UNIVERSITÉ DE GENÈVE
FACULTÉ DES SCIENCES

INRS Institut national de la recherche scientifique

QICAR as a tool to address the lack of toxicological data for technology-critical metals

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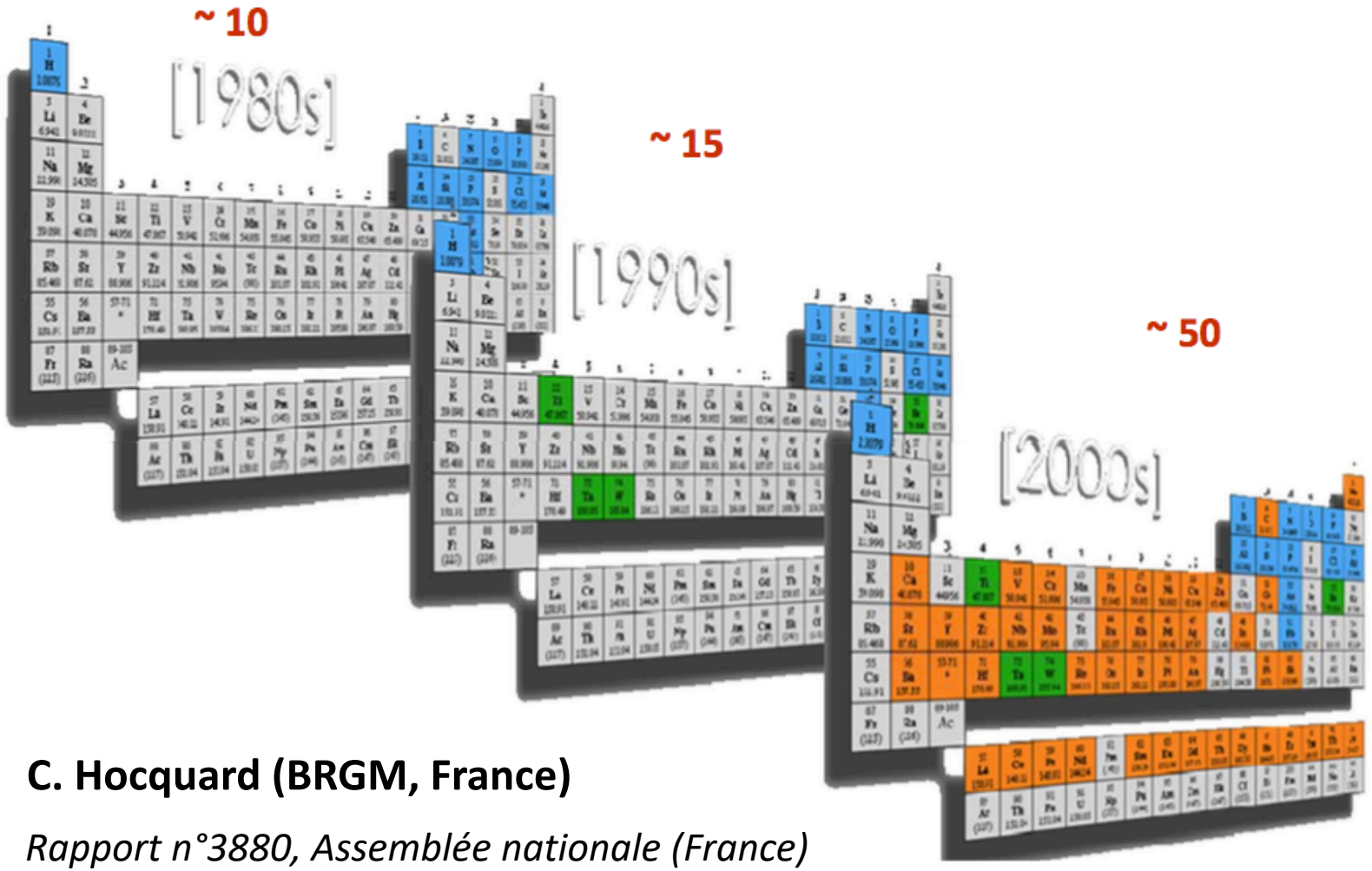
High demands in technology-critical metals



C. Hocquard (BRGM, France)

Rapport n°3880, Assemblée nationale (France)

Solar panels

In Se
Ga Te
Ge Cd

Catalytic converters

Pt
Pd
Rh

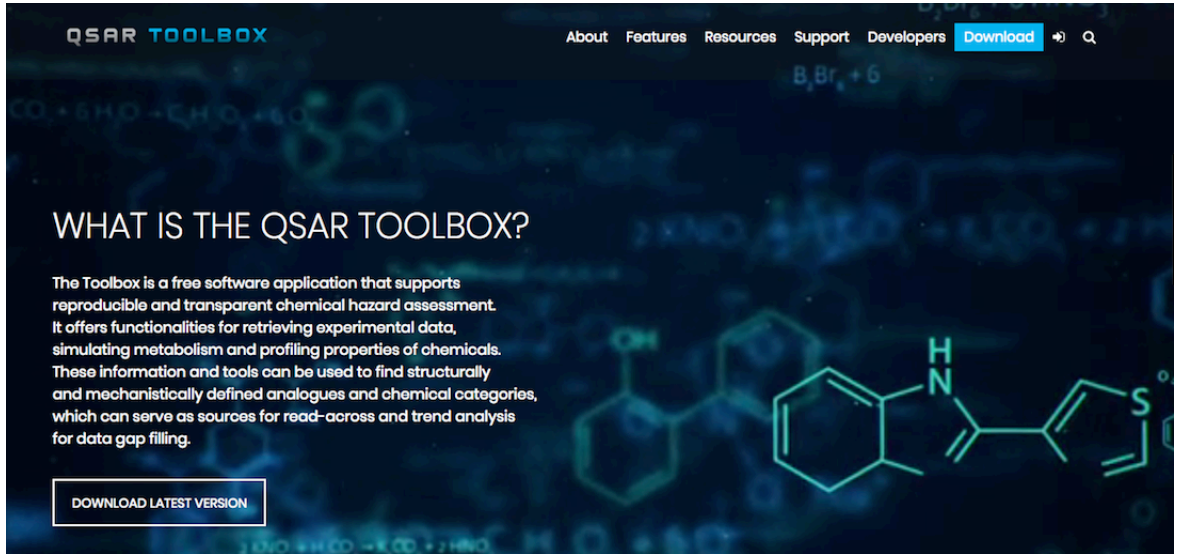
Turbine blades

Re

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?

