Quantitative Ion Character Activity Relationships (QICARs)

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1 Background

To deal with the less common metal-containing compounds on the Domestic Substances List, Environment Canada will require information about the speciation and the inherent toxicity of many “data-poor” elements. In this context, we explored the possible use of quantitative ion character-activity relationships (QICARs) to predict the relative toxicity of these rarely studied elements in model natural waters and their speciation in solution. **Such information should be invaluable for designing new toxicity tests for these elements and also for determining priorities based on which metals are likely to be most problematic.**

Various quantitative structure-activity relationships (QSARs) have been used for estimating the properties of "new" organic substances, with correlations using molecular properties ranging in sophistication from bulk properties through structure-dependent techniques and quantum chemical considerations. Applications to metal compounds (salts and neutral inorganics) have been much less frequent, at least in part because the range of "new" inorganic substances is much narrower and the incentive to develop extrapolation tools has been less pervasive. The highest linear correlations for acute toxicity (including endpoints for EC_{50}, reproductive inhibition, etc.) make use of one to two parameters relating to metal ion characteristics such as electronegativity, ionisation potential, and/or the "hardness / softness" of the metal atom involved. For this reason, we refer here not to QSARs but rather to QICARs (quantitative ion character-activity relationships), following the suggestion of Ownby and Newman (2003).

Possible uses of QICARs for metals and metal-containing substances might include:

- As a screening tool, to review existing toxicity data and identify "outliers", i.e. toxicity values that depart from the QICAR predictions: These outliers might be LC or EC values that are abnormally low (and are driving regulation setting), or values that are unusually high; in either case, the QICARs could be used to flag values that merit further scrutiny.
- As an extrapolation tool, to estimate speciation (complexation) and the toxicity of little-studied metals for which the existing geochemistry and toxicity data base is limited.

In the first phase of the work, in collaboration with Environment Canada personnel, we identified the range of elements to be investigated: Bi, the Platinum Group Elements and the Lanthanides. Note that in parallel two other CNTC working groups have reviewed the existing literature on the toxicity of the Platinum Group Elements (Claude Fortin and Feiyue Wang) and the Lanthanides (Mike Wilkie, Scott Smith and Jim McGeer). The results of their studies should be compared with the QICAR predictions presented in the present report.

The present project had two main components, the first of which focused on the toxicity of the elements of interest towards (aquatic) organisms. We reviewed the existing literature to choose the best models which permit the prediction of metal toxicity using metal ion characteristics, and we then ran the models and ranked the little-studied elements in terms of their predicted relative toxicities. The second component related to the prediction of the speciation (complexation) of the little-studied elements in natural waters. We screened the available geochemistry databases (Martell and Smith 2004; Academic Software 2001), looking for the complexation constants between the metals and the dominant inorganic ligands present in natural waters (i.e., hydroxide, chloride, carbonate, sulphate, fluoride), and then used chemical equilibrium models to predict the inorganic speciation of the elements of interest, i.e., their speciation in natural waters in the absence of natural organic matter.

2 Toxicity predictions – methods and results

2.1 Description of the studied elements

The names and symbols of the little-studied metals are listed in **Table 1**. Except for bismuth, the studied elements belong to the platinum (Pt) and the lanthanide (La) groups.

Table 1: Names and symbols of the studied elements.

	Name	**Symbol**
	Bismuth	Bi
Platinum group	Ruthenium	Ru
	Rhodium	Rh
	Palladium	Pd
	Osmium	Os
	Iridium	Ir
	Platinum	Pt
Lanthanide group	Lanthanum	La
	Cerium	Ce
	Praseodymium	Pr
	Neodymium	Nd
	Promethium	Pm
	Samarium	Sm
	Europium	Eu
	Gadolinium	Gd
	Terbium	Tb
	Dysprosium	Dy
	Holmium	Ho
	Erbium	Er
	Thulium	Tm
	Ytterbium	Yb
	Lutetium	Lu

2.2 Brief literature review of models used to predict metal toxicity

Although the use of QICAR to predict metal toxicity has not been nearly as widespread as the use of QSAR for organic molecules, several predictive models for metals can nevertheless be found in the environmental toxicology literature (see review by Walker *et al.* (2003)). These models are often based on one or two explanatory metal characteristics and applied to a range of toxicological responses (Kinraide 2009; Veltman et al. 2008; Ownby and Newman 2003; Wolterbeek and Verburg 2001; Tartara et al. 1997; Newman and McCloskey 1996; Barbich et al. 1986; Fisher 1986; Kaiser 1980; Jones and Vaughn 1978; Biesinger and Christensen 1972) – see **Table** 2 for a list of the physical and chemical properties of metals that have been used for predicting their toxicity.

Table 2: Physical and chemical properties of metals that have been used for predicting their toxicity.[a]

Metal properties		Symbol	Definition
Physical properties	- Atomic weight, atomic volume, density	**AW**,V, ρ	Properties that can be measured without changing the basic identity of the studied element.
	- Melting point	MP	
	- Polarizability	A	
	- Molar refractivity	MR	
Electronic structure	- Position on the periodic table (atomic number)	AN	**AN** is the number of protons in an atom, which defines its position in the periodic table.
	- Electronic configuration (electron shells)		The electronic configuration represents the arrangement of electrons in the orbitals of an atom.
	- Ionization energy (potential)	IP, ΔIP	The **ionization energy** (or potential) is the energy required to remove an electron from a gaseous atom or ion. ΔIP is the difference between the ion's IP with the oxidation number (OX) and the IP of the next lower oxidation number (OX-1).
	- Electron affinity	E*	The electron affinity is the energy change that occurs when an electron is added to a gaseous atom or ion.
Redox capacities	- Oxidation number	OX	Elements can lose electrons and be oxidized, or gain electrons to be reduced. $\mathbf{E^0}$ is the standard reduction potential. $\mathbf{\Delta E^0}$ is the absolute value of the electrochemical potential between the ion and the first stable reduced state.
	- Standard electrode potential	E^0	
	- Electrochemical potential	ΔE^0	
Binding properties	- Ionic radius	IR or r	$\mathbf{X_m}$ is the ability of an atom to attract electrons to itself in a chemical bond. **Z** is the ion's charge. Z^2/r (polarizing power) is a measure of electrostatic interaction strength between an ion and a ligand. X_m^2r is a measure for a metal ion of the importance of covalent interactions relative to ionic interactions.
	- Atomic radius, Covalent radius	**AR**, CR	
	- Electropositivity, electronegativity	X_m	
Indices	- Ionic potential	Z/r	
	- Ionic index	Z^2/r	
	- Covalent index	X_m^2r	
	- Covalent bond stability	Δß	Δß is an empirical parameter, which reflects covalent bond stability of the metal-ligand complex.
	- Log AN/ΔIP, AN/ΔIP		
	- Log of the first hydrolysis constant	log K_{OH}	**HSAB theory** categorizes the ions depending on their resistance to deformation in response to electric forces.
	- Hard and soft acids and bases (HSAB) theory	σ_p, σ_w	

[a] Properties indicated in **bold** are those used in the models that we have selected for QICAR toxicity predictions for the little-studied elements.

Among the ion properties compiled in **Table 2**, the binding tendencies or ligand preferences of the different metals have been used successfully in several models. In contrast to the other characteristics, they define the ion with respect to its interactions with potential biotic ligands. For example, hard ions (high σ_p) or class A ions (high Z^2/r) bind preferentially to O-donor atoms whereas soft ions or class B ions seek S-donor ligands.

One of the first models was developed by Kaiser in 1980 to express 16% reproductive impairment in *Daphnia magna* induced by the exposure to 21 different metals (Kaiser 1980). The general equation was:

$$pT = \alpha_0 + \alpha_1 \log \frac{AN}{\Delta IP} + \alpha_2 \Delta E^0 \quad (1)$$

where *pT* is the negative logarithm of a metal ion concentration with a certain toxicity expressed in $\text{mol}\cdot\text{L}^{-1}$, AN is the metal's atomic number, ΔIP is the difference between the ion's ionization potential with the oxidation number (OX) and the ionization potential of the next lower oxidation state (OX-1), and ΔE^0 is the absolute value of the electrochemical potential between the ion and the first stable reduced state. The values of α_0, α_1 and α_2 depended on ion class or category, the organisms and the tested endpoints. Further studies showed that this model was also effective in predicting express acute EC_{50} values for nine metals for a marine bacterium (Newman and McCloskey 1996) but gave variable results for the response of *Caenorhabditis elegans* to metal exposure (Tartara *et al*. 1997) (note that *AN/ΔIP* was used instead of log (*AN/ΔIP*)). Wolterbeek and Verburg (2001) developed a more robust model, also based on fixed metal properties, by modelling toxicity results from 30 literature data sets, which varied widely in exposure times, test organisms, effects and effect levels. We used this as our first tested model; its general equation is:

$$pT = a_0 + a_1 \Delta E^0 + a_2 \log_{10} IP + a_3 X_m + a_4 \log_{10} \frac{AR}{AW} \quad (2)$$

The definition of ΔE^0 is similar to that in equation 1, whereas *IP* is the ion's ionization potential at the oxidation state (OX), X_m the electronegativity, *AR* the atomic radius and *AW* the atomic weight. These metal properties are generally easily available and, in contrast to Kaiser's original model, metals do not need to be separated into basic classes (A, B, intermediate) to model toxicity. Moreover the relative contribution of each parameter to the calculated toxicities allows some mechanistic understanding of metal toxicity.

The second selected model is a more recently published equation, which uses a "consensus scale of softness" (σ_{con}) and a "consensus scale for toxicity" (T_{con}) to predict the toxicity of 92 ions (Kinraide 2009). Softness parameters have been extensively used in recent years, with more or less success, to model the toxicity of metal ions (Walker et al. 2003; Ownby and Newman 2003; Tartara et al. 1997; Newman and McCloskey 1996; Williams and Turner 1980; Jones and Vaughn 1978). One of the most studied has been the softness parameter as defined by Ahrland (1968), σ_p, with:

$$\sigma_p = \frac{CBE(F) - CBE(I)}{CBE(F)} \quad (3)$$

where *CBE(F)* and *CBE(I)* are the coordinate bond energy of the metal-fluoride and metal-iodide complexes, respectively. Based on this definition, σ_p reflects the ability of a metal ion to give up its valence electron, i.e. to form a covalent bond (Jones and Vaughn 1978). Kinraide constructed the consensus scale of softness, σ_{con}, from eight published scales of softness, such as σ_p, as well as from the logarithm of the solubility products of metal sulphides and the negative logarithm of the stability constant for metal ion binding to seven soft ligands. These different scales were normalized and averaged to obtain a consensus constant defined as:

$$\sigma_{con} = aE^0 I_p + b\rho_{Metal} \quad (4)$$

where E^0 is the electrode standard potential, I_p the first ionization potential of the metal and ρ_{Metal} is the bulk metal density. As in the first model, these three ion characteristics are easily retrievable. The calculated constants *a* and *b* are 0.0607 and 0.0454, respectively. A consensus scale of toxicity was derived from ten different toxicity studies[1] and is described by the following equation:

$$T_{con} = a\sigma_{con} + b\sigma_{con} Z + cZ \quad (5)$$

where *Z* is the ion charge, *a*=2.16, *b*=-0.521 and *c*=0.0778. This equation implies that toxicity of a given ion depends on its charge and its softness.

Based on our literature review of the various approaches that have been used to explain differences in toxicity among metals, we selected the Wolterbeek and Verburg (2001) model and the Kinraide (2009) model for use in our simulations of the toxicity of the data-poor elements of interest. Our selection criteria were that the models had been developed and used with a sufficient number of metals, with a broad range of ion property values, and that they leant themselves to mechanistic interpretations (McKinney *et al.* 2000). From the cited literature, one can easily see that Newman and his co-workers have been active in the modelling of metal toxicity in relation to ion characteristics. However, we have decided not to use any of their developed models because of the much smaller pool of studied metals compared to the two models described above. In **Table 2**, properties indicated in **bold** are those used in the models that we have selected for QICAR toxicity predictions for the little-studied elements.

The ion characteristics used in equations 2, 4 and 5, as compiled for the data-poor elements of interest in the present study, can be found in **Table 3**. Most of these metal properties were retrieved from the Handbook of Chemistry and Physics (Lide 2004). Values that were not available in this handbook were obtained, when possible, from other sources. The ionization potential of Ir, electronegativity values of Eu(II), Tb(III) and Yb as well as the atomic radii of most of the elements were retrieved from Wolterbeek and Verburg's original article. The atomic radii of Pm, Sm and Tm were found in Cordero et al. (2008). No values of electrochemical and ionization potentials were found for osmium; the same situation prevailed for electronegativity values for Pm. Accordingly, toxicity values for these two elements could not be calculated.

An important limitation of the Wolterbeek and Vereburg model, as pointed out by the authors themselves, is that it can only be applied to metals whose properties (ΔE^0, *IP*, X_m, *AR* and *AW*) fall within a calibration matrix representing the minimum and maximum numerical values of these properties for the metals used in the calibration of the model. In other words, the metal ion parameters for the data-

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[1] Kinraide (2009) used three of the 30 datasets used by Wolterbeek and Verburg (2001), and added seven additional studies – see Appendix 1 for a list of all these studies.

Table 3: Compilation of the data-poor elements characteristics used in equations 2, 4 and 5.

Element	Z	AR (Å)[a,b]	AW ($g \cdot mol^{-1}$)[c]	ρ_{Metal} ($g \cdot cm^{-3}$)[c]	ΔE^0 (V)[c]	IP (eV)[a,c]	Xm[a,c]	E^0 (V)[c]	First Ip (eV)[c]
Bi	3	1.46	208.98038(2)[d]	10.05	0.2	25.56	1.9	0.308	7.2856
Ru	2	1.33	101.07(2)	10.65	0.455	16.76	2.2	0.455	7.36050
	3	1.33	101.07(2)	10.65	0.249	28.47	2.2	0.2487	7.36050
Rh	3	1.35	102.90550(3)	10.7	0.758	31.06	2.28	0.758	7.45890
Pd	2	1.38	106.42(1)	10.38	0.951	19.43	2.20	0.951	8.3369
Os		1.44	190.23(3)	20	-[e]	-	2.2	-	8.4382
Ir	3	1.36	192.217(3)	19	1.156	27	2.2	1.156	8.9670
Pt	2	1.38	195.078(2)	19.77	1.18	18.563	2.2	1.18	8.9587
La	3	1.87	138.91	6.15	-2.379	19.1773	1.10	-2.379	5.5769
Ce	3	1.82	140.115(4)	6.55	-2.336	20.198	1.12	-2.336	5.5387
	4	1.82	140.115(4)	6.55	1.72	36.758	1.12	1.72	5.5387
Pr	3	1.82	140.90765(2)	6.50	-3.1	21.624	1.13	-2.353	5.473
Nd	3	1.83	144.24(3)	6.89	-2.7	22.1	1.14	-2.323	5.5250
Pm	3	1.99	(145)	6.50	-2.6	22.3	-	-2.30	5.582
Sm	3	1.98	150.36(3)	7.16	-1.55	23.4	1.17	-2.304	5.6436
Eu	2	1.98	151.964(1)	5.13	-2.812	11.241	1.15	-2.812	5.6704
	3	1.98	151.964(1)	5.13	-0.36	24.92	1.15	-1.991	5.6704
Gd	3	1.79	157.25(3)	7.4	-2.279	20.63	1.20	-2.279	6.1501
Tb	3	1.76	158.92534(2)	7.65	-2.28	21.91	*1.20*	-2.28	5.8638
Dy	3	1.76	162.50(3)	8.37	-2.6	22.8	1.22	-2.295	5.9389
Ho	3	1.75	164.93032(2)	8.34	-2.8	22.84	1.23	-2.1	6.0215
Er	3	1.74	167.26(3)	8.86	-3.0	22.74	1.24	-2.331	6.1077
Tm	3	1.90	168.93421(3)	8.56	-2.2	23.68	1.25	-2.319	6.18431
Yb	3	1.94	173.04(3)	6.21	-1.05	25.05	*1.25*	-2.19	6.25416
Lu	3	1.72	174.967(1)	9.3	-2.28	20.9594	1.0	-2.28	5.4259

[a] Wolterbeek and Verburg (2001); [b] Cordero *et al*. (2008); [c] Lide (2004) – the absolute values of ΔE^0 are used in the simulations ; [d] In column 4, the final number (in parentheses) represents an uncertain value; [e] The symbol "-" means that no data were found.

poor elements of interest should fit within this calibration matrix. The limits within which the Wolterbeek and Verburg model is applicable are shown in **Table 4**. Fortunately, all of the elements of interest in the present study fall within these limits.

