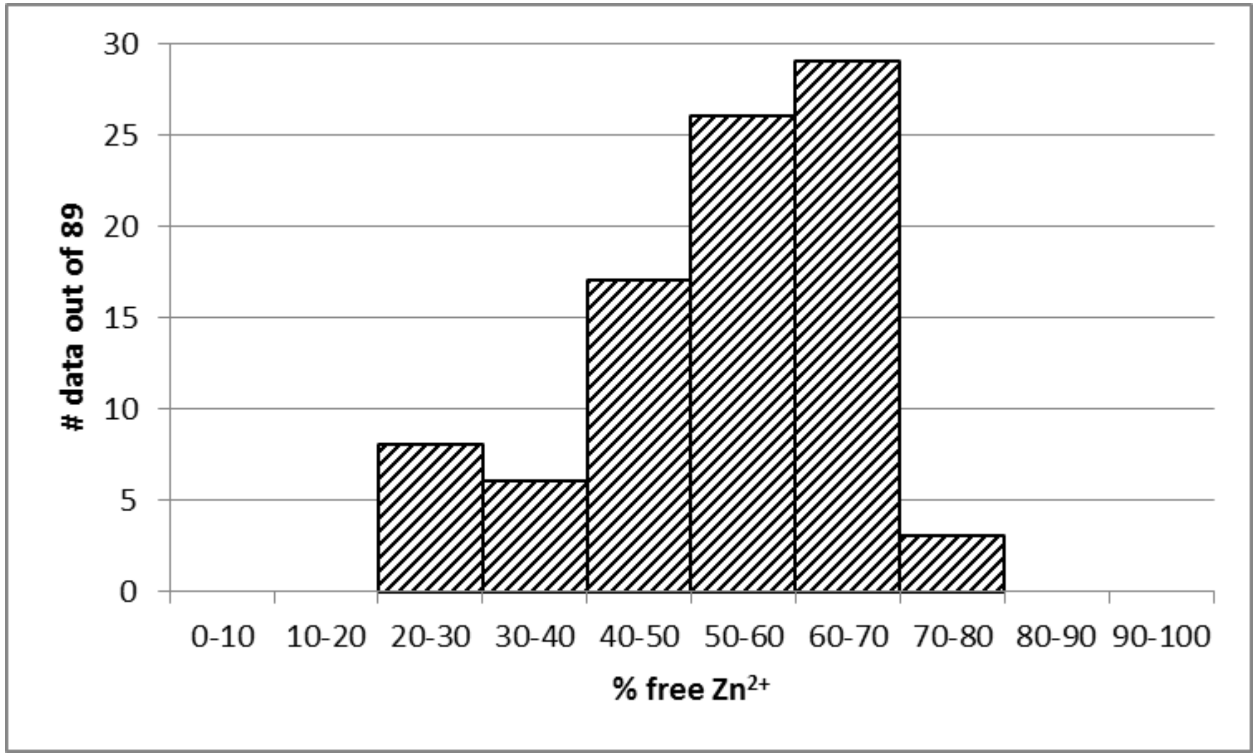
  - Modest improvement for data-rich metals

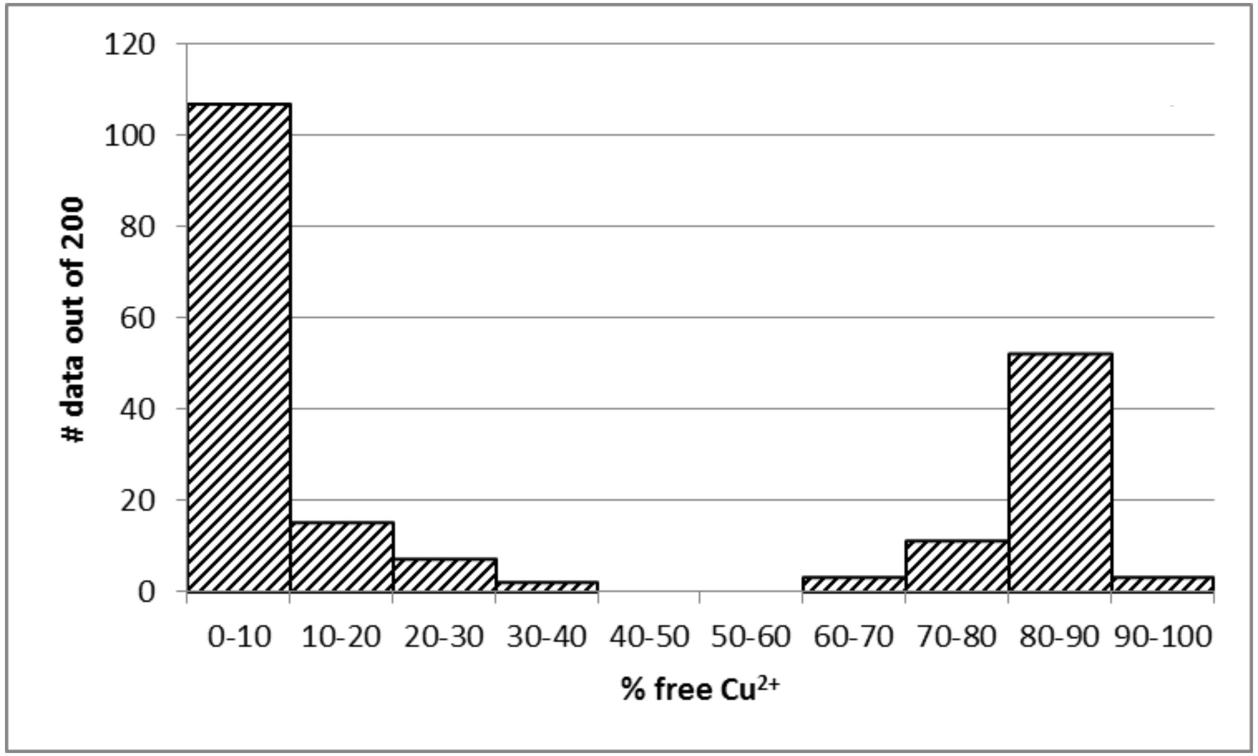
  - Range of speciation *vs.* average speciation

  - Marked deterioration in the prediction of data-poor metal toxicity

Conclusions and recommendations

Frequency distribution plots – calculated speciation in *Daphnia magna* experimental media





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Conclusions and recommendations

- Maintain toxicity database: high quality tests performed under optimal exposure and realistic environmental conditions
- Need additional toxicological data for data-poor metals
- Need thermodynamic data for data-poor metals
- Careful scrutiny of original data (extreme EC_{50} values, effects of pH, hardness, [DOC]…)

Acknowledgment

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European Precious Metals Federation

RioTinto

international zinc association

NiPERA NICKEL HEALTH AND ENVIRONMENTAL SCIENCES

Cu International Copper Association Copper Alliance

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- Jasim Chowdhury (International Lead Association)
- Rebecca Dalton (Environment Climate Change Canada)
- Bob Gensemer (GEI Consultants Inc.)
- Paul Marsh (Cobalt Development Institute)
- Bob Santore (Windward Environmental)
- Bill Stubblefield (Oregon State University)

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- Mike Bank (Norwegian Inst. Marine Research)
- Kevin Brix (U. of Miami)
- Dorothea Hug Peter (U. of Geneva)
- Pierre Marle (U. of Geneva)
- Geneviève Rioux (INRS-ETE)

Continue the discussion on PGMs:

Poster 21

Environmental fate and toxicology of Platinum Group Metals (PGMs): areas for improvement

Jelle Mertens [1], Maxime Eliat[1] and Séverine Le Faucheur [2]