- Metal intrinsic characteristics (23 in total):
  - Atomic weight
  - Density
  - Ionization potential
  - Ionic radius
  - …

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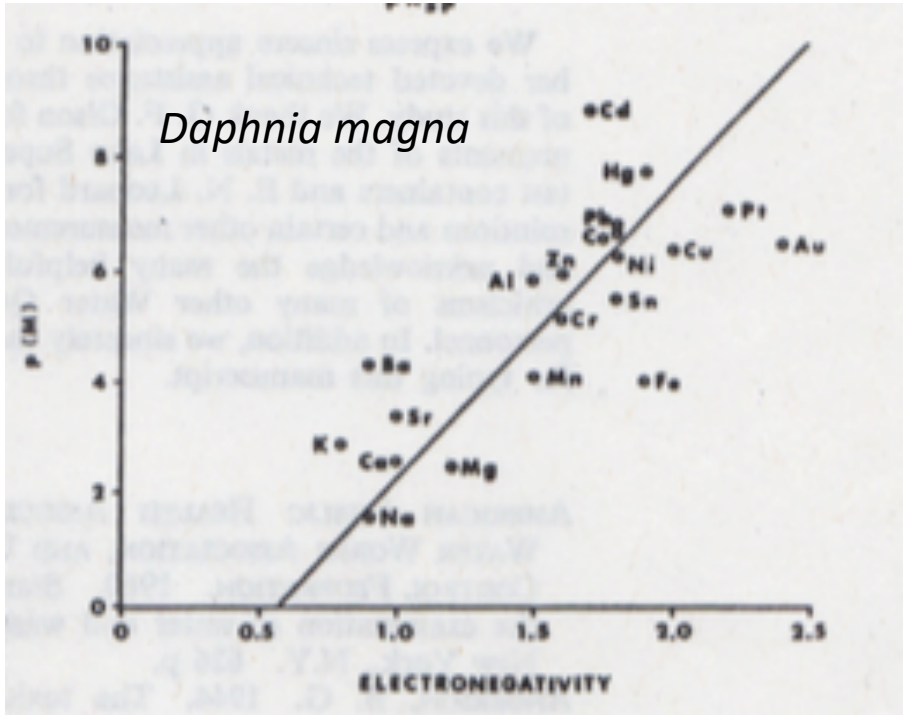
- Example of QICAR

Endpoint: 16% reproductive impairment concentration



Electronegativity (χ_m)

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

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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- 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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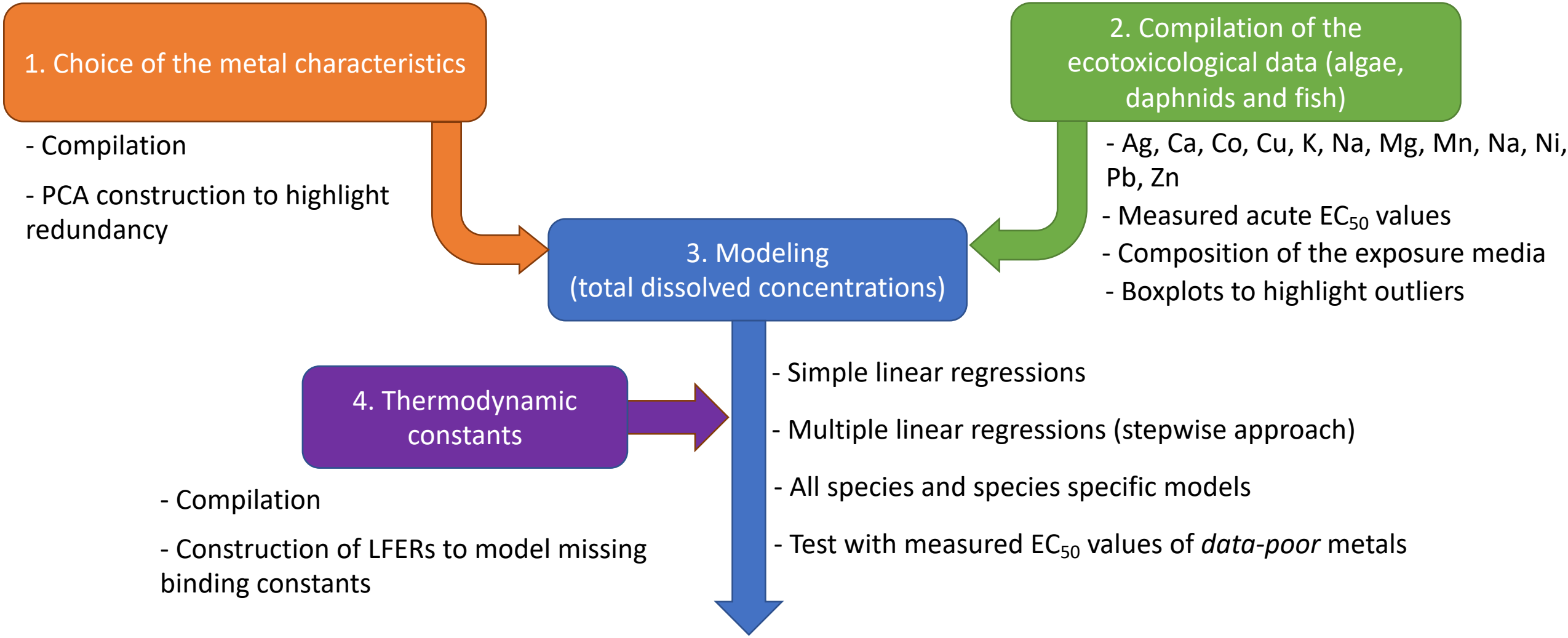
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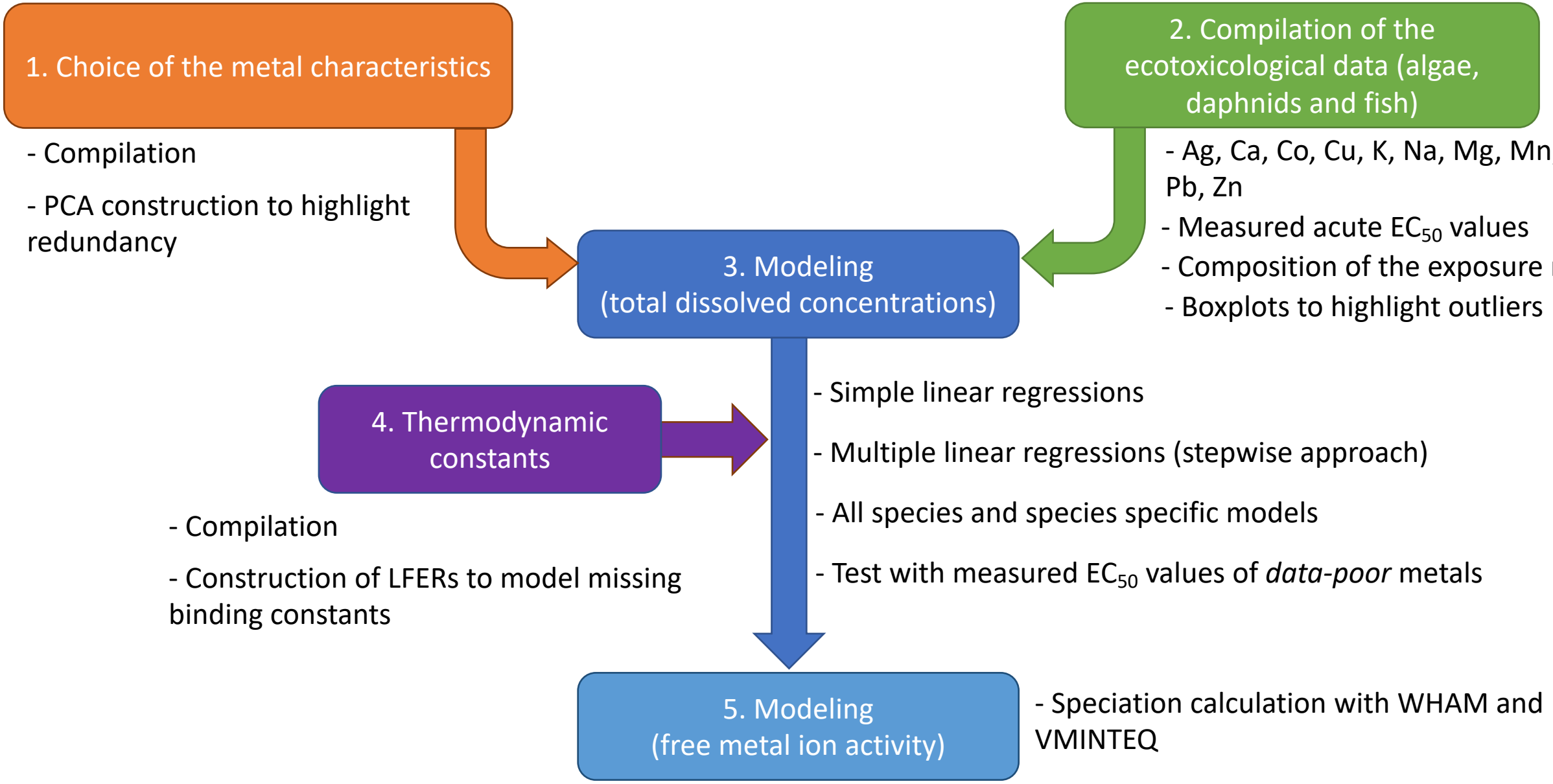
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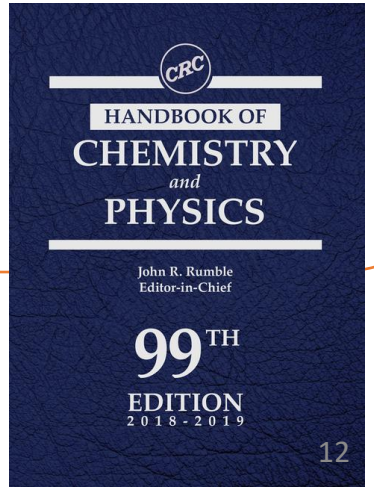
- Speciation calculation with WHAM and VMINTEQ