Table 4: Limits within which the Wolterbeek and Verburg model is applicable.

Minimum	Properties	Maximum
0 (Ge^{4+})	ΔE0	3.045 (Li^{+})
3.89390 (Cs^{+})	IP	119.203 (Mn^{7+})
0.79 (Cs)	Xm	2.55 (Se)
0.006986 (Bi)	AR/AW	0.218989 (Li)

Note: The values are for the elements in parentheses, which represent the limits within which the model is applicable.

2.3 Results of the toxicity predictions

2.3.1 Wolterbeek and Verburg model

Wolterbeek and Verburg (2001) present comparisons between observed toxicities and predicted toxicities for 30 different data sets, corresponding to different organisms and different toxicity endpoints (Table 4 in their paper). Professor Wolterbeek kindly communicated to us the optimized values of a_0, a_1, a_2, a_3, a_4 that were obtained by fitting equation (2) to each of their data sets (**Table 5**; the mice, rat and drosophila data sets were not used because these organisms were not considered to be sufficiently “aquatic”). We then used these values to calculate the predicted toxicities of our data-poor elements, as applied to several organisms and several endpoints. The obtained results are presented below. Note that elements which appear below in **bold** in the text are those that occupy the first position in the toxicity ranking tables (i.e., the most toxic).

2.3.1.1 Enzyme inactivation

Inactivation of six different enzymes (*fish carbonic anhydrase*, *glutamic oxalacetic transaminase*, *lactic dehydrogenase*, *fish acetylchlolinesterase, ribonuclease* and *lipase*) by the elements of interest has been predicted with the present model (**Figures 1 to 8**). For three of these six studied enzymes (*fish carbonic anhydrase, fish acetylchlolinesterase and lipase)*, the ten most toxic elements belong to the La group, with **Er**, **Lu**, **Eu(II)** or **Pr** (prediction with lipase was performed with two endpoints) as first toxicant (**Table 6**). For the *fish carbonic anhydrase* and *acetylchlolinesterase* (**Figures 1, 4**)*,* the range of inactivating concentrations is very narrow for these first elements. For example, *fish carbonic anhydrase* is inactivated at 2.6 x 10^{-5}M with **Er** (first element) to 5.1 x 10^{-5}M with Gd (10th element) (**Figure 1**). The first element of the La group in the toxicity ranking for the same enzyme is Ir with a predicted concentration close to the range for the first ten elements (5.9 x 10^{-5} M; 11th element). For the *lipase* enzyme, the range of inactivating concentration of the first ten elements is wider by about one order of magnitude (**Figures 7, 8**). The first element of the Pt group in the toxicity ranking is Pt (15th and 16th) with an inactivating concentration of about 25 and 500 times higher than the most toxic element of the La group, for the endpoints I_1 and I_{50}, respectively. For the three other enzymes (*glutamic oxalacetic transaminase*, *lactic dehydrogenase* and *ribonuclease*), the first ten elements belong to the Pt and La group, with **Pt** being predicted to be the most toxic metal for these enzymes (**Table 6**). The other members of the group of five most toxic metals are Ru(II), Pd, Ir and Rh. Europium(II), which is a La group element, also ranks in the first five metals with an inactivating concentration about three times higher than Pt for *lactic dehydrogenase* and ten times higher for *glutamic oxalacetic transaminase* and *ribonuclease* (expressed as I_1).

Table 5: Optimized constants (a_{0-4}) used in the Wolterbeek and Verburg (2001) model.

Target	Enzyme or Species	Exposure time	R^2	Effect	n	a0	a1	a2	a3	a4
Enzymes	Fish carbonic anhydrase		0.69	I_{50}	21	-2.357	0.217	1.057	-0.512	-2.768
	Glutamic oxalacetic transaminase		0.80	I_{20}	16	0.540	0.325	-2.918	1.799	-1.251
	Lactic dehydrogenase		0.89	I_{20}	15	0.543	0.138	-2.188	0.611	-2.106
	Fish acetylcholinesterase		0.63	I_{50}	17	1.525	0.076	-0.360	-0.819	-1.716
	Ribonuclease		0.70	I_1	14	2.046	0.645	-2.610	2.253	-0.171
	Ribonuclease		0.64	I_{50}	14	-1.187	0.792	-0.503	1.815	-0.242
	Lipase		0.71	I_1	17	3.027	1.053	-2.348	-0.968	-2.834
	Lipase		0.73	I_{50}	14	0.190	1.559	-1.248	-1.796	-3.659
Bacteria	*Vibrio fischeri (M)*	15 m	0.93	EC_{50}	20	-1.535	-0.533	-0.382	2.185	-1.555
	Vibrio fischeri (N)	15 m	0.97	EC_{50}	9	-34.032	1.990	15.305	4.278	-5.844
Algae	*Selenastrum capricornutum*	96 h	0.99	EC_{50}	9	1.677	-0.775	-0.782	0.792	-2.554
Fungi	*Alternaria tenuis*	18 h	0.72	ED_{50}	22	-4.214	-0.066	2.399	2.119	-0.819
	Botrytus fabea	18 h	0.83	ED_{50}	22	-2.076	-0.406	1.454	1.767	-0.875
Protozoans	*Spirostomum ambiguum*	24 h	0.83	LC_{50}	11	4.049	1.227	1.275	1.296	2.216
	Spirostomum ambiguum	48 h	0.84	LC_{50}	11	4.020	1.218	1.266	1.287	2.201
Copepods	*Cyclops abyssorum*	48 h	0.95	LC_{50}	12	0.310	-0.679	0.012	-0.422	-2.698
	Eudiaptomus padonus	48 h	0.92	LC_{50}	12	3.345	-1.061	-0.911	-0.782	-2.439
Nematodes	*Caenorhabditis Elegans-1*	24 h	0.93	LC_{50}	9	-20.444	0.869	12.080	0.677	-3.356
	Caenorhabditis Elegans-2	24 h	0.78	LC_{50}	18	-3.888	0.316	1.062	1.341	-1.201
Crustaceans	*Daphnia magna*	21 d	0.88	RI_{16}	21	1.403	-0.942	-0.128	-0.397	-3.411
	Daphnia magna	21 d	0.88	RI_{50}	21	1.557	-0.961	-0.065	-0.544	-3.278
	Daphnia magna	21 d	0.83	LC_{50}	21	1.855	-0.950	0.217	-0.790	-2.913
	Daphnia magna-1	48 h	0.90	LC_{50}	15	1.654	-1.016	-0.453	-0.707	-3.616
	Daphnia magna-2	48 d	0.71	LC_{50}	22	2.511	-0.614	-0.846	0.022	-1.949
	Daphnia hyalina	48 h	0.88	LC_{50}	12	-0.207	-1.263	2.284	-2.757	-4.930
Fish	Rainbow trout	96 h	0.91	TL_{50}	9	6.273	1.110	-2.588	-5.098	-6.126

I_x: Inactivation - toxicant concentration that reduces (enzyme) activity by x %; I_1 values are taken to be the effect-no effect threshold; **EC_{50}**: Effective toxicant concentration that reduces a response of an organism by 50 %; **LC_{50}**: Lethal toxicant concentration that kills half of organisms; **RI_x**: Reproductive impairment – toxicant concentration that reduces reproductive ability of an organism by x %; **TL_{50}**: Tolerance limit = toxicant concentration that causes the mortality of 50% of the test organisms.

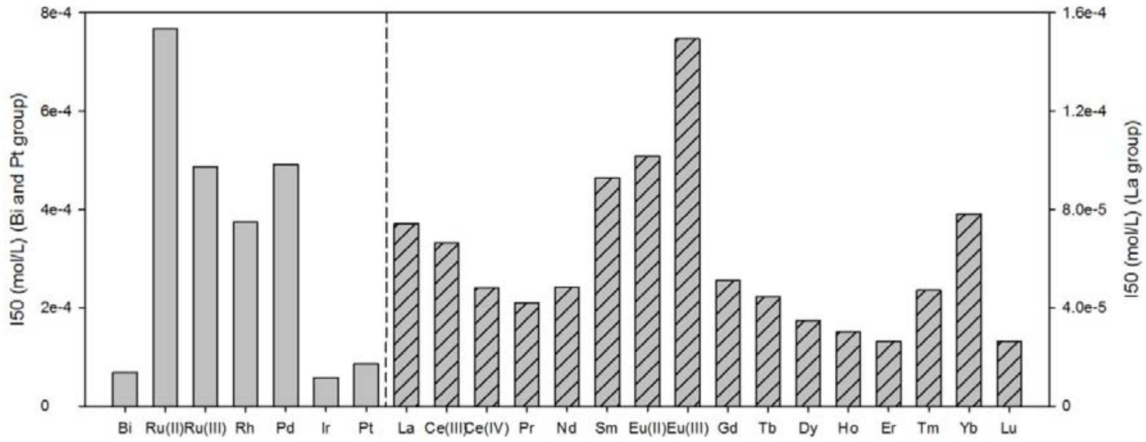

Figure 1: Predicted metal concentrations inhibiting *fish carbonic anhydrase* activity by 50%.

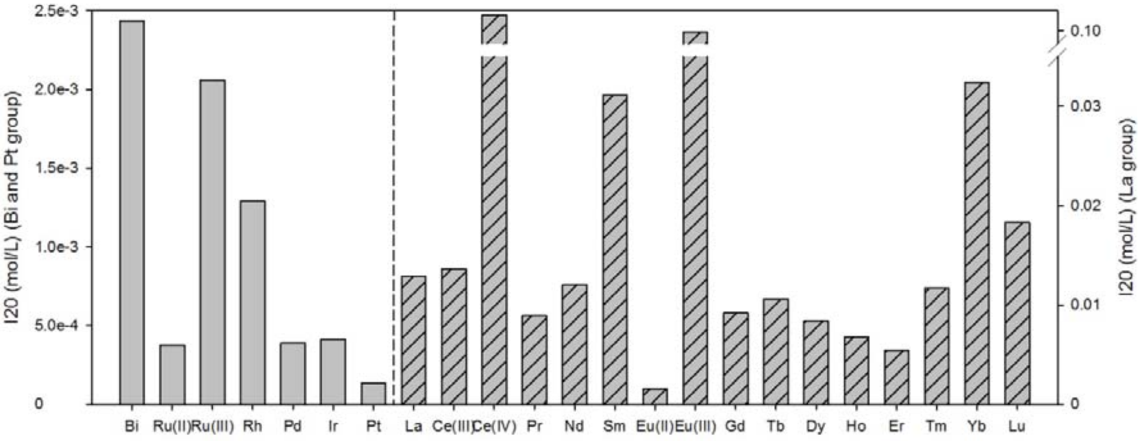

Figure 2: Predicted metal concentrations inhibiting *glutamic oxalacetic transaminase* activity by 20%.

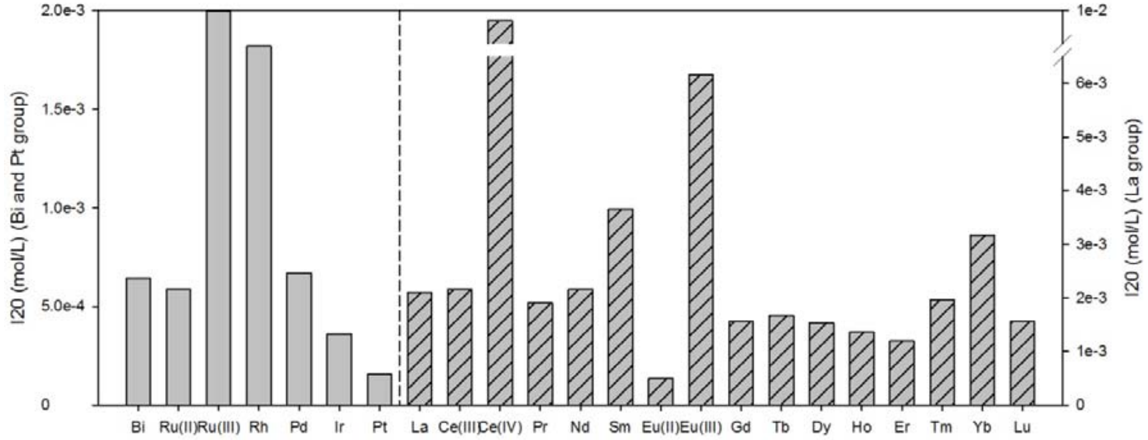

Figure 3: Predicted metal concentrations inhibiting *lactic dehydrogenase* activity by 20%.

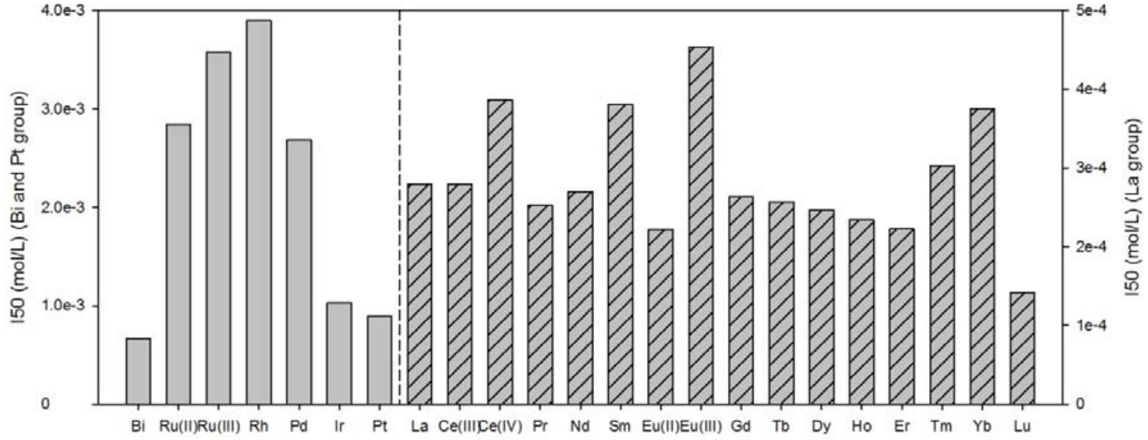

Figure 4: Predicted metal concentrations inhibiting *fish acetylchlolinesterase* activity by 50%.

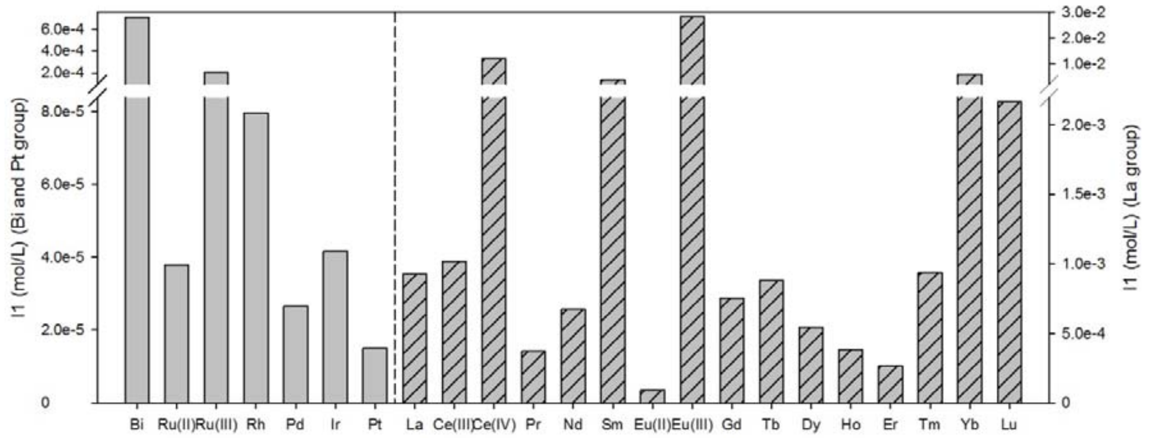

Figure 5: Predicted metal concentrations inhibiting *ribonuclease* activity by 1%.

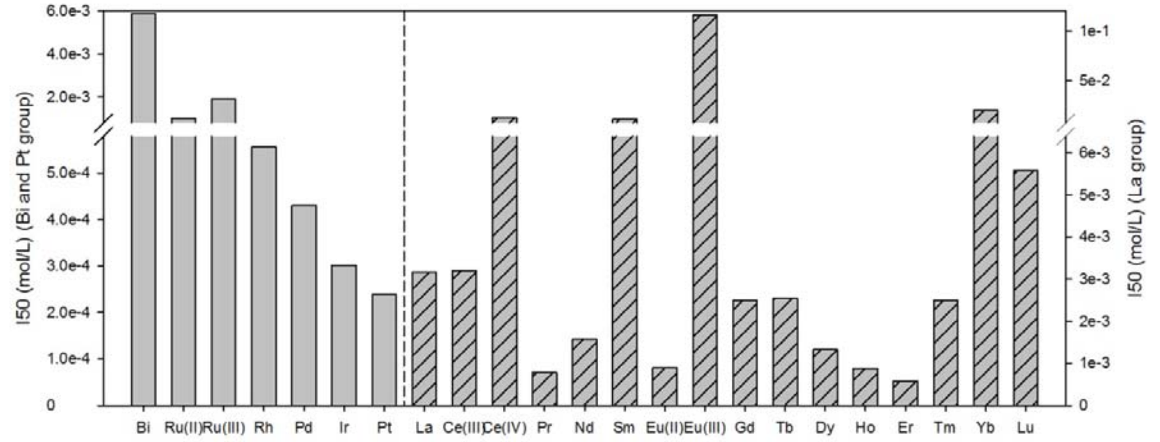

Figure 6: Predicted metal concentrations inhibiting *ribonuclease* activity by 50%.

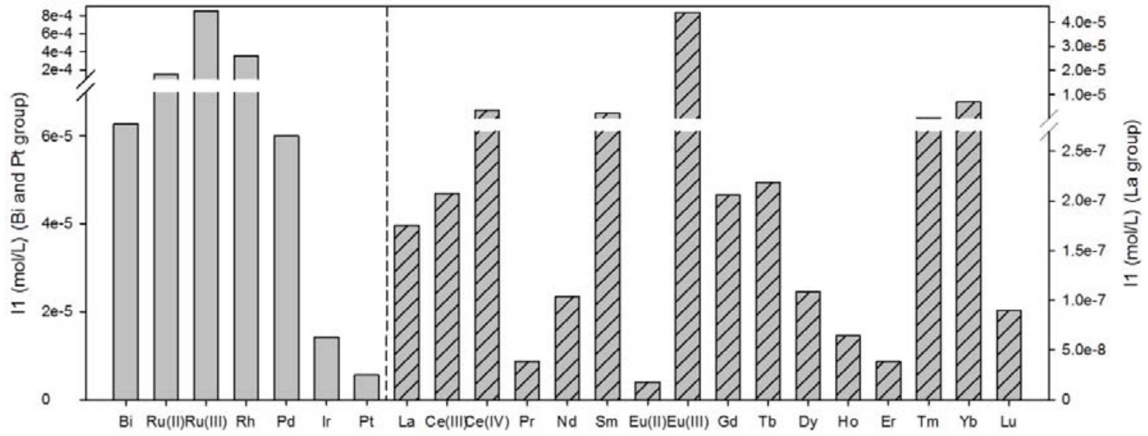

Figure 7: Predicted metal concentrations inhibiting *lipase* activity by 1%.

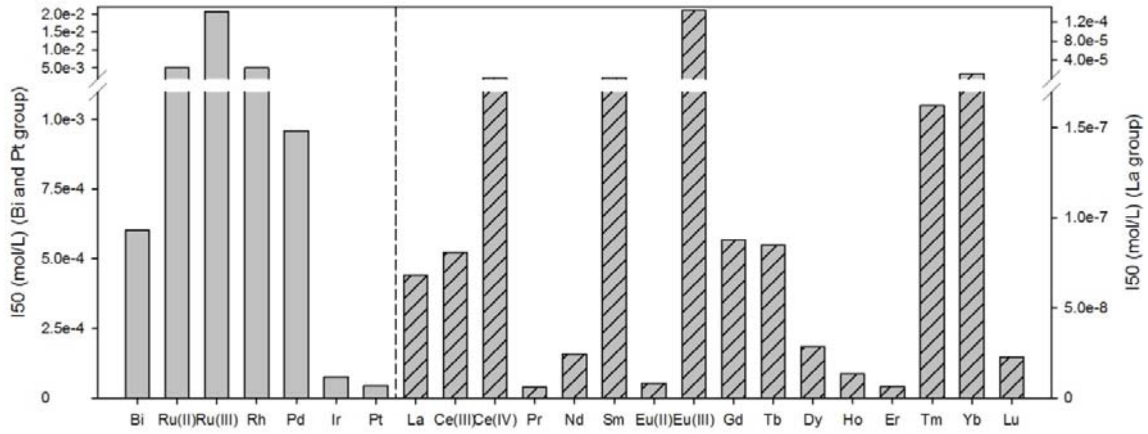

Figure 8: Predicted metal concentrations inhibiting *lipase* activity by 50%.

Table 6: Toxicity ranking of the first ten elements towards enzymes (1: most toxic element).

Enzymes	1	2	3	4	5	6	7	8	9	10
fish carbonic anhydrase	Er	Lu	Ho	Dy	Pr	Tb	Tm	Ce(IV)	Nd	Gd
glutamic oxalacetic transaminase	Pt	Ru(II)	Pd	Ir	Rh	Eu(II)	Ru(III)	Bi	Er	Ho
lactic dehydrogenase	Pt	Ir	Eu(II)	Ru(II)	Bi	Pd	Er	Ho	Dy	Gd
fish acetylchlolinesterase	Lu	Eu(II)	Er	Ho	Dy	Pr	Tb	Gd	Nd	La
ribonuclease-I$_1$	Pt	Pd	Ru(II)	Ir	Rh	Eu(II)	Ru(III)	Er	Pr	Ho
ribonuclease-I$_{50}$	Pt	Ir	Pd	Rh	Er	Pr	Ho	Eu(II)	Ru(II)	Dy
lipase-I$_1$	Eu(II)	Er	Pr	Ho	Lu	Nd	Dy	La	Gd	Ce(III)
lipase-I$_{50}$	Pr	Er	Eu(II)	Ho	Lu	Nd	Dy	La	Ce(III)	Tb

2.3.1.2 Bacteria

Effects of our data-poor elements on *Vibrio fischeri* (EC_{50}) were modelled using two sets of $a_{0\text{-}4}$ parameters (**Table 5**). The effective concentration, EC_{50}, corresponds to the concentration resulting in a 50% decrease of bacterial luminescence after 15 min of exposure to the metals. As was done by Wolterbeek and Verburg (2001), the two series of predicted toxicities were called *V. fischeri* (M) (for data from McCloskey et al. (1996)) and *V. fischeri* (N) (for data from Newman and McClosey (1996)). These two studies differed in the number of metals used to construct the models (nine in Newman and McCloskey (1996) and 20 in McCloskey et al. (1996)) and also in the exposure conditions (marine conditions in Newman and McCloskey (1996) and freshwater conditions in McCloskey et al. (1996). In both cases, the authors calculated the speciation of their metals and expressed the metal concentrations in terms of the free metal ion.

Bismuth and the elements of the Pt group are the most toxic for *V. fischeri* (M) with EC_{50} values about 1000 times lower than those of the La group (except for Eu(III) and Yb, which have an EC_{50} about 100 times higher) (**Figure 9**). The most toxic element is **Ru(III)** followed by Pt, Ru(II), Ir and Rh with a narrow range of predicted EC_{50}s from 3.3×10^{-6} M to 4×10^{-6} M (**Table 7**). Bismuth is the next element after Rh with an EC_{50} of 4.7×10^{-6}M. In *V. fischeri* (N), **Ir** and Rh are the most toxic metals with very low EC_{50}s of 7.0×10^{-13} M and 8.6×10^{-12} M, respectively (**Figure 10**). The third to the sixth elements in the ranking are Pt, Er, Ce(IV) and Ho with EC_{50}s between 1.9 and 7.3×10^{-10} M. The following metals in the toxicity ranking have predicted EC_{50}s that are about 1000 times higher, starting with Ru(II) at 9.7×10^{-7} M.

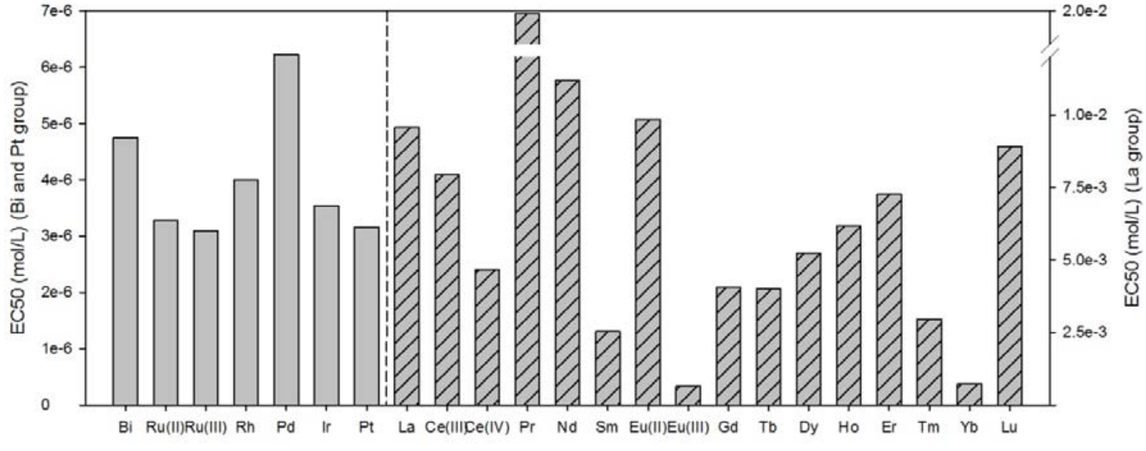

Figure 9: Predicted metal concentrations inhibiting light emission by *Vibrio fischeri (M)* by 50%.

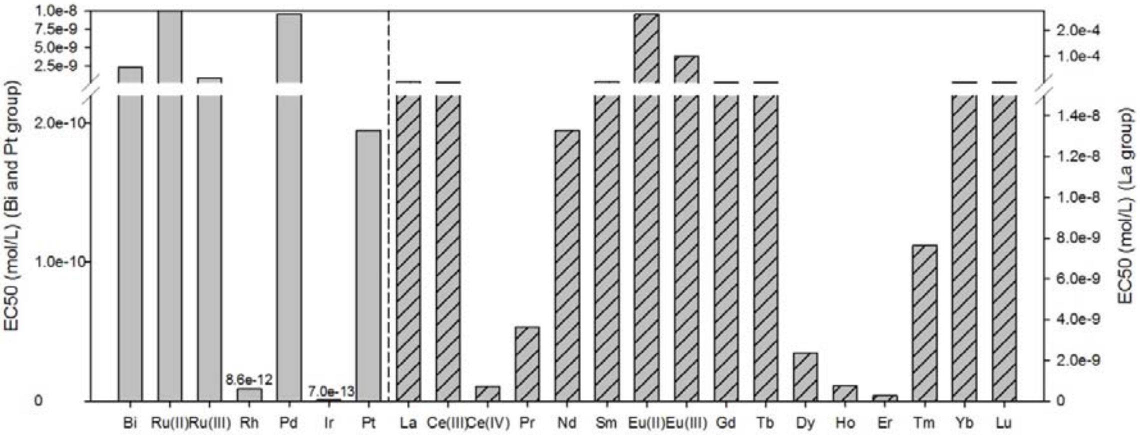

Figure 10: Predicted metal concentrations inhibiting light emission by *Vibrio fischeri (N)* by 50%.

Table 7: Toxicity ranking of the first ten elements towards bacteria (1: most toxic element).

	1	2	3	4	5	6	7	8	9	10
V. fischeri M	Ru(III)	Pt	Ru(II)	Ir	Rh	Bi	Pd	Eu(III)	Yb	Sm
V. fischeri N	Ir	Rh	Pt	Er	Ce(IV)	Ho	Ru(II)	Bi	Dy	Pr

2.3.1.3 Algae

Growth inhibition by the studied elements was predicted for the unicellular green alga, *Selenastrum capricornutum* (now known as *Pseudokirchneriella subcapitata*). **Bismuth** and Pt with EC_{50}s of 3.7 x 10^{-8} M and 9.9 x 10^{-8} M, respectively, are the most toxic elements for the alga, followed by other elements of the Pt group (**Figure 11**, **Table 8**). The most toxic element in the La group is Eu(III) (8th; EC_{50}=9.3 x 10^{-7} M), followed by Yb (9th; EC_{50}=1.8 x 10^{-6} M) and Sm (10th; EC_{50}=7.3 x 10^{-6} M).

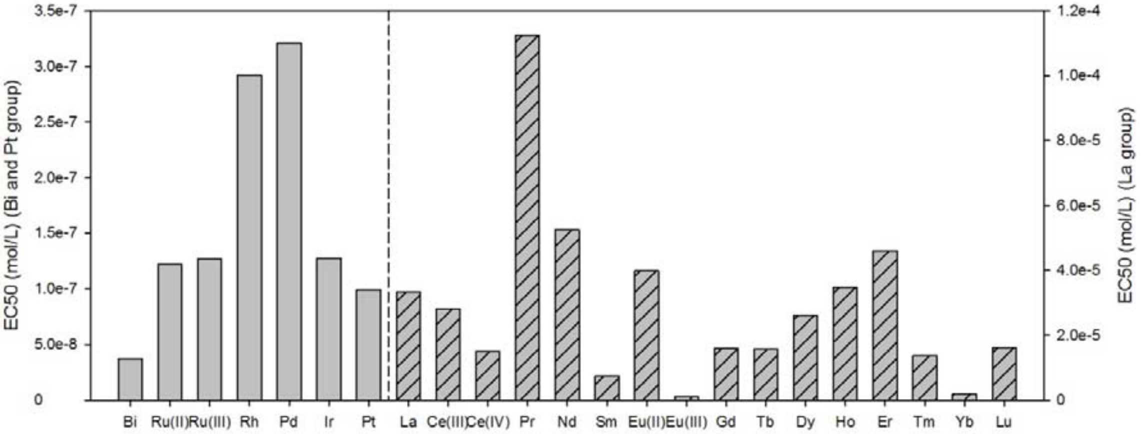

Figure 11: Predicted metal concentrations reducing growth of *S. capricornutum* by 50%.

Table 8: Toxicity ranking of the first ten elements towards algae (1: most toxic element).

	1	2	3	4	5	6	7	8	9	10
Algae	Bi	Pt	Ru(II)	Ru(III)	Ir	Rh	Pd	Eu(III)	Yb	Sm

2.3.1.4 Fungi

Metals of the Pt group and Bi are predicted to be the most toxic elements for two species of fungi (*Alternaria tenuis* and *Botrytus fabea*) (**Figure 12**). **Rhodium**, Ir and **Ru(III)** are ranked as the three first toxicants in the toxicity ranking with an ED_{50} range between 2.0 x 10^{-6} M and 4.9 x 10^{-6} M (**Table 9**). Cerium(IV) (8th) and Eu(III) (8th) are the most toxic metals of the La group with ED_{50} values 100 times higher than for elements of the Pt group, with a concentration of 4.5 x 10^{-4} M (*A. tenuis*) and 3.2 x 10^{-4} M (*B. fabea*), respectively.

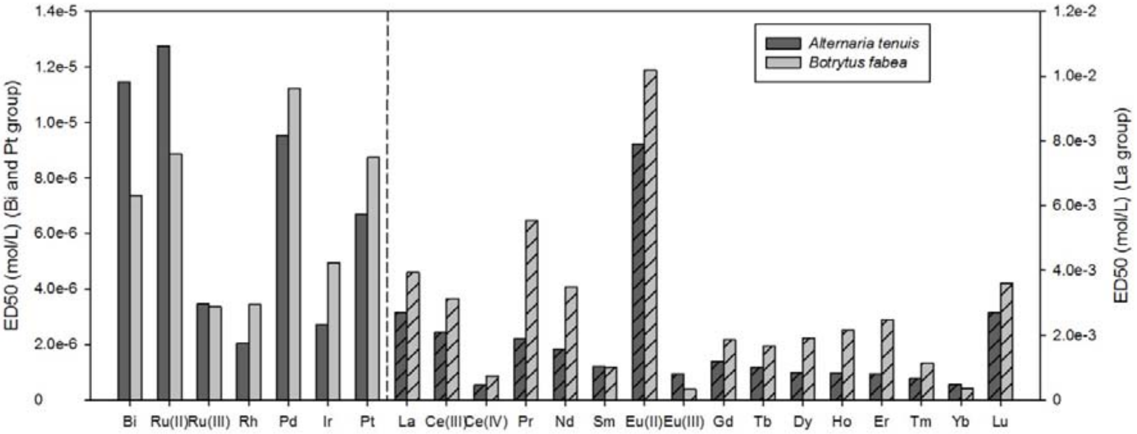

Figure 12: Predicted metal doses reducing germination of *A. tenuis* and *B. fabea* by 50%.