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 (Δß)~~
- ~~Log of the first hydrolysis constant (log K_{OH})~~
- ~~Hard and soft acids and bases (HSAB)~~ theory (σp)

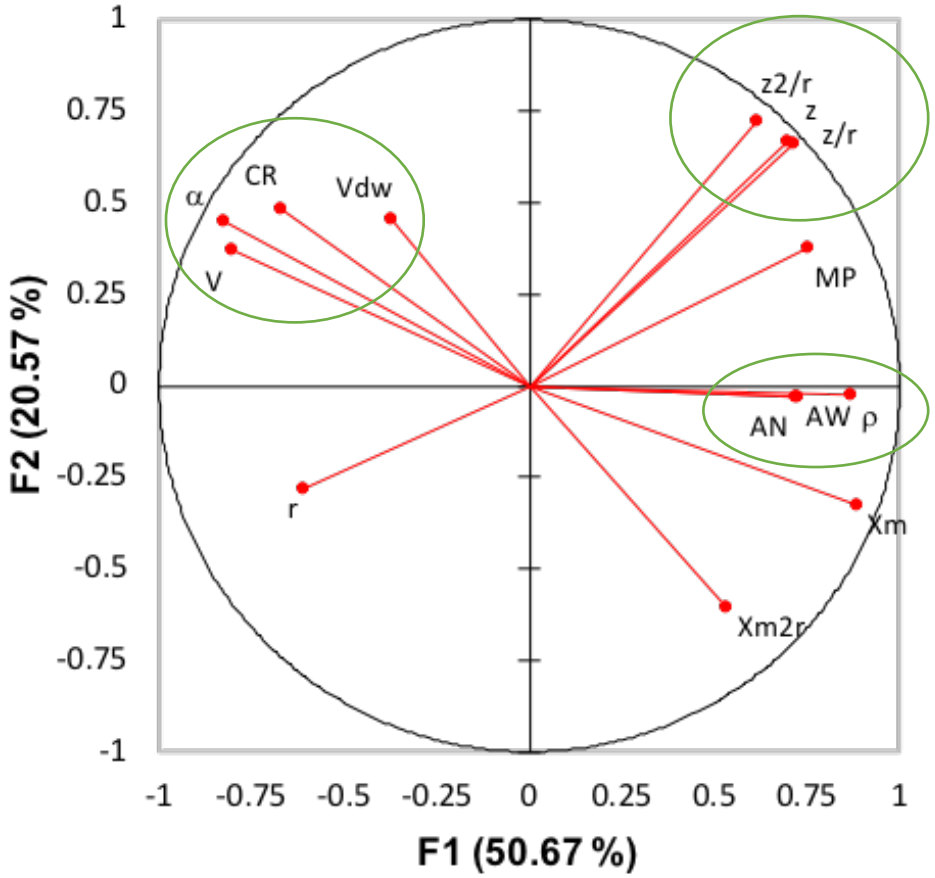
15

~~23~~ metal characteristics



Results – Metal characteristics database

- Construction of PCA to highlight redundancy



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

Results – EC_{50} values database for QICAR building

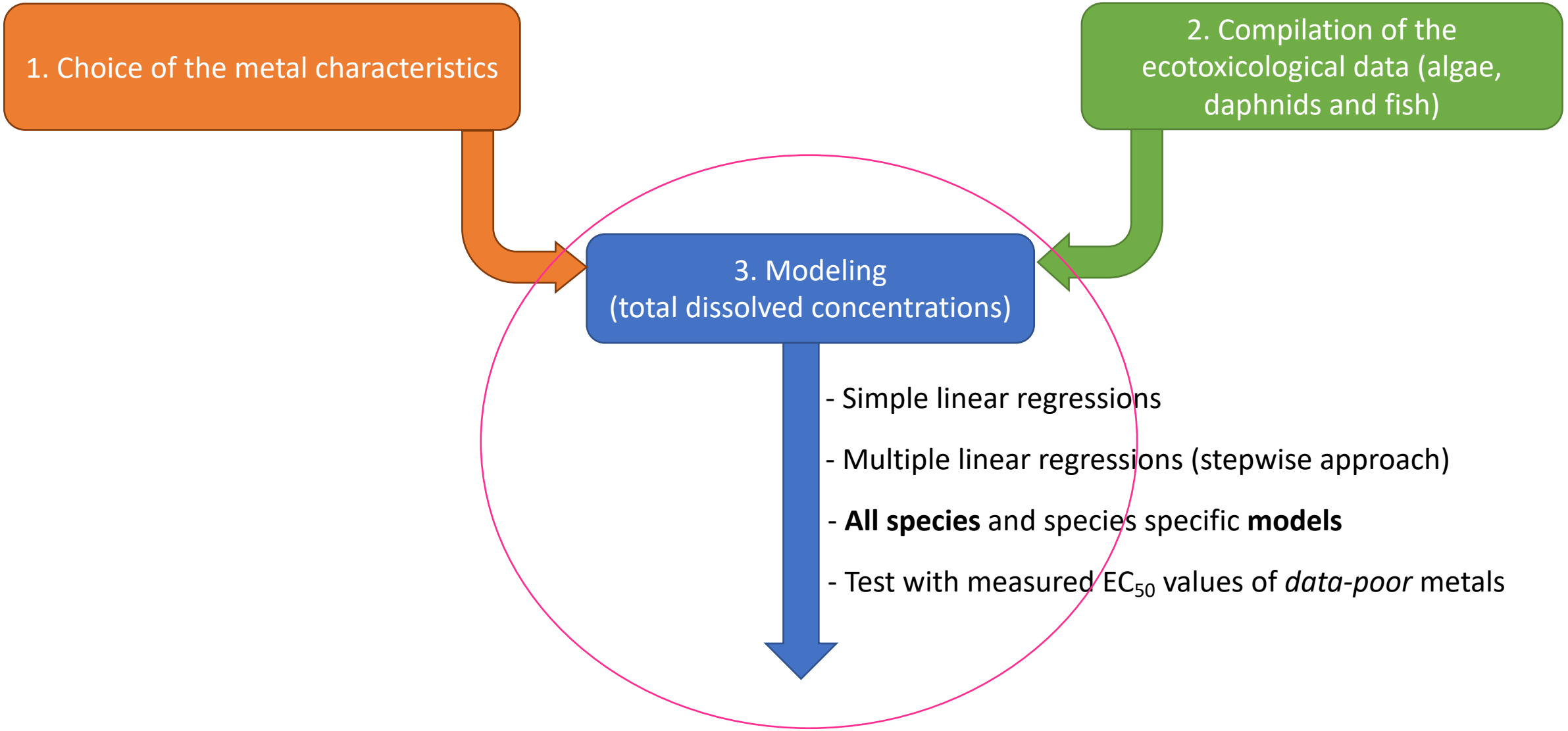
Number of tests	Algae	Daphnids	Fish
Ag	9	10	8
Ca	1	10	1
Cd	4	90	100
Co	31	41	2
Cu	61	239	201
K	2	27	2
Mg	2	45	2
Mn	2	14	4
Na	2	72	3
Ni	27	172	77
Pb	17	61	56
Zn	46	94	18

- 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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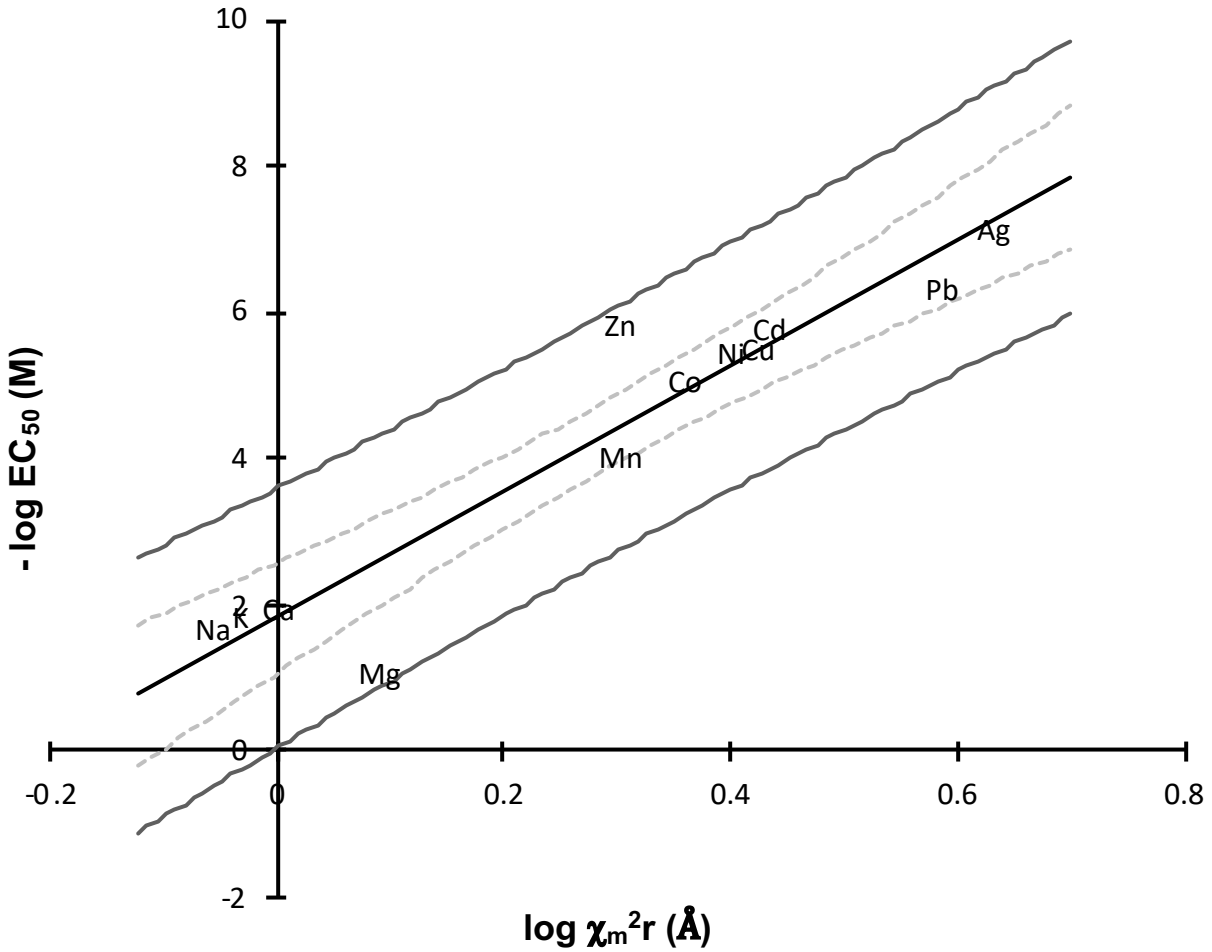
Results – QICAR for algae – total dissolved concentration

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

(r^2_{adj}=0.89)



- $\chi_m^2 r$: covalent index
- Composite parameter:
  - χ_m: electronegativity
  - r: ionic radius
- Introduced by Nieboer and Richardson (1980)

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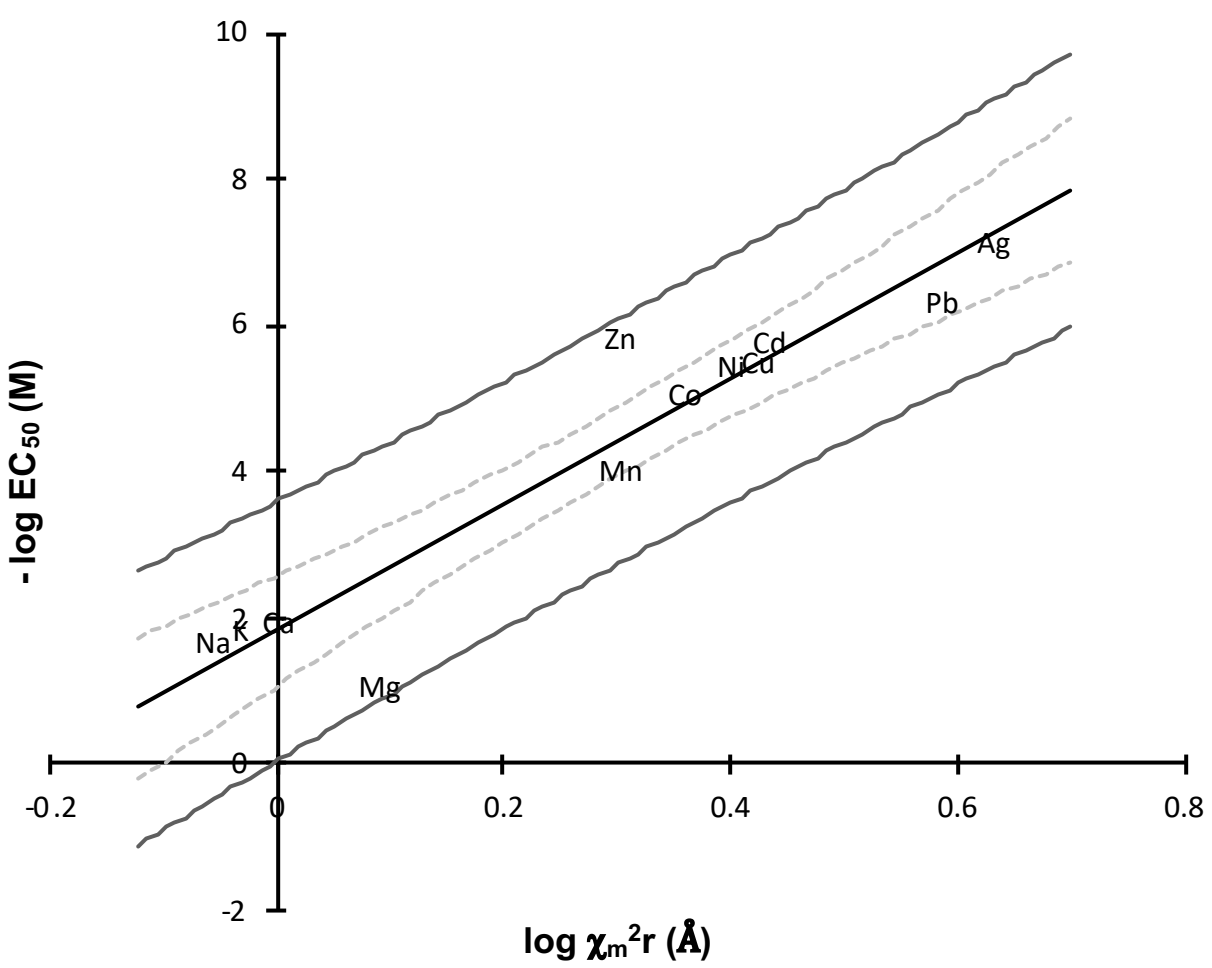