Table 9: Toxicity ranking of the first ten elements towards fungi (1: most toxic element).

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
A. tenuis	Rh	Ir	Ru(III)	Pt	Pd	Bi	Ru(II)	Ce(IV)	Yb	Tm
B. fabea	Ru(III)	Rh	Ir	Bi	Pt	Ru(II)	Pd	Eu(III)	Yb	Ce(IV)

2.3.1.5 Protozoa

From the model calculations, the protozoan *Spirostomum ambiguum* is expected to be more impacted by elements belonging to the La group than those of the Pt group and Bi after 24 and 48 hours of exposure (**Figure 13**). The first ten metals in the toxicity ranking are similar after 24 and 48 h of exposure with LC_{50} values of **Pr**, Er and Ho ranging from 1.7 x 10^{-7} M to 4.1 x 10^{-7} M (**Table 10**). Rhodium is the most toxic element in the Pt group (12th position) with a LC_{50} of 2.4 x 10^{-6} M.

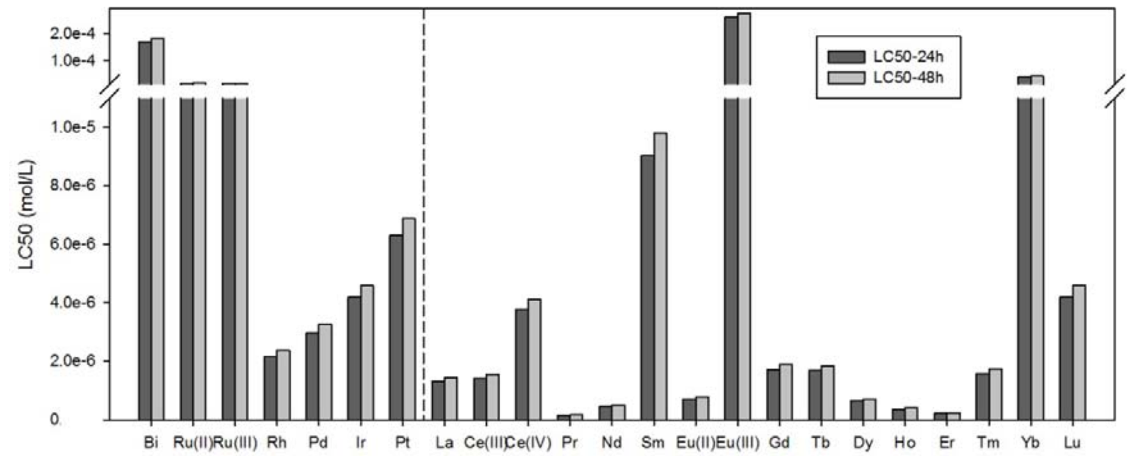

Figure 13: Predicted metal concentrations causing 50% mortality of *S. ambiguum*.

Table 10: Toxicity ranking of the first ten elements towards protozoa (1: most toxic element).

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
S. ambiguum	Pr	Er	Ho	Nd	Dy	Eu(II)	La	Ce(III)	Tm	Tb

2.3.1.6 Copepods

Metal concentrations leading to 50% mortality (LC_{50}) were modelled for *Cyclops abyssorum* and *Eudiaptomus padonus* (**Figure 14**). In both organisms, **Bi** is predicted to be the most toxic element with a LC_{50} of 6.2×10^{-6} M and 2.4×10^{-6} M for *C. abyssorum* and *E. padonus*, respectively. Europium(III) ranks in second place in both copepods but with a much higher concentration for *C. abyssorum* ($LC_{50}=2.1 \times 10^{-5}$ M) than for *E. padonus* (4.1×10^{-6} M). The next elements in the ranking list are Ir, Pt, Yb, Ru(III), Ru(II), Rh, Sm and Pd; their position in the toxicity ranking table depends on the studied copepods (**Table 11**).

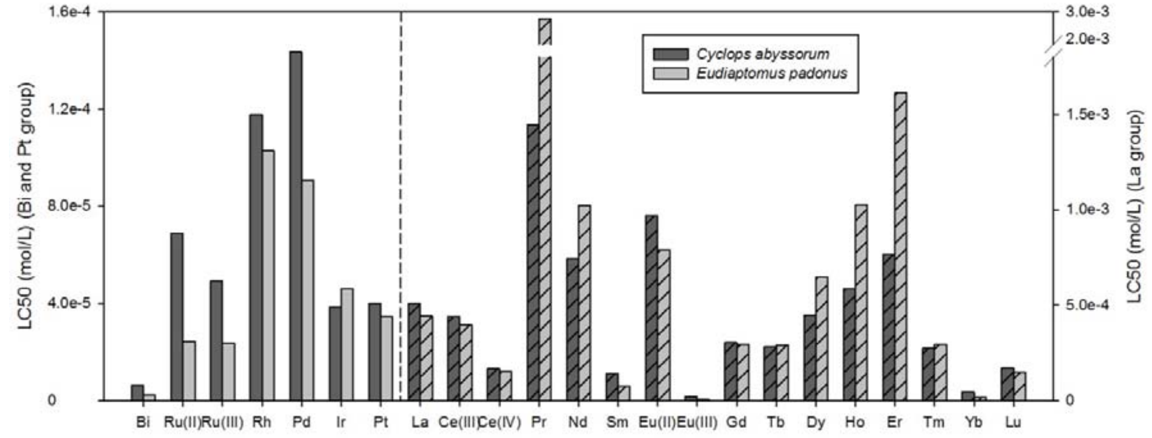

Figure 14: Predicted metal concentrations causing 50% mortality of *C. abyssorum* and *E. padonus*.

Table 11: Toxicity ranking of the first ten elements towards copepods (1: most toxic element).

	1	2	3	4	5	6	7	8	9	10
C. abyssorum	Bi	Eu(III)	Ir	Pt	Yb	Ru(III)	Ru(II)	Rh	Sm	Pd
E. padonus	Bi	Eu(III)	Yb	Ru(III)	Ru(II)	Pt	Ir	Sm	Pd	Rh

2.3.1.7 Nematodes

Toxicity (LC_{50}) of the studied elements towards *Caenorhabditis elegans* was modelled using two sets of a_{0-4} parameters, designated as *C. elegans*-1 and -2 (**Figures 15, 16**). In the first series of toxicity data (**Figure 15**), **Ce(IV)** is predicted to be the most lethal element with an EC_{50} of 8.9 x 10^{-9} M, followed by metals from both the Pt and La groups, with Ir (EC_{50} of 2.8 x 10^{-7} M) and Rh (7.9 x 10^{-7} M) ranking at second and third position, respectively (**Table 12**). In the second series of modelled toxicity data (**Figure 16**), the elements of the Pt group are more toxic than those of the La group with the first five elements being Ir (1st; LC_{50}=3.0 x 10^{-4} M), Pt (2nd; LC_{50}=4.3 x 10^{-4} M), Rh (3rd; LC_{50}=5.6 x 10^{-4} M), Pd and Ru(III) (**Table 12**). The first element from the La group is Er (8th) with a LC_{50} about ten times higher than Ir.

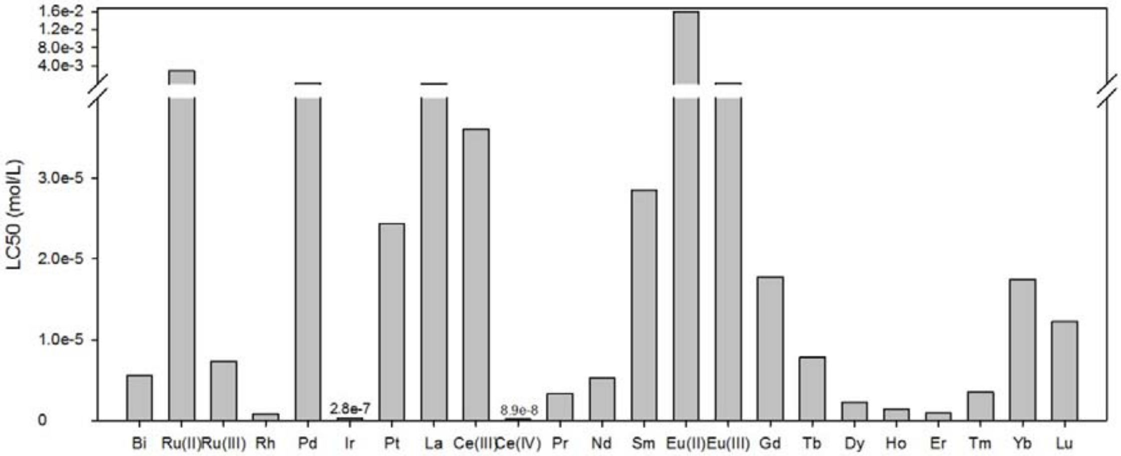

Figure 15: Predicted metal concentrations causing 50% mortality of *C. elegans*-1.

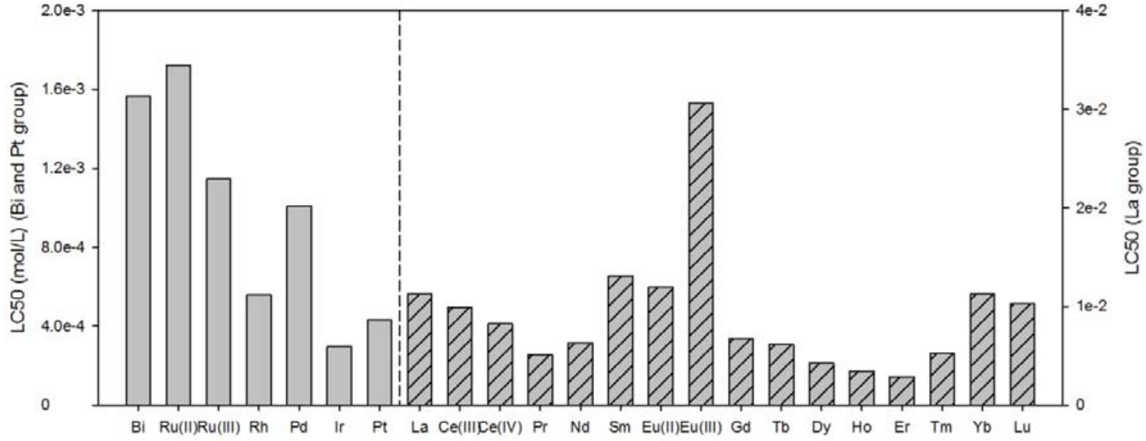

Figure 16: Predicted metal concentrations causing 50% mortality of *C. elegans*-2.

Table 12: Toxicity ranking of the first ten elements towards nematodes (1: most toxic element).

	1	2	3	4	5	6	7	8	9	10
C. elegans-1	Ce(IV)	Ir	Rh	Er	Ho	Dy	Pr	Tm	Nd	Bi
C. elegans-2	Ir	Pt	Rh	Pd	Ru(III)	Bi	Ru(II)	Er	Ho	Dy

2.3.1.8 Crustaceans

Parameters (a_{0-4}) to model the toxicity of our studied metals towards crustaceans are available for short- and long-term exposures (**Table 5**).

Short-term exposure

Metal concentrations leading to the death of 50% of the crustaceans after an exposure period of 48 h were modelled for *Daphnia magna* with two series of a_{0-4} parameters, called *D. magna*-1 and -2 (**Table 5**) and *Daphnia hyalina* (**Figures 17 to 19**). **Bismuth** is predicted to be the most toxic metal for both *D. magna*-1 and -2 with LC_{50} values of 5.4 x 10^{-8} M and 3.6 x 10^{-6} M, respectively, whereas Bi is in 2nd place in the toxicity ranking for *D. hyalina* (LC_{50}=7.1 x 10^{-9}M), for which the most toxic element is **Eu(III)** (LC_{50} = 2.2 x 10^{-9} M). Europium(III) is also predicted to be among the more toxic elements for *D. magna* with a 2nd (LC_{50}=2.2 x 10^{-7} M) and 6th place for the data series 1 and 2, respectively. Platinum is the second most lethal element for *D. magna-2* with a LC_{50} of 1.1 x 10^{-5} M. The third element in the toxicity ranking table is Yb for *D. magna-1* (LC_{50}=7.6 x 10^{-7} M) and *D. hyalina* (LC_{50}=1.5 x 10^{-8} M), whereas it is Ru(II) for *D. magna-2* (LC_{50}=1.2 x 10^{-5} M). Iridium and Sm are common elements present among the ten most toxic elements for the three daphnids (**Table 13**).

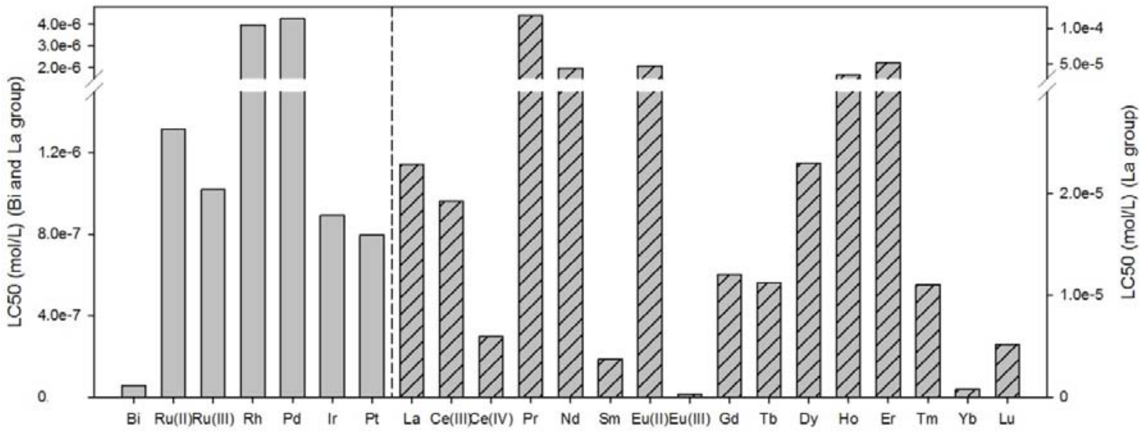

Figure 17: Predicted metal concentrations causing 50% mortality of *D. magna*-1.

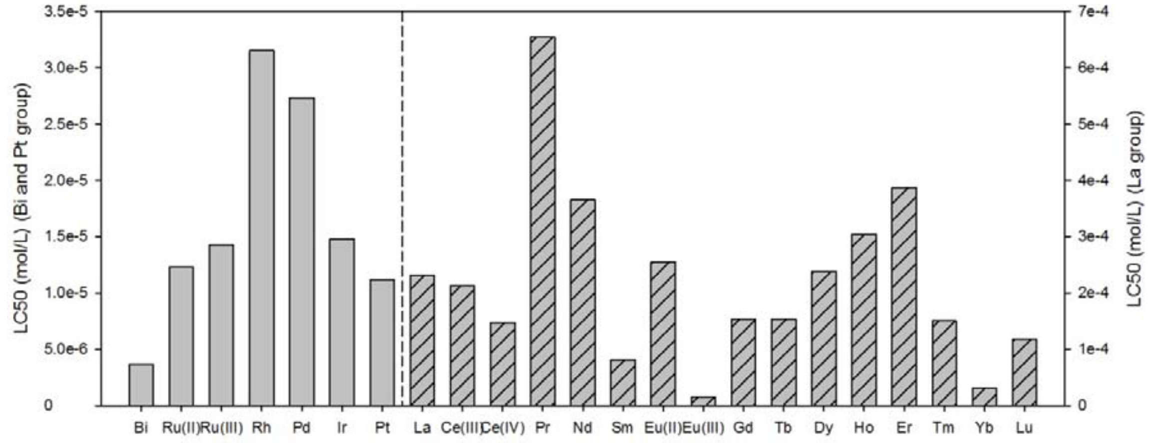

Figure 18: Predicted metal concentrations causing 50% mortality of *D. magna*-2.