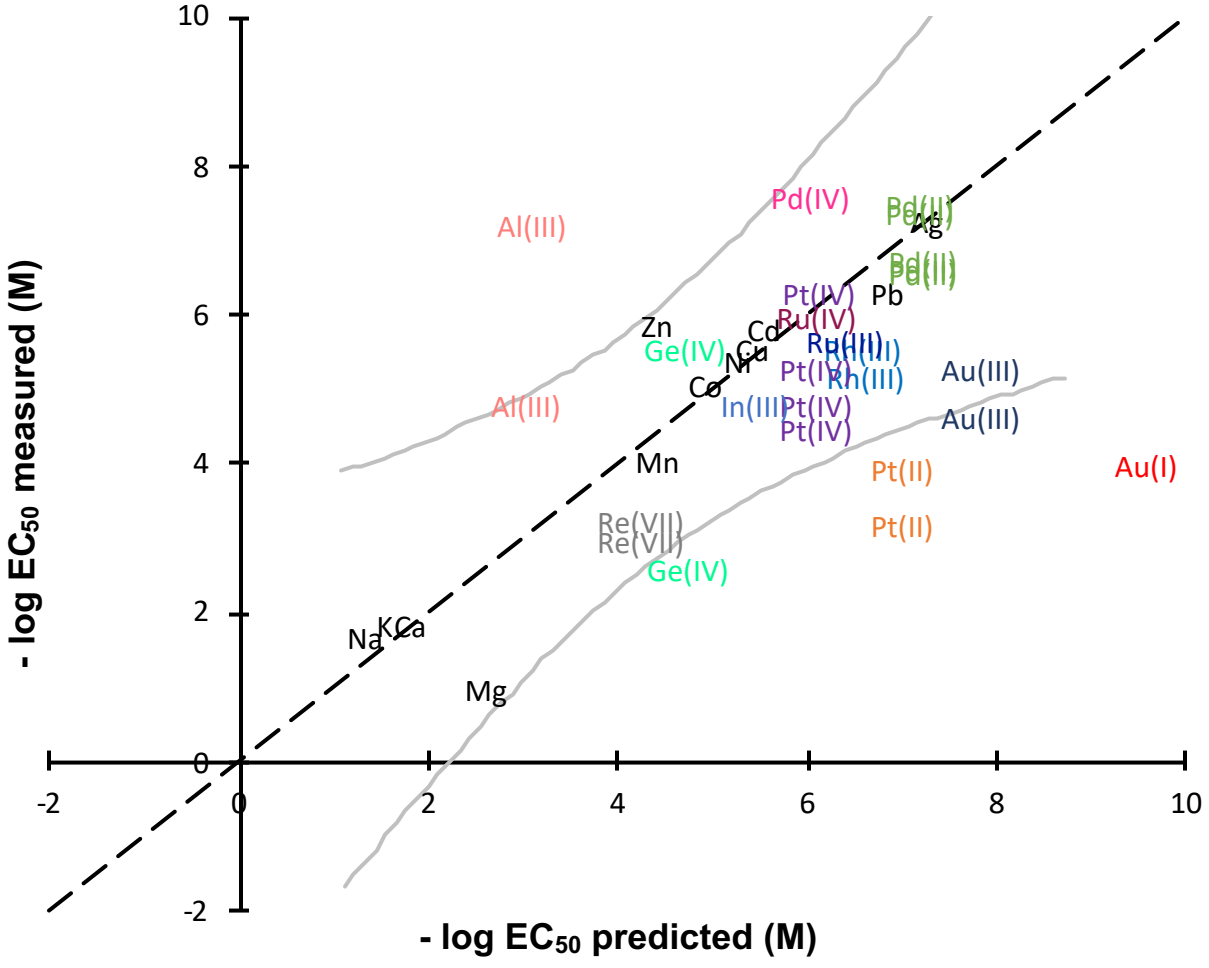

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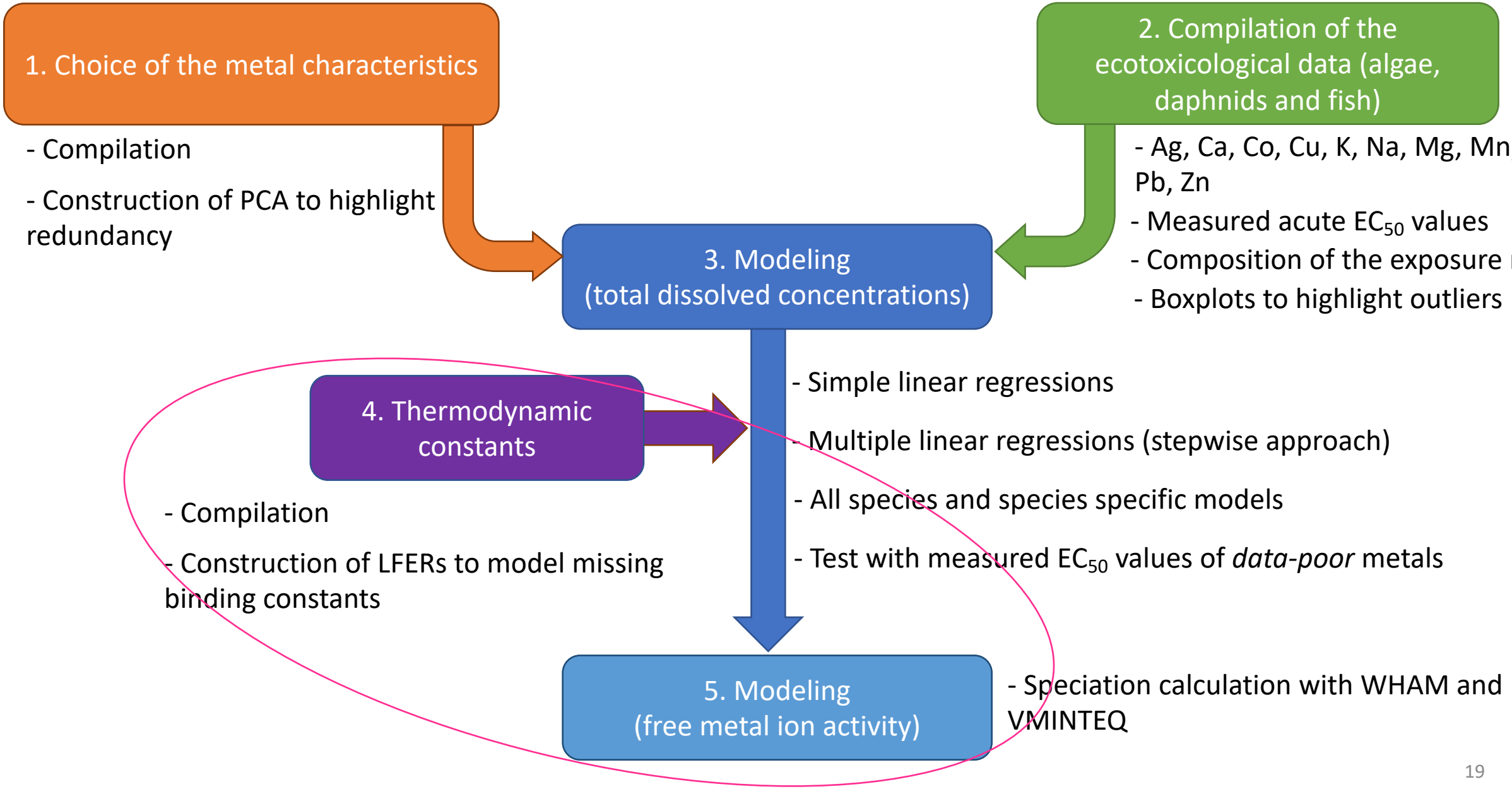
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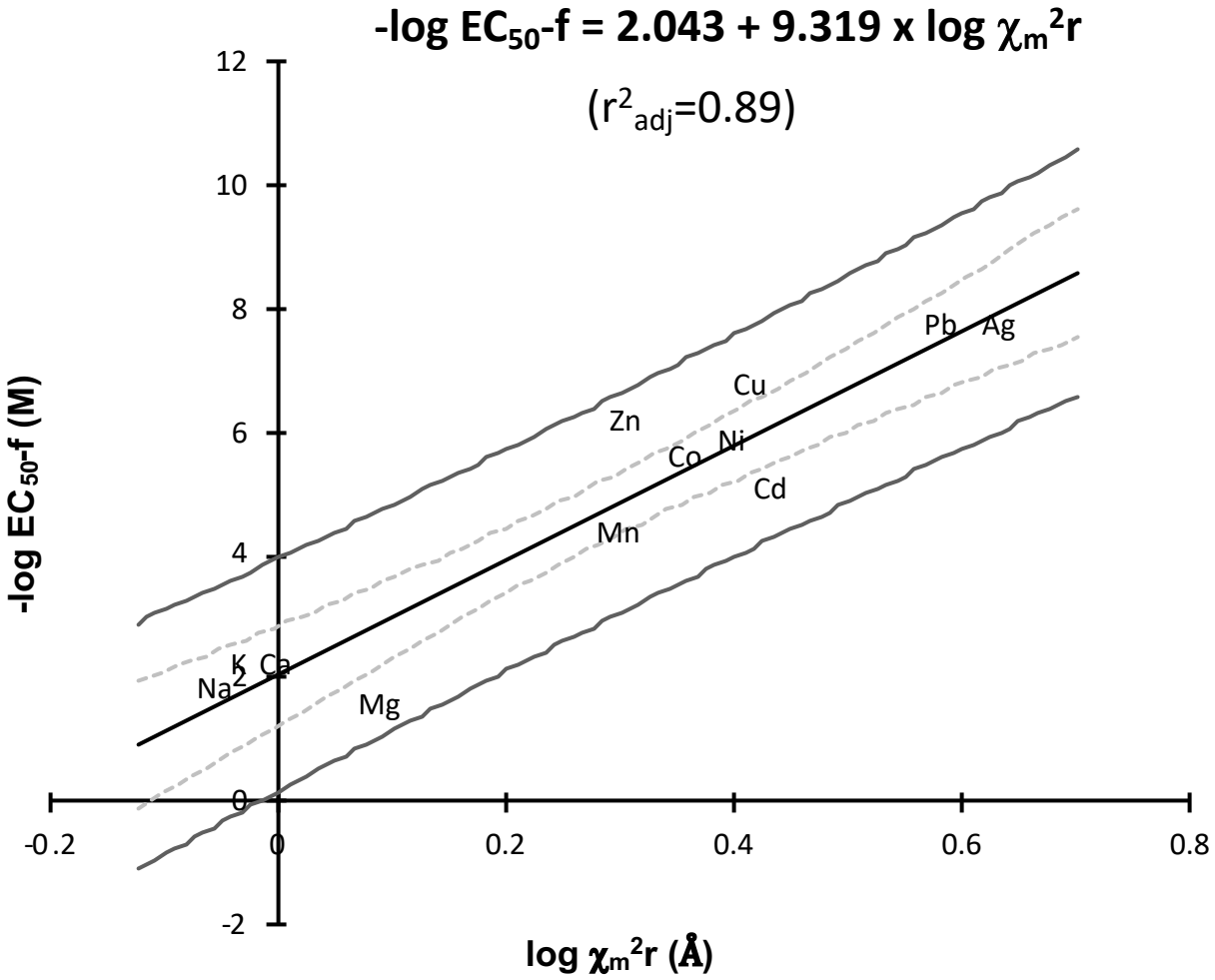
Results – Speciation calculation (algae exposure media)