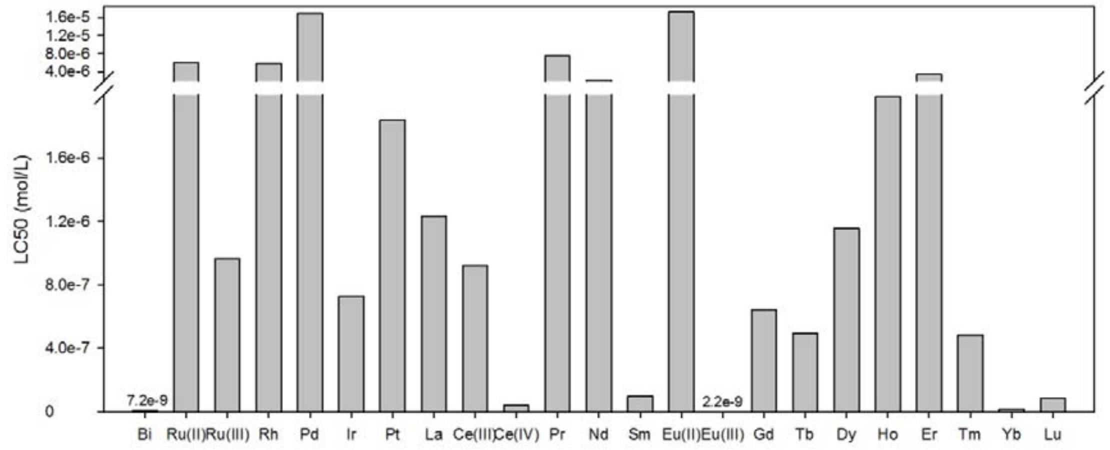

Figure 19: Predicted metal concentrations causing 50% mortality of *D. hyalina*.

Table 13: Toxicity ranking of the first ten elements towards crustaceans in short-term exposures (1: most toxic element).

	1	2	3	4	5	6	7	8	9	10
D. magna-1	Bi	Eu(III)	Yb	Pt	Ir	Ru(III)	Ru(II)	Sm	Rh	Pd
D. magna-2	Bi	Pt	Ru(II)	Ru(III)	Ir	Eu(III)	Pd	Yb	Rh	Sm
D. hyalina	Eu(III)	Bi	Yb	Ce(IV)	Lu	Sm	Tm	Tb	Gd	Ir

Chronic exposure

Three chronic toxicity endpoints (RI_{16}, RI_{50} and LC_{50}) in *Daphnia magna* were predicted with the present model (**Figures 20 to 22**). Similar to the case for short-term exposure, **Bismuth** and **Eu(III)** are also predicted to be the most toxic elements for *D. magna* for longer exposure times. Reduction of daphnid reproduction by Bi is predicted at 2.8×10^{-8} M (RI_{16}) and 4.9×10^{-8} M (RI_{50}) whereas the predicted LC_{50} value is 1.8×10^{-7} M. Impacts of Eu(III) on the daphnids are predicted for concentrations of 1.4×10^{-7} M (RI_{16}), 2.1×10^{-7} M (RI_{50}) and 4.0×10^{-7} M (LC_{50}). Depending on the toxicity endpoints, the next metals in the toxicity ranking table are Ir, Pt, Ru(III), Yb and Pt (**Table 14**).

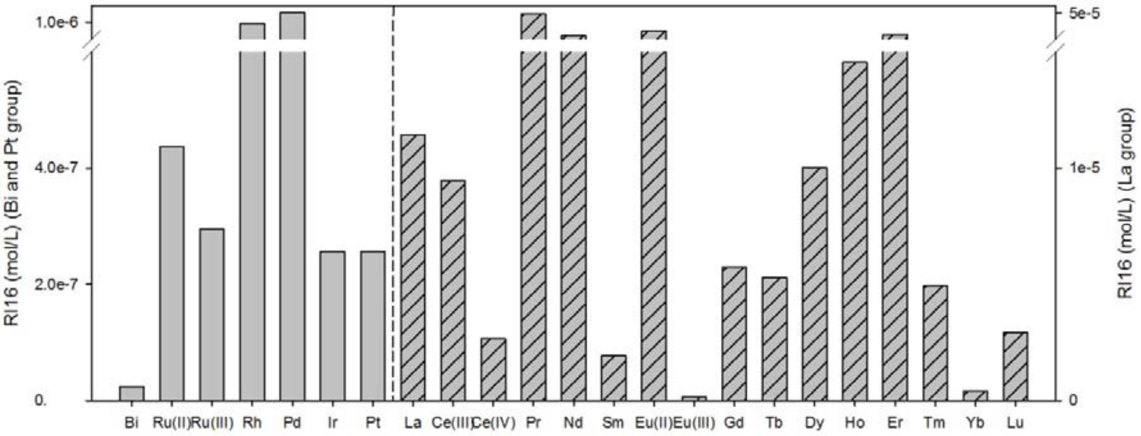

Figure 20: Predicted metal concentrations reducing *D. magna* reproduction by 16%

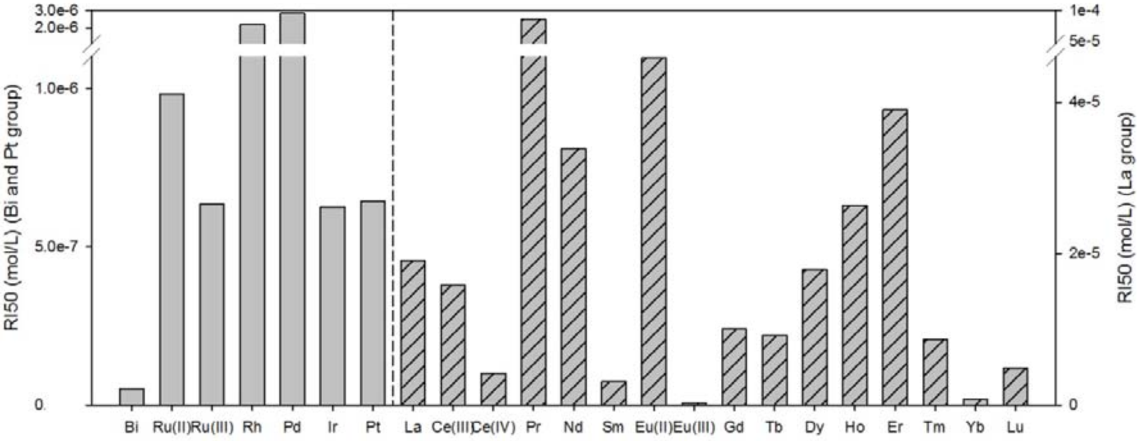

Figure 21: Predicted metal concentrations reducing *D. magna* reproduction by 50%

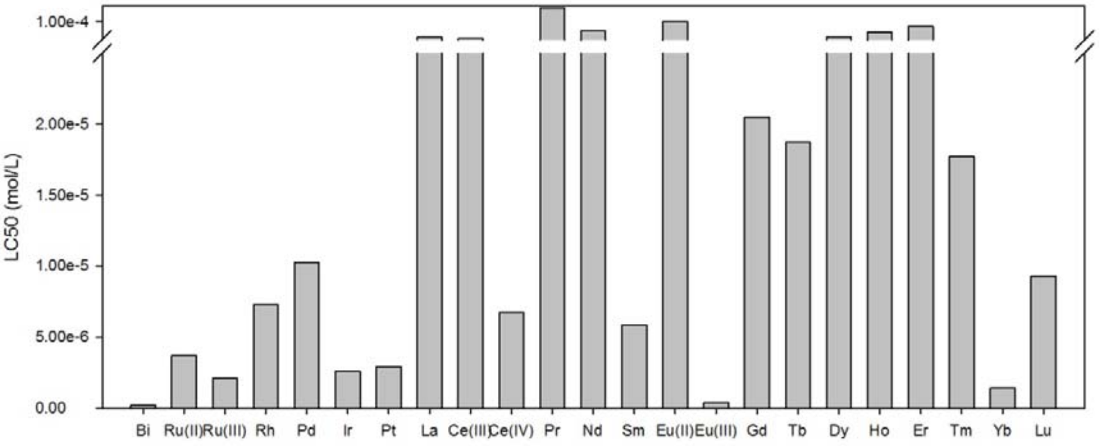

Figure 22: Predicted metal concentrations causing 50% mortality of *D. magna*

Table 14: Toxicity ranking of the first ten elements towards crustaceans in long-term exposure (1: most toxic element)

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
D. magna RI_{16}	Bi	Eu(III)	Ir	Pt	Ru(III)	Yb	Ru(II)	Rh	Pd	Sm
D. magna RI_{50}	Bi	Eu(III)	Ir	Ru(III)	Pt	Yb	Ru(II)	Rh	Pd	Sm
D. magna LC_{50}	Bi	Eu(III)	Yb	Ru(III)	Ir	Pt	Ru(II)	Sm	Ce(IV)	Rh

2.3.1.9 Fish

The elements of the La group are predicted to be more toxic for the rainbow trout than those of the Pt group and Bi (**Figure 23; Table 15**). The predicted TL_{50} values are very low for the first ten elements, ranging from 2.6 x 10^{-13} M (1st; **Lu)** to 6.3 x 10^{-12} M (10th; Tb). The most toxic element of the Pt group has a modelled TL_{50} of 5.5 x 10^{-7} M (Pt, 18th). Bismuth is 17th with a TL_{50} of 4.2 x 10^{-7} M.

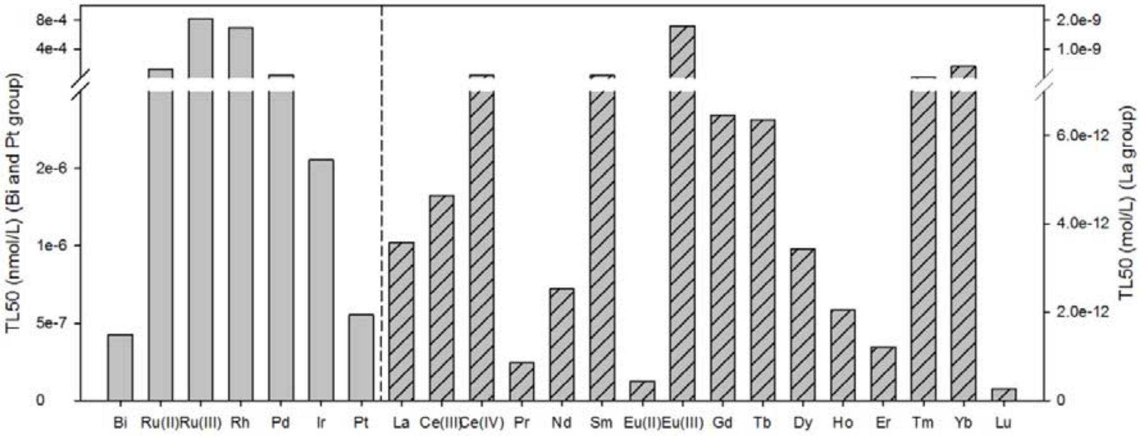

Figure 23: Predicted metal concentrations causing 50% mortality of rainbow trout (*Oncorhynchus mykiss*)

Table 15: Toxicity ranking of the first ten elements towards rainbow trout (1: most toxic element).

	1	2	3	4	5	6	7	8	9	10
O. mykiss	Lu	Eu(II)	Pr	Er	Ho	Nd	Dy	La	Ce(III)	Tb

2.3.1.10 General ranking

The estimated toxicity of our little-studied metals towards aquatic organisms with the Wolterbeek and Verburg model depends on the organism, the exposure time and the measured effect. In other words, the ranking of an individual metal varies from one combination of toxicological endpoint and test organism to another. In order to conclude which metals could potentially be problematic among those studied, an average position for each metal has been calculated (**Table 16**).

Overall, the elements of the Pt group and Bi are predicted to be more toxic than those of the La group. **Iridium** is the metal with the lowest average position (i.e., the most toxic), which reflects the various toxicity rankings (**Tables 6-15**) since Ir is present in 19 out of 23 rankings. Two enzymes (*fish carbonic anhydrase* and *lipase*), protozoa and fish seem to be less sensitive to Ir than are the other tested organisms. The second most toxic element is **Pt,** which is positioned 16 times out of 23 among the ten most toxic metals. In addition to the less sensitive endpoints mentioned for Ir, *D. hyalina* and *C. elegans*-1 are predicted to be less impacted by Pt than the other test organisms. Finally, **Bi** is predicted to be the third most toxic element for aquatic organisms and is present 16 times out of 23 in the toxicity ranking tables. As in the case of Ir and Pt, enzymes, protozoa and rainbow trout are predicted to be the least sensitive targets for Bi.

Table 16: Average metal position in the toxicity ranking tables (Tables 6-15) with minimum and maximum values.

Ranking	Element	Average position	SD	minimum	maximum
1	Ir	7.1	5.9	1	19
2	Pt	7.7	6.5	1	18
3	Bi	8.7	7.5	1	22
4	Rh	10.1	6.9	1	23
5	Ru(III)	10.3	7.5	1	23
6	Pd	11.2	6.4	2	22
7	Ru(II)	11.3	7.7	2	23
8	Er	11.3	8.1	1	22
9	Ho	11.4	6.5	3	21
10	Dy	11.6	4.8	4	18
11	Tm	11.9	2.4	7	17
12	Tb	12.2	2.5	6	15
13	Lu	12.3	6.0	1	22
14	Yb	12.5	6.5	3	22
15	Ce(IV)	12.7	5.3	1	23
16	Gd	12.9	2.4	8	17
17	Eu(III)	13.2	8.5	1	23
18	Pr	13.8	8.6	1	23
19	Sm	14.0	4.8	6	22
20	Nd	14.5	6.0	4	22
21	Eu(II)	14.8	8.5	1	23
22	Ce(III)	14.8	3.6	8	20
23	La	15.5	4.5	7	21

2.3.2 Kinraide model

As described in section 2.2, the Kinraide (2009) model uses a consensus scale of softness and toxicity to describe metal toxicity. The main difference with the Wolterbeek and Verburg (2001) model is that the Kinraide approach does not provide an estimated toxic concentration for each metal; rather, it provides an overall toxicity ranking of the metals. Based on equations (4) and (5) and the needed metal characteristics (**Table 3**), the consensus scale of softness and toxicity have been calculated for the elements of interest (**Table 17**).

The elements of Pt group are predicted to be more toxic than those of the La group due to a higher softness parameter. Bismuth is also estimated to be more toxic than metals form the La group.

Table 17: Calculated consensus scale of softness (σ_{con}), of toxicity (T_{con}) and toxicity ranking (1: most toxic) of the studied metals.

Element	σ_{con}	T_{con}	**Ranking**
Pt	1.54	1.876	**1**
Pd	0.95	1.221	**2**
Ir	1.49	1.124	**3**
Ru (II)	0.69	0.923	**4**
Rh	0.83	0.728	**5**
Ru(III)	0.59	0.588	**6**
Bi	0.59	0.587	**7**
Ce(IV)	0.88	0.378	**8**
Lu	-0.33	0.037	**9**
Dy	-0.45	-0.034	**10**
Pm	-0.45	-0.035	**11**
Eu(III)	-0.45	-0.037	**12**
Er	-0.46	-0.042	**13**
Sm	-0.46	-0.044	**14**
Tb	-0.46	-0.044	**14**
Nd	-0.47	-0.045	**16**
Ho	-0.47	-0.049	**17**
Tm	-0.48	-0.054	**18**
Pr	-0.49	-0.057	**19**
Gd	-0.51	-0.074	**20**
Ce(III)	-0.49	-0.058	**21**
La	-0.53	-0.081	**22**
Yb	-0.55	-0.095	**23**
Eu(II)	-0.73	-0.666	**24**

2.3.3 Model comparisons and identification of the most problematic elements

The use of the models developed by Wolterbeek and Verburg (2001) and Kinraide (2009) allowed us to classify our little-studied elements as a function of their potential toxicity towards aquatic organisms (**Tables 16, 17**). Both models predict that the elements of the Pt group as well as Bi should be more toxic than the elements of the La group. Iridium and Pt are expected to be the most potent metals among the studied elements, both ranking among the three most toxic metals for both models; Bi falls third in the Wolterbeek and Verburg ranking, whereas the second rank in the Kinraide scale is occupied by Pd. Thus, the four main elements that have been identified as potentially problematic for aquatic ecosystems on the basis of their inherent toxicity are **Pt**, **Ir**, **Pd** and **Bi**.

In order to get a better picture of the potential toxicity of these four selected elements, we have compared their estimated toxicity with that of three "common" metals (i.e., Cd, Hg and Pb). To this end, the ion characteristics of these "common" metals were compiled **(Table 18)** and applied in equations 2, 4 and 5. The results obtained with the Wolterbeek and Verburg model are presented in **Table 19**, to which we have added Pt, Ir, Pd and Bi to facilitate the comparisons.