	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



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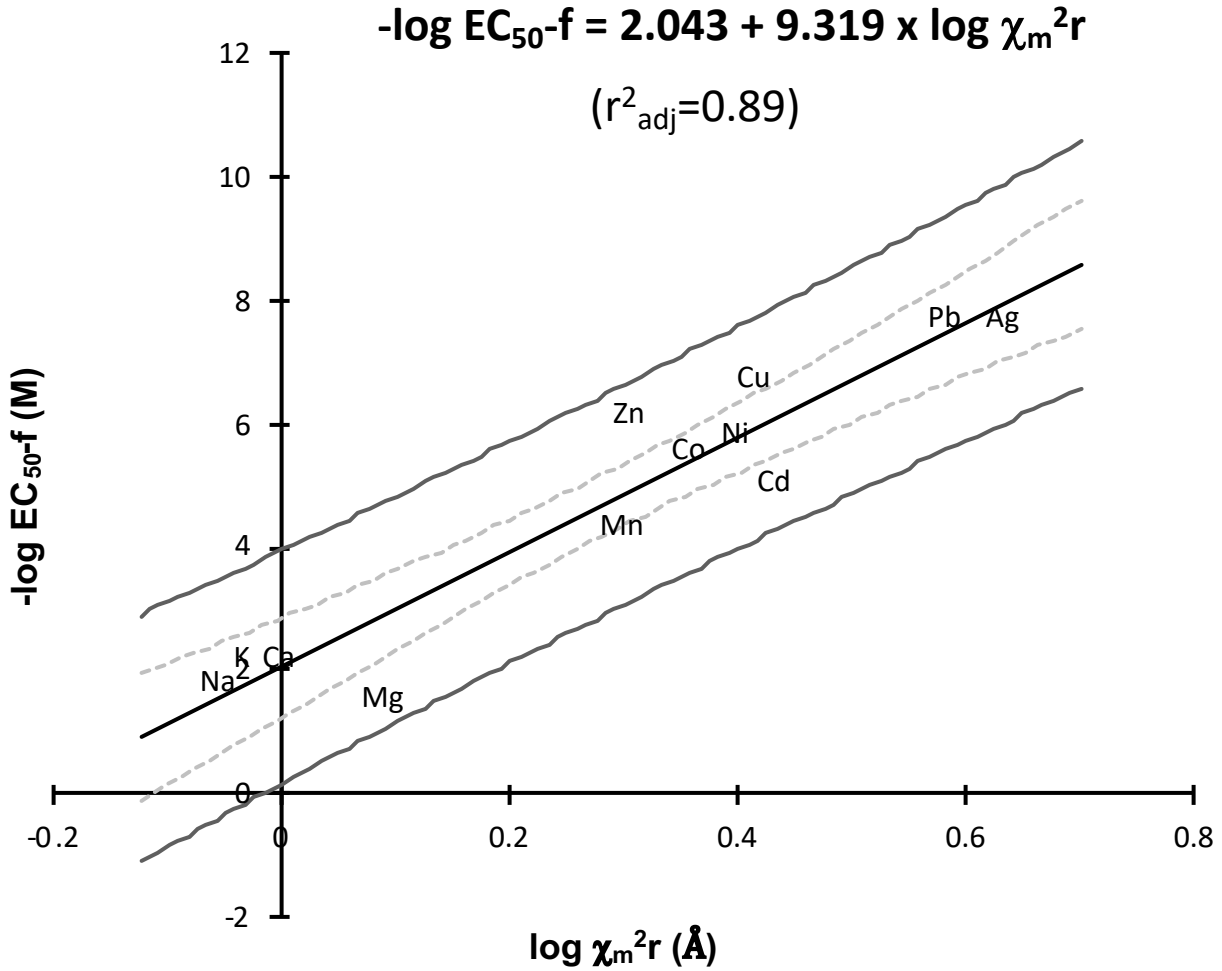
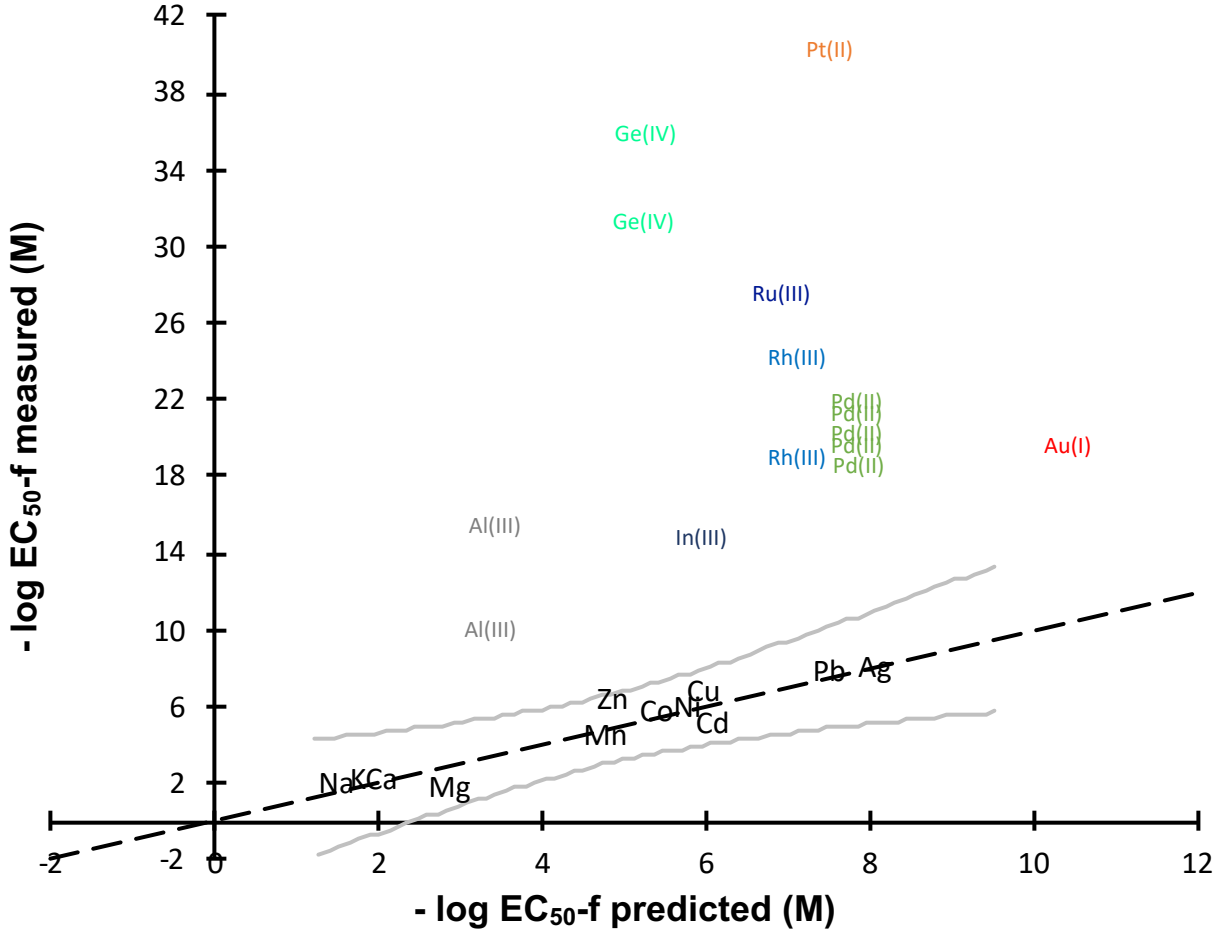