Our selected elements were found to be more toxic towards enzymes, bacteria, fungi, protozoa and nematodes than Cd, Hg and Pb. In only one of the eight enzymatic studies (*fish acetylchlolinesterase*) was one of the "common" metals (i.e. Pb) found to be more toxic than Bi, Pd, Ir and Pt, with an I_{50} value (5.1×10^{-4} M) close to those of Bi (6.6×10^{-4} M) and Pt (9.0×10^{-4} M). In contrast, Pt is predicted to be the most toxic element in six out of the eight enzymatic tests. Its inhibitory concentrations are very similar to those of Hg and Pb for *glutamic oxalacetic transaminase* and *lactic dehydrogenase*, and to that for Hg alone in *lipase*, whereas it is ten times lower than those of the three "common" metals for *ribonuclease*. Iridium is also predicted to be more toxic than Cd, Hg and Pb towards *fish carbonic anhydrase* with an I_{50} value close to that of Hg. In *V. fischeri* M and N, Pt and Ir, respectively, are also predicted to be more toxic than Cd, Hg and Pb. In *V. fischeri* M, the EC_{50} of Pt (3.2×10^{-6} M) is of the same order of magnitude as the EC_{50} of Pb (6.5×10^{-6} M), whereas in *V. fischeri* N, Ir is found to be much more toxic (7.0×10^{-13} M) than Hg (1.8×10^{-8} M), the most toxic of the "common" metals. Iridium is also predicted to be more toxic than Hg (most toxic element of the "common" metals) towards fungi (~ 10 x) and nematodes (~ 10 to 100 x), whereas Pd is predicted to be more toxic (~ 10 x) than Hg (most toxic "common" element) in protozoa.

In algae, copepods and crustaceans, Pb is found to be more toxic than the selected little-studied metals. However, its predicted toxic concentrations are very close to those of Bi. For example, in algae, the EC_{50} of Pb is 3.0×10^{-8} M and the EC_{50} of Bi is 3.7×10^{-8} M. In the copepod *C. abyssorum*, the LC_{50} of Pb is 6.0×10^{-6} M and LC_{50} of Bi is 6.2×10^{-6} M. This tendency is also observed in crustaceans. In fish, Cd, Hg and Pb are predicted to be more toxic than the selected little-studied elements.

A similar exercise was carried out for the Kinraide (2009) model. The consensus softness and toxicity values for the "common" metals were calculated according to equation (5) and are presented in **Table 20**. The values of our selected metals are included in the table to facilitate comparisons. Platinum is predicted to be the most toxic element among all the studied metals, followed by Hg, Pd and Ir.

Table 18: Compilation of the ion characteristics used in equations (2), (4) and (5) for the three "common" metals (Cd, Hg, Pb).

Element	Z	AR (Å)[a,b]	AW (g·mol^{-1})[c]	ρ_{Metal} (g·cm^{-3})[c]	ΔE^0 (V)[c]	IP (eV)[c]	Xm[a,c]	E^0 (V)[c]	First Ip (eV)[c]
Cd	2	1.48	112.4	8.65	-0.403	16.9083	1.69	-0.403	8.9938
Hg	2	1.48	200.59	13.7	0.851	18.756	1.9	0.851	10.4375
Pb	2	1.54	207.19	11.34	-0.1262	15.0322	1.8	-0.1262	7.41666

[a] Wolterbeek and Verburg (2001); [b] Cordero et al. (2008); [c] Lide (2004) – the absolute values of ΔE0 are used in the simulations ; [d] The symbol "-" means that no data were found.

Table 19: Estimated toxic metal concentrations (M) calculated with the Wolterbeek and Verburg (2001) model.

	Bi	**Pd**	**Ir**	**Pt**	**Cd**	**Hg**	**Pb**
Enzymes							
fish carbonic anhydrase	6.8E-05	4.9E-04	5.9E-05	8.6E-05	4.3E-04	7.9E-05	1.3E-04
glutamic oxalacetic transaminase	2.4E-03	3.9E-04	4.1E-04	1.3E-04	3.3E-03	6.5E-04	8.9E-04
lactic dehydrogenase	6.4E-04	6.7E-04	3.6E-04	1.6E-04	1.2E-03	3.0E-04	2.7E-04
fish acetylchlolinesterase	6.6E-04	2.7E-03	1.0E-03	9.0E-04	1.1E-03	5.8E-04	5.1E-04
ribonuclease-I$_1$	7.1E-04	2.7E-05	4.2E-05	1.5E-05	5.9E-04	1.2E-04	3.4E-04
ribonuclease-I$_{50}$	5.9E-03	4.3E-04	3.0E-04	2.4E-04	9.2E-03	1.6E-03	7.9E-03
lipase-I$_1$	6.3E-05	6.0E-05	1.4E-05	5.6E-06	5.5E-05	7.3E-06	2.1E-05
lipase-I$_{50}$	6.0E-04	9.6E-04	7.6E-05	4.3E-05	7.4E-04	4.8E-05	3.4E-04
Bacteria							
V. fischeri M	4.8E-06	6.2E-06	3.5E-06	3.2E-06	4.0E-05	1.0E-05	6.5E-06
V. fischeri N	2.3E-09	9.6E-09	7.0E-13	1.9E-10	1.6E-04	1.8E-08	4.2E-05
Algae							
S. capricornutum	3.7E-08	3.2E-07	1.3E-07	9.9E-08	2.9E-07	1.1E-07	3.0E-08
Fungi							
A. tenuis	1.1E-05	9.5E-06	2.7E-06	6.7E-06	1.5E-04	2.8E-05	6.9E-05
B. fabea	7.4E-06	1.1E-05	5.0E-06	8.7E-06	6.6E-05	2.2E-05	2.4E-05
Protozoa							
S. ambiguum-24h	1.7E-04	3.0E-06	4.2E-06	6.3E-06	7.4E-05	3.5E-05	4.8E-04
S. ambiguum-48h	1.8E-04	3.3E-06	4.6E-06	6.9E-06	7.9E-05	3.8E-05	5.1E-04
Copepods							
C. abyssorum	6.2E-06	1.4E-04	3.8E-05	4.0E-05	3.9E-05	2.0E-05	6.0E-06
E. padonus	2.4E-06	9.0E-05	4.6E-05	3.5E-05	8.7E-06	1.0E-05	1.2E-06
Nematodes							
C. elegans-1	5.6E-06	1.7E-04	2.8E-07	2.4E-05	6.4E-03	7.6E-05	5.7E-03
C. elegans-2	1.6E-03	1.0E-03	3.0E-04	4.3E-04	8.6E-03	1.4E-03	4.3E-03
Crustaceans							
short-term							
D. magna-1	5.5E-08	4.3E-06	8.9E-07	8.0E-07	5.1E-07	2.6E-07	3.8E-08
D. magna-2	3.6E-06	2.7E-05	1.5E-05	1.1E-05	1.2E-05	7.8E-06	2.4E-06
D. hyalina	7.2E-09	1.7E-05	7.3E-07	1.8E-06	2.0E-07	1.3E-07	1.4E-08
long-term							
D. magna RI$_{16}$	2.3E-08	1.2E-06	2.6E-07	2.6E-07	2.5E-07	1.1E-07	2.1E-08
D. magna RI$_{50}$	4.9E-08	2.8E-06	6.2E-07	6.4E-07	4.6E-07	2.4E-07	4.4E-08
D. magna LC$_{50}$	1.8E-07	1.0E-05	2.6E-06	2.9E-06	1.3E-06	9.3E-07	1.7E-07
Fish							
O. mykiss	4.2E-07	4.6E-05	1.6E-06	5.5E-07	3.6E-07	5.0E-08	5.9E-08

Table 20: Calculated consensus scale of softness (σ_{con}), of toxicity (T_{con}) and toxicity ranking (1: most toxic) of the "common" and the predicted most toxic little-studied metals.

Element	σ_{con}	T_{con}	Ranking
Pt	1.54	1.876	**1**
Hg	1.16	1.454	**2**
Pd	0.95	1.221	**3**
Ir	1.49	1.124	**4**
Pb	0.46	0.668	**5**
Bi	0.59	0.587	**6**
Cd	0.17	0.349	**7**

3 Speciation predictions – methods and results

3.1 Brief literature review

To estimate the inorganic speciation of the metals of interest, one first needs the complexation constants for the metal and the dominant inorganic ligands present in natural waters, e.g. HO^-, Cl^-, SO_4^{2-}, HCO_3^- and CO_3^{2-}, as extrapolated to an ionic strength I=0 (i.e., at infinite dilution). To that end, one of our first challenges was to identify the stable oxidation states of the little-studied elements in aqueous solutions. Lanthanides are predominantly trivalent with the exception of cerium and europium, which can exist as Ce(IV) and Eu(II) (Elderfield and Greaves 1982). Bismuth is also predominantly trivalent as are rhodium and iridium (Filella 2010; Richens 1997). Ruthenium exists as Ru(II) and Ru(III) whereas platinum and palladium are mainly present in the oxidation state (II) (Richens 1997). Osmium is a very complex element that has no characterised cationic aquo ions (Richens 1997). These oxidation states were used to guide the compilation of the relevant stability constant data for the metal complexes with inorganic ligands.

Once compiled, the stability constant data can be used as input to a chemical equilibrium model[2]. Such models take into account the various reactions in which metal cations can participate. Examples include complexation reactions, oxidation and reduction reactions, and precipitation reactions:

complexation reactions, e.g.

$$Dy^{3+} + HO^{-1} \rightleftarrows DyOH^{2+}$$

precipitation reactions, e.g.

$$Dy^{3+} + 3HO^{-1} \rightleftarrows Dy(OH)_3(s) \downarrow$$

oxidation-reduction reactions, e.g.

$$Fe^{2+} - e^{-1} \rightleftarrows Fe^{3+}$$

In addition, the models can be set up to take into account gas exchanges between the atmosphere and the aqueous solution:

gas exchanges, e.g.

$$CO_2 + H_2O \rightleftarrows H_2CO_3 \rightleftarrows H^+ + HCO_3^{-1}$$

The models do not consider just one cation, but rather are able to solve the equilibrium equations simultaneously for <u>all</u> the cations and anions in solution. The process of solving chemical equilibrium problems involves the following steps (Schecher and McAvoy 2001): (i) selection of the chemical components that will define the system; (ii) definition of the chemical species that can be formed by these components; (iii) setting the total concentrations of the individual components; and (iv) solving the simultaneous equilibria. To perform these calculations, the model needs the equilibrium constant for each of the reactions to be considered; for each model, these constants are normally supplied as part of a default thermodynamic database that comes with the software package. Normally these

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[2] This description of chemical equilibrium models has been adapted from INRS-ETE (2010).

constants are given for dilute solution (I=ionic strength → 0, T=298 K), and the model then "adjusts" the constants to take into account the true ionic strength and temperature of the solution and the effect of the ionic strength and temperature on the activity coefficients of the cations and ions present in solution. To run the model, one must provide the total concentrations of each cation and anion, including those that do not interact with the metal of interest but nevertheless affect the overall ionic strength of the solution (e.g., Ca, Mg, Na, K; Cl, SO_4, HCO_3^{-1}, CO_3^{-2}). In addition, one normally fixes the pH, the redox potential and the temperature of the solution. Note that 25 °C is the reference temperature used for the thermodynamic data; choosing a temperature other than 25 °C would require having ΔH values for the various (precipitation) reactions – these latter data are not widely available.

For a given aqueous solution, each model should in principle yield the same results. When this is not the case, the differences in predictions from one model to another can normally be traced to differences in the underlying thermodynamic data (e.g., the formation constant for a particular complexation reaction may differ from one model to another). In addition, the models may differ in how they correct the equilibrium constants as a function of ionic strength; for concentrated solutions these differences may yield different equilibrium concentrations (e.g., relatively simple ionic strength correction models such as the Davies equation should in principle only be applied to dilute waters). Finally, it is important to emphasize that these models are equilibrium models (i.e., they do not consider the kinetics of the various reactions). This constraint is usually ignored for complexation reactions (which are usually relatively fast for monovalent and divalent metals, with the notable exception of some elements such as Pt and Pd).

There is no shortage of chemical models designed to calculate metal speciation (Turner 1995). The available models differ in how the water quality data are entered, how the data are processed, and how the results of the equilibrium calculations are presented. More importantly, the default thermodynamic data used for the calculations (i.e., the solubility products and the complexation constants that are included in the model's database) may differ from one model to another. We have used Visual MINTEQ (version 3.0 beta); http://www2.lwr.kth.se/English/OurSoftware/vminteq/download.html) for the present study. The main advantages of this model are that it already includes almost all the lanthanide elements in its default data base (which is not the case for MINEQL+ (Schecher and McAvoy 2001)), and that it offers the possibility of running simulations of the interactions of these trace elements with natural organic matter (which is not presently the case for WHAM VI (Centre for Hydrology and Ecology 2001)).

3.2 Chemical equilibrium calculations for two typical Canadian surface waters

The simulations were run on two typical Canadian surface waters. The first test water corresponded to the average composition of Lake Ontario water (Dove 2009; Borgmann et al. 2005), whereas the second test water was chosen to represent the much more dilute waters draining off the Canadian Precambrian Shield, e.g., Quebec hydrographic region 7 (Bobée et al. 1977) – see **Table 21**. The trace elements of interest were all added at an arbitrary total concentration of 10^{-7} M; this concentration represents a compromise between the concentrations likely to be found in surface waters (e.g., 10^{-8} to 10^{-9} M or lower) and those that are likely to used in toxicity tests (10^{-5} to 10^{-6} M). Note that this choice of 10^{-7} M will not affect the relative distribution of inorganic metal species, since the inorganic ligands are all present in considerable excess (Morel and Hering 1993).

The initial simulations were run with the Visual MINTEQ default database; the following elements do not appear in this default database – Ir, Os, Pt, Ru, Rh (Platinum Group); Ce(IV), Eu(II) and Pm (Lanthanides).

The simulations were run in the absence of natural organic matter (yielding the inorganic speciation of the elements), and then in the presence of natural organic matter (with the Nica-Donnan subroutine, the default ratio of DOC : active DOM of 1:1.65, and the assumption that this active DOM was 100% fulvic acid. Note that these simulations were run in the mode where precipitation of all inorganic solids was prohibited, with the exception of $Fe(OH)_3(s)$ as ferrihydrite and $Al(OH)_3(s)$ as amorphous aluminum trihydroxide.

Table 21: Chemical composition of the typical surface waters used to model the speciation of the elements of interest.

Water quality parameter	Lake Ontario Water[a]	Canadian Shield Water[b]
Ca	9.22×10^{-4} M	5.00×10^{-5} M
Mg	3.55×10^{-4} M	2.06×10^{-5} M
Na	5.70×10^{-4} M	4.78×10^{-5} M
K	4.22×10^{-5} M	1.03×10^{-5} M
Cl	7.02×10^{-4} M	3.39×10^{-5} M
SO_4	3.21×10^{-4} M	3.13×10^{-5} M
F	2.50×10^{-6} M	2.50×10^{-6} M
dissolved inorganic carbon	open to the atmosphere	open to atmosphere
pH	8.20	6.30
Al	5.46×10^{-7} M	2.00×10^{-6} M
Fe	4.81×10^{-7} M	1.00×10^{-6} M
dissolved organic carbon	1.9 mg $C \cdot L^{-1}$	10 mg $C \cdot L^{-1}$

[a] Data from Borgmann et al. (2005); [b] data from Bobée et al. (1977).

In parallel with the simulations run with the Visual MINTEQ default database, we screened the available geochemistry databases (Martell and Smith 2004; Academic Software 2001). **Table 22** represents a summary of the availability of stability constants for the inorganic complexes. The complexation constants of the lanthanides with OH^-, Cl^-, HCO_3^- and CO_3^{-2} are almost all available, except for Eu(II) for which no data could be retrieved. Binding constants for the possible chloro-complexes of Ce^{+4}, Tb^{+3} and Dy^{+3} are missing, as well as those for the binding of HCO_3^-, CO_3^{-2} and SO_4^{-2} with Pm^{+3}. In the case of bismuth and elements from the Pt group, constants are available for hydroxo- and chloro-complexes but could not be found for the carbonato-, sulphato- and fluoro-metal species. No data were found for Os or Ir. The complexation constants between the metals and the dominant inorganic ligands present in natural waters (i.e., hydroxide, chloride, carbonate, sulphate, fluoride) have been compiled in **Appendix 2** and compared with the default constants in Visual MINTEQ .

Table 22: Existence of stability constants for the complexes formed between the elements of interest and the dominant inorganic ligands in natural waters («√» indicate available data; «-» indicates that no data were found).

Elements	**OH^-**	**Cl^-**	**HCO_3^-**	**CO_3^{2-}**	**SO_4^{2-}**	**F^-**
Bi^{+3}	√	√	-	-	-	-
Ru^{+2}/ Ru^{+3}	-	√	-	-	√ (Ru^{+2})	-
Rh^{+3}	√	√	-	-	-	-
Pd^{+2}	√	√	-	-	√	-
Os	-	-	-	-		
Ir^{+3}	-	-	-	-	-	-
Pt^{+2}	√	√	-	-	-	-
La^{+3}	√	√	√	√	√	√
Ce^{+3}/Ce^{4+}	√	√ (Ce^{+3})	√	√	√	√ (Ce^{+3})
Pr^{+3}	√	√	√	√	√	√
Nd^{+3}	√	√	√	√	√	√
Pm^{+3}	√	√	-	-	-	√
Sm^{+3}	√	√	√	√	√	√
Eu^{+2}/Eu^{+3}	√ (Eu^{+3})	√ (Eu^{+3})	√ (Eu^{+3})	√ (Eu^{+3})	√ (Eu^{+3})	√ (Eu^{+3})
Gd^{+3}	√	√	√	√	√	√
Tb^{+3}	√		√	√	√	√
Dy^{+3}	√	-	√	√	√	√
Ho^{+3}	√	√	√	√	√	√
Er^{+3}	√	√	√	√	√	√
Tm^{+3}	√	√	√	√	√	√
Yb^{+3}	√	√	√	√	√	√
Lu^{+3}	√	√	√	√	√	√

3.3 Calculated speciation of Bi, the lanthanides and the platinum group elements in two typical Canadian surface waters

The results of the chemical equilibrium calculations for Bi^{+3} and for Pd^{+2} indicate that the speciation of these two elements is relatively unaffected by the differences in water quality between Lake Ontario and the Canadian Shield (**Tables 23** to **26**). For both elements, the hydroxo-complexes are predicted to be the dominant species in solution ($Bi(OH)_3^0$ and $PdOH^+$), and this result is insensitive to the differences in pH between the two test waters. It should be noted, however, that neither the Visual MINTEQ default database nor the other thermodynamic databases (IUPAC; NIST) include constants for carbonate complexation of either Bi^{+3} or Pd^{+2}. In addition, the Visual MINTEQ default database does not include binding constants for these elements with DOM (see the discussion of DOM-metal interactions below for the lanthanides).

The results of the speciation calculations are much more complete for the lanthanides than for the platinum group elements. Given their position in the periodic table of the elements (where the changes in atomic weight from Ce to Lu are relatively unimportant, compared to the earlier periods), and their high positive charge (the simulations were run for the trivalent forms), it is not surprising that for a given water composition, all the lanthanides show quite similar speciation in solution. For example, for Lake Ontario water in the absence of natural organic matter the carbonate complexes account for 95 to 98% of the dissolved metal (**Table 23**), and the proportion of free M^{+3} is consistently less than 2%. The addition of organic carbon (1.9 mg $C{\cdot}L^{-1}$) only affects two of the lanthanides (Eu^{+3} and Dy^{+3}) (**Table 24**); for these cations, the contribution of the carbonate complexes drops to 25% (Eu^{+3}) or <1% (Dy^{+3}), but for all the other lanthanides the carbonate complexes remain the dominant species in solution.

The lanthanide results for the Canadian Shield water contrast markedly with those for Lake Ontario (compare **Tables 23** and **25**, **Tables 24** and **26**), but again all the lanthanides show similar speciation trends. In the absence of natural organic matter, the free M^{+3} cation is the dominant species (70 to 87%; **Table 25**) and the contribution of the carbonate complexes is less than 4%. This result reflects the lower pH (6.3 versus 8.2) and the correspondingly lower concentration of carbonate and bicarbonate ions in the Canadian Shield waters. The addition of organic carbon (10 mg $C{\cdot}L^{-1}$) has a marked effect on all the lanthanides, the contribution of the free metal ion drops to ≤2%, and the fulvic acid complexes dominate the speciation in solution (>98%; **Table 26**).

To understand the apparent influence of natural organic matter on the predicted speciation of the lanthanides, as calculated with Visual MINTEQ, it is necessary to consider how Visual MINTEQ deals with interactions between DOM and metal cations. The Nica-Donnan subroutine considers two phases, the bulk solution phase and a DOM or humic “gel” phase, and the partitioning between the two phases is governed by a Donnan equilibrium. Within the humic phase, the model further distinguishes between cations that are electrostatically bound to the humic material and cations that are complexed to the humic molecules. In effect, the negative charge of the humic molecules attracts counterions, which accumulate in a diffuse layer close to the surface of the humic molecules. These ions retain their water of hydration and are weakly bound to the humic material by electrostatic forces; ions with the same positive charge bind unselectively to the humic material. In addition, some of these cations (i.e., those with a high affinity for the humic binding sites) will form coordination complexes with the humic molecules, losing at least two molecules of water of hydration in the process; these cations are bound much more strongly to the humic material.

Since the initial Donnan equilibrium is non selective (governed by ion charge only), Visual MINTEQ is able to calculate weak electrostatic binding to DOM for all our little studied elements. However, for the second type of binding (i.e., true metal complexation reactions at the humic surface), the Visual MINTEQ default database has only a limited number of binding constants. For example, among the lanthanide elements, complexation constants are only available for Eu^{+3} and Dy^{+3}. As a result, when DOM is added to Lake Ontario water (compare **Tables 23** and **24**), the only elements for which the calculated speciation changes are Eu^{+3} and Dy^{+3}… **but this is an artefact of the Visual MINTEQ default database.** Given the earlier observation that the inorganic speciation of all the lanthanides follows the same trends, it is highly likely that the DOM-induced changes predicted for Eu^{+3} and Dy^{+3} will also apply to the other lanthanide elements.

At first glance, the speciation results for the lanthanides in Canadian Shield water in the presence of DOM appear very different than those for Lake Ontario water, in that the addition of DOM appears to influence all the lanthanides, not just Eu^{+3} and Dy^{+3} (see **Table 26**). However, these results are somewhat misleading, since the final columns in **Tables 24** and **26** include both metals bound electrostatically and metals complexed with DOM. In effect, the Canadian Shield water is much less mineralized than the lake Ontario water, and the ratio of major cations (Ca^{+2}, Mg^{+2}, Na^{+} and K^{+}) to lanthanides is much lower than in the Lake Ontario water; in addition the DOM concentration is five times higher in the Canadian Shield water. As a result, the diffuse double layer contains a much higher proportion of lanthanides in the Canadian Shield water simulations than in the Lake Ontario simulations. If the weakly bound lanthanides are discounted, then once again only Eu^{+3} (98% Eu-DOM) and Dy^{+3} (>99% Dy-DOM) are significantly affected by the addition of DOM to the Canadian Shield water... but as was the case earlier for Lake Ontario, this result is an artefact of the Visual MINTEQ default database.

Table 23: Calculated inorganic speciation of the elements of interest (%) – Lake Ontario water, no DOM

Metal	**M^{z+}**	**$M(OH)_n$**	**$M(CO_3)_n$**	**$M(Cl)_n$**	**$M(SO_4)_n$**	**$M(X)_n$**
Bi^{+3}	<1	100				
Pd^{+2}	<1	91		9		
La^{+3}	4		93		2	
Ce^{+3}	2		95			2 (PO_4)
Pr^{+3}	1		98			
Nd^{+3}	1		98			
Sm^{+3}	<1		98			
Eu^{+3}	<1		98			
Gd^{+3}	1		97			
Tb^{+3}	<1		98			
Dy^{+3}	<1		99			
Ho^{+3}	<1		99			
Er^{+3}	<1		99			
Tm^{+3}	<1		99			
Yb^{+3}	<1		97			2 (PO_4)
Lu^{+3}	<1		99			

Table 24: Calculated speciation of the elements of interest (%) – Lake Ontario water with DOM

Metal	M^{z+}	$M(OH)_n$	$M(CO_3)_n$	$M(SO_4)_n$	$M(X)_n$	M-DOM [a]
Bi^{+3}	<1	100				<1
Pd^{+2}	<1	91			9 (Cl)	<1
La^{+3}	4	1	94	2		<1
Ce^{+3}	2	1	95	1	1 (PO_4)	<1
Pr^{+3}	1	1	98	1		<1
Nd^{+3}	1	1	98			<1
Sm^{+3}	1	1	98			<1
Eu^{+3}	<1		25			75
Gd^{+3}	<1	1	97		1 (PO_4)	<1
Tb^{+3}	<1	1	98			<1
Dy^{+3}	<1		<1			>99
Ho^{+3}	<1	1	99			<1
Er^{+3}	<1	1	99			<1
Tm^{+3}	<1	1	99			<1
Yb^{+3}	<1	1	97		2 (PO_4)	
Lu^{+3}	<1	1	99			<1

[a] In Visual MINTEQ, inner sphere complexation constants are only available for Eu^{+3} and Dy^{+3}.

Table 25: Calculated inorganic speciation of the elements of interest (%) – Canadian Shield water, no DOM

Metal	M^{z+}	$M(OH)_n$	$M(CO_3)_n$	$M(Cl)_n$	$M(SO_4)_n$	$M(X)_n$
Bi^{+3}	<1	>99				
Pd^{+2}	<1	97		3		
La^{+3}	89	<1	1		10	1 (F)
Ce^{+3}	87	1	1		9	1 (PO_4), 2 (F)
Pr^{+3}	86	1	2		9	2 (F)
Nd^{+3}	85	1	2		10	2 (F)
Sm^{+3}	83	2	2		10	3 (F)
Eu^{+3}	82	3	3		10	3 (F)
Gd^{+3}	81	2	2		9	2 (PO_4) 3 (F)
Tb^{+3}	81	3	2		9	5 (F)
Dy^{+3}	80	4	3		8	5 (F)
Ho^{+3}	80	4	3		8	5 (F)
Er^{+3}	79	4	3		8	6 (F)
Tm^{+3}	77	6	3		7	6 (F)
Yb^{+3}	70	7	4		6	7 (PO_4) 5 (F)
Lu^{+3}	76	7	4		6	6 (F)

Table 26: Calculated speciation of the elements of interest (%) – Canadian Shield water with DOM

Metal	M^{z+}	$M(OH)_n$	$M(CO_3)_n$	$M(SO_4)_n$	$M(X)_n$	M-DOM [a]
Bi^{+3}	<1	100				<1
Pd^{+2}	<1	97			3 (Cl)	<1
La^{+3}	2					98 [b]
Ce^{+3}	2					98
Pr^{+3}	2					98
Nd^{+3}	2					98
Sm^{+3}	2					98
Eu^{+3}	<1					>99
Gd^{+3}	2					98
Tb^{+3}	2					98
Dy^{+3}	<1					>99
Ho^{+3}	2					98
Er^{+3}	2					98
Tm^{+3}	2					98
Yb^{+3}	2					98
Lu^{+3}	2					98

[a] In Visual MINTEQ, inner sphere complexation constants are only available for Eu^{+3} and Dy^{+3}.
[b] Misleading value (outer sphere, electrostatically bound metal) – see text for explanation.

4 Summary and recommendations

4.1 Predicted speciation

The use of chemical equilibrium models to predict metal speciation obviously depends on the availability of reliable thermodynamic data. Stability constants for Bi and the platinum group elements proved to be scarcer than for the lanthanides, and thus the calculated speciation of Bi and the PGEs is not as well constrained as that of the elements in the La group. This is a troubling result, since the PGEs are generally predicted to be more toxic than the lanthanides (see section 4.2). For example, iridium is classified among the most toxic of the studied elements but no thermodynamic constants for its interactions with inorganic ligands could be retrieved and thus its speciation in natural waters could not be predicted.

For the lanthanides, and from an ecotoxicological perspective, the following results seem particularly relevant:

- For Lake Ontario water (with or without DOM) and for all the metals for which thermodynamic complexation data are available, the contribution of the free metal ions to the solution speciation is low (<2%), suggesting that the bioavailability of the metals will also be low under these conditions (due to complexation by carbonate or by DOM). Experimental confirmation of this anticipated protective role of carbonate and DOM would be invaluable , cf. Ng et al. (2011).

- For Canadian Shield water without DOM, the contribution of the free metal ions is much more important and metal bioavailability would be expected to be correspondingly high. However, this case is environmentally unrealistic, since such waters normally include appreciable concentrations of dissolved organic matter.
- For Canadian Shield water with added DOM, the results for the two lanthanides for which complexation constants are available in the Visual MINTEQ database (i.e., Eu^{+3} and Dy^{+3}) suggest that the free ion concentrations would be very low (< 1% of the total dissolved metal). As mentioned earlier, it is highly likely that the other trivalent lanthanides will also be strongly bound to the natural DOM.

4.2 Predicted toxicity

Among the studied elements, the platinum group elements and Bi are predicted to be potentially problematic for aquatic ecosystems; their predicted EC_{50} concentrations are lower than those for recognized environmental contaminants (Pb, Cd, Hg) for bacteria, fungi, protozoa and nematodes. For the other test organisms, Pb is predicted to be the most toxic element. However, its predicted toxic concentration is very similar to that of Bi for algae, copepods and crustaceans (except *D. hyalina*). The lanthanides generally do not rank near the top of the predicted toxicity rankings, but the predicted EC_{50} for rainbow trout with the Wolterbeek and Verburg (2001) model is as low as ca. 10^{-13} M, whereas the predicted EC_{50} for Cd is 5×10^{-8} M.

When considering the predicted toxicity of the little studied elements, it is important to remember that almost all of the Wolterbeek and Verburg (2001) predictions were based on the total metal concentrations to which the various test organism were exposed (only in the studies of the bacterium *Vibrio fischeri* by Newman and collaborators was the free-metal concentration used as the predictor). In addition, for many of the older literature studies, Wolterbeek and Verburg had to rely upon the nominal metal concentrations rather than measured exposure concentrations. In other words, it is highly likely that metal speciation in the original toxicity tests differed from that which would be expected to prevail in natural waters. It would accordingly be unwise to use the results of the simulations with the Wolterbeek and Verburg (2001) model to predict actual toxicity thresholds for natural waters. The toxicity values predicted by the Wolterbeek and Verburg model should clearly not be used for regulatory purposes, but the modelled values can be used to guide future ecotoxicological tests.

4.3 Recommendations

The following recommendations should be considered together with those in the parallel reports submitted on the toxicity of the lanthanides (Ng et al. 2011) and on the geochemistry and toxicity of the platinum group elements (Fortin et al. 2011).

- *For the elements that rank among the most toxic in the Wolterbeek and Verburg (2001) toxicity rankings (see Section 2.3.3), and for which the thermodynamic data base needed for the speciation calculations is incomplete (see Table 22 and Appendix 2), explore the possibility of estimating these constants with a QICAR approach*. Elements in this class would include Bi and the platinum group elements.

- *For the elements that rank among the most toxic in the Wolterbeek and Verburg (2001) toxicity rankings (see Section 2.3.3), verify the speciation predictions in the laboratory.* This recommendation is deceptively simple, since for many of the elements it would first be necessary to develop or adapt the analytical techniques needed to determine their solution speciation.

- *Revisit the toxicity studies used by Wolterbeek and Verburg (2001) to develop their predictive regressions (see Appendix 1) and determine whether metal speciation could be estimated in the original toxicity tests.* If this proves feasible, the Wolterbeek and Verburg "pT" values could be converted from total metal concentrations to free-metal ion concentrations, and then compared to predicted free-metal ion concentrations in the receiving environment.

- *In any future toxicity tests, ensure that metal exposure concentrations are measured (not nominal) and that all necessary water chemistry measurements are performed so as to allow calculations of metal speciation in the exposure solutions.* Note that care should be taken to avoid exceeding the solubility limit of the element of interest (e.g., by modifying the composition of the exposure solution and/or by limiting the total added metal concentration). In planning these toxicity tests, the merits of monitoring bioaccumulation of the element of interest, in addition to the usual toxicity endpoints, should be considered.

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6 Appendices

6.1 Appendix 1

Datasets used by Wolterbeek and Verburg (2001) to construct their toxicity models
(Note: The studies of Lewis et al. (1999) and Williams et al. (1982) were not used in the present project).

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Datasets used by Kinraide (2009) to construct his toxicity model

(Note: Kinraide also used the studies of Tartara *et al*. (1998), McCloskey *et al*. (1996), Lewis *et al*. (1999))

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6.2 Appendix 2

Compilation of the thermodynamic constants available for the interaction of the elements of interest and the inorganic ligands present in natural waters

In parallel with the simulations run with the Visual MINTEQ default database, we screened the available geochemistry data bases (Martell and Smith 2001; Academic Software 2001), compiled the complexation constants between the metals and the dominant inorganic ligands present in natural waters (i.e., hydroxide, chloride, carbonate, sulphate, fluoride) and compared these to the default constants in Visual MINTEQ (pink-coloured cases) (**Table A-2**). Note that in order to facilitate comparisons among databases for a given complex, all the retrieved thermodynamic constants were expressed in a manner similar to that used in the VMINTEQ data base.