Conclusions and recommendations

- $\chi_m^2 r$ 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 :

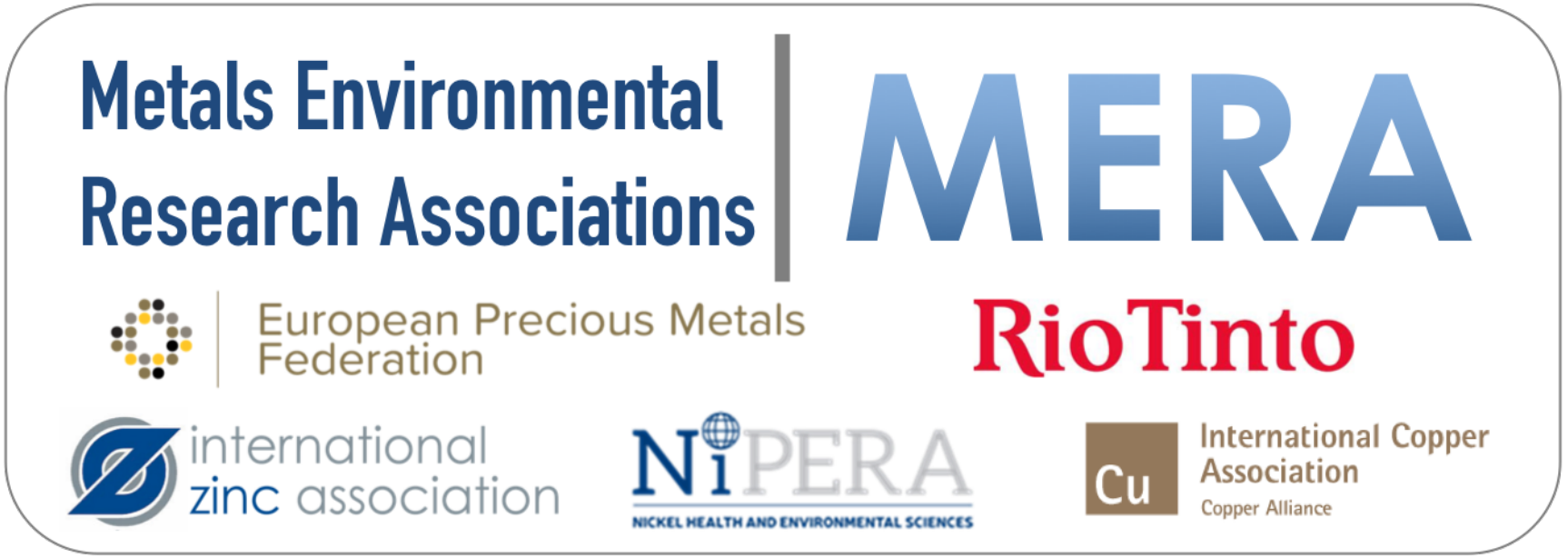
  - Modest improvement for data-rich metals

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

    - Speciation calculations inaccurate?
    - Toxicity test data inaccurate?
    - Other contributing metal forms?

Acknowledgments

- Financial support:



- Additional data providers:

- 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)
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- Dorothea Hug Peter (U. of Geneva)
- Pierre Marle (U. of Geneva)
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