Equations defining binding constants between metals and inorganic ligands in Table A-2

$*K1: Me^{z+} + H_2O \Leftrightarrow Me(OH)^{(z-1)} + H^+$	$K1: Me^{z+} + L^- \Leftrightarrow MeL^{(z-1)}$
$*\beta_2 : Me^{z+} + 2H_2O \Leftrightarrow Me(OH)^{(z-2)} + 2H^+$	$K2: MeL^{(z-1)} + L^- \Leftrightarrow MeL^{(z-2)}$
$*\beta_n : Me^{z+} + nH_2O \Leftrightarrow Me(OH)^{(z-n)} + nH^+$	$\beta_2 : Me^{z+} + 2L^- \Leftrightarrow MeL_2^{(z-2)}$
	$\beta_n : Me^{z+} + nL^- \Leftrightarrow MeL_n^{(z-n)}$

Thermodynamic constants between the studied metals and OH^- can be expressed with $*\beta$ or β. These constants are linked by the following equation: $\beta_n = *\beta_n \times K_e$ with $K_e = 10^{-13.997}$.

Table A-2: Thermodynamic constants between the metals and the predominant inorganic ligands present in natural waters.

Note that "Ref 1" refers to the IUPAC database (Academic Software 2001); "Ref 2" corresponds to the NIST database (Martell and Smith 2004).

Bi	***K1**	***β2**	***β3**	***β4**	**Ref**	***K1**	***β2**	***β3**	***β4**
OH$^-$[a,b]	-0.87	-1.38	-2.05	-12.54	**1**	-1.097	-3.474	-8.991	-21.188
	K1	**K2**	**β2**	**β3**		**K1**	**K2**	**β2**	**β3**
Cl$^-$	3.6	5.5	7.1	8.1	**2**	3.6	5.5	7.1	8.1
CO_3^{2-}	-	-	-	-		-	-	-	-
HCO_3^-	-	-	-	-		-	-	-	-
SO_4^{2-}	-	-	-	-		-	-	-	-
F$^-$	-	-	-	-		-	-	-	-

[a,b] Compiled data originally available at I=0.25 M for OH$^-$; default constants in VMINTEQ are calculated values from β constants at I=0.

Ru(II)[a]	**K1**	**K2**	**β2**	**β3**	**Ref**
OH$^-$	-	-	-	-	
Cl$^-$	1.43	-	-	-	**1**
CO_3^{2-}	-	-	-	-	
HCO_3^-	-	-	-	-	
SO_4^{2-}	2.72	-	-	-	**2**
F$^-$	-	-	-	-	

[a] No data are available in VMINTEQ

Ru(III)[a]	**K1**	**K2**	**β2**	**β3**	**Ref**
OH$^-$	-	-	-	-	
Cl$^-$	2.98	1.83	-	-	**1**
CO_3^{2-}	-	-	-	-	
HCO_3^-	-	-	-	-	
SO_4^{2-}	-	-	-	-	
F$^-$	-	-	-	-	

[a] No data are available in VMINTEQ

Rh(III)[a]	***K1**	***K2**	***K3**	***K4**	***K5**	***K6**	***β2**	***β3**	***β4**	***β5**	***β6**	**Ref**
OH$^-$	- 2.34	-	-	-	-	-	-5.47	-9.21	-16.44	-25.86	-36.98	**1**
	K1	**K2**	**K3**	**K4**	**K5**	**K6**	**β2**	**β3**	**β4**	**β5**	**β6**	
Cl$^-$	-	-	-	1.39	0.34	-0.66	-	-	-	-	-	**1**
CO_3^{2-}	-	-	-	-	-	-	-	-	-	-	-	
HCO_3^-	-	-	-	-	-	-	-	-	-	-	-	
SO_4^{2-}	-	-	-	-	-	-	-	-	-	-	-	
F$^-$	-	-	-	-	-	-	-	-	-	-	-	

[a] Compiled data originally available at I=0.1 M for OH$^-$ and as β constants

Pd(II)	***K1**	***K2**	***K3**	***K4**	***β2**	**Ref**	***K1**			
OH^{-}[a]	-1.60	0.10	-	-	-1.49	**1**	-2.79	-	-	-
	K1	**K2**	**K3**	**K4**	**β2**		**K1**	**β2**	**β3**	**β4**
Cl^{-}[b]	5.08	3.475	2.1	0.902	8.56	**1**	6.1	10.7	13.1	15.4
CO_3^{2-}	-	-	-	-	-		**-**	-	-	-
HCO_3^{-}	-	-	-	**-**	**-**		**-**	-	-	-
SO_4^{2-}	-	-	-	-	4.18	**1**	2.2	-	-	-
F^{-}	-	-	-	-	-		**-**	**-**	**-**	**-**

[a] Compiled data originally available as β constants for OH^{-}

Pt(II)	***K1**	***K2**	***β2**	***β3**	***β4**	**Ref**
OH^{-}[a]	-	-	29.9	-	-	**1**
	K1	**K2**	**β2**	**β3**	**β4**	
Cl^{-}	5.54	4.27	9.81	12.61	14.34	**1**
CO_3^{2-}	-	-	-	-	**-**	
HCO_3^{-}	-	-	-	-	**-**	
SO_4^{2-}	-	-	-	-	**-**	
F^{-}	-	-	-	-	**-**	

[a] Compiled data originally available at I indicated as var. for OH^{-}; [b] Compiled data originally available at I=0.5M for Cl^{-}

La(III)	***K1**	***K2**	***β2**	***β3**	***β4**	**Ref**	***K1**	
OH^{-}	-8.81					**1**	-8.81	
	K1	**K2**	**β2**	**β3**	**β4**		**K1**	**β2**
Cl^{-}	-0.82	-	-	-	**-**	**1**	0.53	
CO_3^{2-}	6.98	-	11.86	-	**-**	**2**	6.73	11.3
HCO_3^{-}	-	-	-	-	**-**		12.67	
SO_4^{2-}	3.50	1.85	5.35	-	**-**	**1**	3.64	5.3
F^{-}	2,66	4,47	7,13	-	**-**	**1**	3.6	

Ce(III)	***K1**	***K2**	***β2**	***β3**	***β4**	**Ref**	***K1**	
OH^{-}[a]	-3.13	-	-7.25	-	-	**1**	-8.34	
	K1	**K2**	**β2**	**β3**	**β4**		**K1**	**β2**
Cl^{-}	0.48	-	-	-	**-**	**1**	0.57	
CO_3^{2-}	7.31	-	12.32			**2**	7.06	11.76
HCO_3^{-}	-	-	-	-	**-**		12.64	
SO_4^{2-}	3.48	1.75	5.23	-	**-**	**1**	3.64	
F^{-}	2.90	3.67	6.57	-	**-**	**1**	3.94	

[a] Compiled data originally available as β constants for OH^{-}

Ce(IV)	*K1	*K2	*β2	*β3	*β4	Ref
OH^-[a]	-1.27	0.70	-	-	-	1
	K1	K2	β2	β3	β4	
Cl^-	-	-	-	-	-	
CO_3^{2-}[b]	21.76	8.36	30.77	-	-	1
HCO_3^-	-	-	-	-	-	
SO_4^{2-}[c]	2.6	-0.4	2.2	-	-	1
F^-	-	-	-	-	-	

[a] [c]Compiled data originally available at I indicated as var. for OH^- and for SO_4^{2-}; [b] Compiled data originally available at I=0.01M for CO_3^{2-}

Pr	*K1	*K2	*K3	*β2	*β3	Ref	*K1	
OH^-[a]	-9.80	-3.70	-3.15	-13.5	-16.65	1	-8.32	
	K1	K2		β2	β3		K1	β2
Cl^-	-2.12	-	-	-	-	1	0.57	
CO_3^{2-}	7.48	-	-	12.63	-	2	7.23	12.08
HCO_3^-	-	-	-	-	-		12.58	
SO_4^{2-}	3.58	1.86	-	5.44	-	1	3.64	4.0
F^-[b]	3.71	2.31	-	6.26	-	1	4.05	

[a] *β2 and *β3 were obtained by the addition of *K1 and *K2, and *K1, *K2 and *K3, respectively;[b] Compiled data originally available at I=0.02M for F^-

Nd	*K1	*K2	*β2	*β3	*β4	Ref	*K1	*K2	*β2	*β3	*β4
OH^-[a]	-5.55	-	-11.73	-18.81	-25.51	1	-8.18				-37.388
	K1	K2	β2	β3	β4		K1	K2	β2	β3	β4
Cl^-	0.06	-0.44	-0.38	-	-	1	-	-	-	-	-
CO_3^{2-}	7.53	12.73	-	-	-	2	7.28	-	12.17	-	-
HCO_3^-	-	-	-	-	-		12.61	-	-	-	-
SO_4^{2-}	3.43	1.74	5.17	-	-	1	3.66	-	5.1	-	-
F^-	2.79	3.82	6.61	-	-	1	4.13	-	-	-	-

[a]Compiled data originally available at I=0.1M for OH^-

Pm	*K1	*K2	*β2	*β3	*β4	Ref
OH^-[a]	-3.6	-4.6	-8.2	-	-	1
	K1	K2	β2	β3	β4	
Cl^-[b]	0.7	-	-	-	-	1
CO_3^{2-}	-	-	-	-	-	
HCO_3^-	-	-	-	-	-	
SO_4^{2-}	-	-	-	-	-	
F^-	3.14	-	-	-	-	2

[a]Compiled data originally available as β constants for OH^-;[b]Compiled data originally available at I indicated as var. for Cl^-

Sm	***K1**	***K2**	***β2**	***β3**	***β4**	**Ref**	***K1**		
OH^{-}[a]	-5.63	-	-	-18.77	-26.11	**1**	-7.84		
	K1	**K2**	**β2**	**β3**	**β4**		**K1**	**K2**	**β2**
Cl^{-}	-2.03	-	-	-	**-**	**1**	-	-	-
CO_3^{2-}	-	-	-	-	**-**		7.46	-	12.53
HCO_3^{-}	-	-	-	-	**-**		12.67	-	-
SO_4^{2-}	3.52	1.67	5.19	-	**-**	**1**	3.67	-	5.1
F^{-}	3.15	3.80	6.95	-	**-**	**1**	4.18	-	-

[a]Compiled data originally available at I=0.1M for OH^{-}

Eu(III)	***K1**	***K2**	***β2**	***β3**	***β4**	**Ref**	***K1**		
OH^{-}[a]	-6,76			-18,01	-24,91	**1**	-7.76		
	K1	**K2**	**β2**	**β3**	**β4**		**K1**	**K2**	**β2**
Cl^{-}	2.88	-	-	-	**-**	**1**	0.57	-	-
CO_3^{2-}	7.11	3.45	10.56	-	**-**	**1**	7.48	-	12.63
HCO_3^{-}	5.41	-	7.81	-	**-**	**1**	12.8	-	-
SO_4^{2-}	3.87	1.88	5.75	5.09	**-**	**1**	3.67	-	5.4
F^{-}	3.07	3.21	6.28	-	**-**	**1**	4.24	-	6.71

[a]Compiled data originally available at I=0.1M for OH^{-}

Gd	***K1**	***K2**	***β2**	***β3**	***β4**	**Ref**	***K1**		
OH^{-}[a]	-7,81	-	-14,75	-	-	**1**	-7.83		
	K1	**K2**	**β2**	**β3**	**β4**		**K1**	**K2**	**β2**
Cl^{-}	-	-	-	-	**-**		0.3	-	-
CO_3^{2-}	7.64	-	13.04	-	**-**	**2**	7.39	-	12.48
HCO_3^{-}	-	-	-	-	**-**		12.69	-	-
SO_4^{2-}	3.48	1.73	5.21	-	**-**	**1**	3.66	-	5.2
F^{-}	3.21	3.35	6.56	-	**-**	**1**	4.31	-	7.2

[a]Compiled data originally available at I=0.1M for OH^{-}

Tb	***K1**	***K2**	***β2**	***β3**	***β4**	**Ref**	***K1**		
OH^{-}	-7.64	-	-	-	-	**1**	-7.64		
	K1	**K2**	**β2**	**β3**	**β4**		**K1**	**K2**	**β2**
Cl^{-}	-	-	-	-	**-**		-	-	-
CO_3^{2-}	7.71	-	13.34	-	**-**	**2**	7.46	-	12.78
HCO_3^{-}	-	-	-	-	**-**		12.79	-	-
SO_4^{2-}	3.47	1.90	5.37	-	**-**	**1**	3.64	-	5.1
F^{-}	3.24	3.42	6.66	-	**-**	**1**	4.45	-	-

Dy	***K1**	***K2**	***β2**	***β3**	***β4**	**Ref**	***K1**		
OH^{-}	-7.59	-	-	-	-	**1**	-7.59		
	K1	**K2**	**β2**	**β3**	**β4**		**K1**	**K2**	**β2**
Cl^{-}	-	-	-	-	**-**		-	-	-
CO_3^{2-}	7.81	-	13.47	-	**-**	**2**	7.56	-	12.91
HCO_3^{-}	-	-	-	-	**-**		12.83	-	-
SO_4^{2-}	3.43	1.75	5.18	-	**-**	**1**	3.61	-	4.8
F^{-}	3.38	3.05	6.43	-	**-**	**1**	4.48	-	-

Ho	***K1**	***K2**	***β2**	***β3**	***β4**	**Ref**	***K1**		
OH^-	-7.56	-	-	-	-	**1**	-7.56		
	K1	**K2**	**β2**	**β3**	**β4**		**K1**	**K2**	**β2**
Cl^-	-2.03	-	-	-	**-**	**1**	-	-	-
CO_3^{2-}	7.8	-	13.56	-	**-**	**2**	7.55	-	13
HCO_3^-	-	-	-	-	**-**		12.79	-	-
SO_4^{2-}	3.38	1.6	4.98	-	**-**	**1**	3.59	-	4.9
F^-	3.31	3.50	6.81	-	**-**	**1**	4.53	-	-

Er	***K1**	***K2**	***β2**	***β3**	***β4**	**Ref**	***K1**		
OH^-	-7.52	-	-	-	-	**1**	-7.52		
	K1	**K2**	**β2**	**β3**	**β4**		**K1**	**K2**	**β2**
Cl^-	-2.03	-	-	-	**-**	**1**	-	-	-
CO_3^{2-}	7.86	-	13.68	-	**-**	**2**	7.61	-	13.13
HCO_3^-	-	-	-	-	**-**		12.82	-	-
SO_4^{2-}	3.38	1.6	4.98	-	**-**	**1**	3.59	-	5.1
F^-	3.31	3.50	6.81	-	**-**	**1**	4.55	-	-

Tm	***K1**	***K2**	***β2**	***β3**	***β4**	**Ref**	***K1**		
OH^-	-7.39	-	-	-	-	**1**	-7.39		
	K1	**K2**	**β2**	**β3**	**β4**		**K1**	**K2**	**β2**
Cl^-	-	-	-	-	**-**	**1**	0.51	-	-
CO_3^{2-}	7.93	-	13.83	-	**-**	**2**	7.68	-	13.27
HCO_3^-	-	-	-	-	**-**		12.85	-	-
SO_4^{2-}	3.41	1.80	5.21	-	**-**	**1**	3.59	-	5.1
F^-	3.25	3.69	6.94	-	**-**	**1**	4.57	-	-

Yb	***K1**	***K2**	***β2**	***β3**	***β4**	**Ref**	***K1**		
OH^-	-7.24	-	-	-	-	**1**	-7.24		
	K1	**K2**	**β2**	**β3**	**β4**		**K1**	**K2**	**β2**
Cl^-	-	-	-	-	**-**	**1**	0.41	-	-
CO_3^{2-}	8.06	-	13.86	-	**-**	**2**	7.81	-	13.3
HCO_3^-	-	-	-	-	**-**		12.86	-	-
SO_4^{2-}	3.33	1.72	5.05	-	**-**	**1**	3.55	-	5.2
F^-	3.31	3.64	6.95	-	**-**	**1**	4.59	-	-

Lu	***K1**	***K2**	***β2**	***β3**	***β4**	**Ref**	***K1**		
OH^-	-7.24	-	-	-	-	**1**	-7.27		
	K1	**K2**	**β2**	**β3**	**β4**		**K1**	**K2**	**β2**
Cl^-	-	-	-	-	**-**	**1**	0.21	-	-
CO_3^{2-}	8	-	13.93	-	**-**	**2**	7.75	-	13.37
HCO_3^-	-	-	-	-	**-**		12.82	-	-
SO_4^{2-}	3.49	1.8	5.29	-	**-**	**1**	3.52	-	5.2
F^-	3.33	3.32	6.65	-	**-**	**1**	4.62	-	-