

Supplementary material

Trace metal speciation predictions in natural aquatic systems: incorporation of dissolved organic matter (DOM) spectroscopic quality

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Ion Exchange Technique (IET) calibration results

The calibration of the IET for Cd²⁺, Ni²⁺ and Zn²⁺ was performed with standard solutions in a pH range of 5.29 to 8.86 and with known concentrations of free Cd²⁺ (0.24 to 405 nM), Ni²⁺ (12.8 to 1750 nM) and Zn²⁺ (4.86 to 1310 nM). Fig. S1 depicts the changes in the distribution coefficient (λ) for Cd, Ni and Zn as a function of the free metal concentration.

Across this pH and concentration range, the distribution coefficients were generally stable. The λ values calculated at the highest pH value of 8.86 (closed squares in Fig. S1), however, are much higher than the remaining λ values. At high pH values, metal hydroxo complexes tend to interact with the resin,^[1] creating a positive interference and increasing the λ values for all three metals. For the remaining pH range (5.29 to 7.88) the λ values can be considered to be constant. For Ni, the λ values were found to be stable across the whole concentration range ($n = 56$, CV < 18 %). For Cd and Zn, the lowest concentration (0.24–0.26 nM for Cd and 4.86–5.42 nM for Zn) introduced a considerable amount of variability in the λ values. At the lowest free metal concentrations, trace amounts of an unidentified (strong) ligand may have complexed the metal, yielding an artificially low value for λ . The λ values for Cd and Zn were, however, found to be stable across the free metal concentration of range of 4.08 to 405 nM Cd²⁺ ($n = 46$, CV < 23 %) and 14.6 to 1310 nM Zn²⁺ ($n = 46$, CV < 34 %) and these values were used for the calculation of the free-metal ion concentrations.

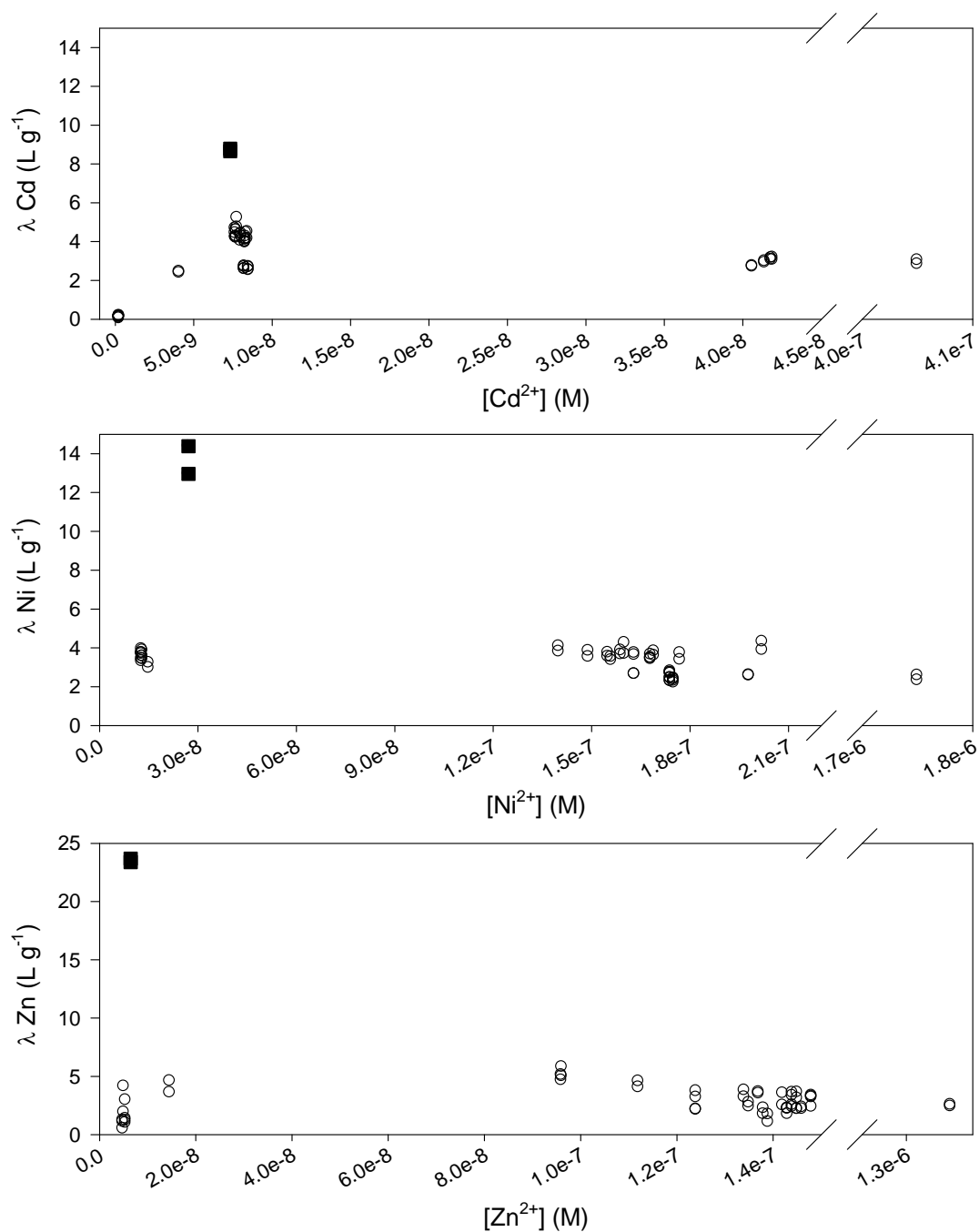


Fig. S1. IET distribution coefficients (λ) for Cd, Ni and Zn as a function of free metal concentration. Open circles represent λ calculated at pH 5.29 to 7.88, whereas closed squares were calculated at pH 8.86.

Ion selective electrode (ISE) calibration results^[2]

Although the calibration curve (Fig. S2) was calculated based on measured free Cu^{2+} concentrations as low as 4.5×10^{-15} M, a method detection limit of 2.6×10^{-11} M Cu^{2+} was calculated based on the three times the standard deviation of six replicate method blank measurements.

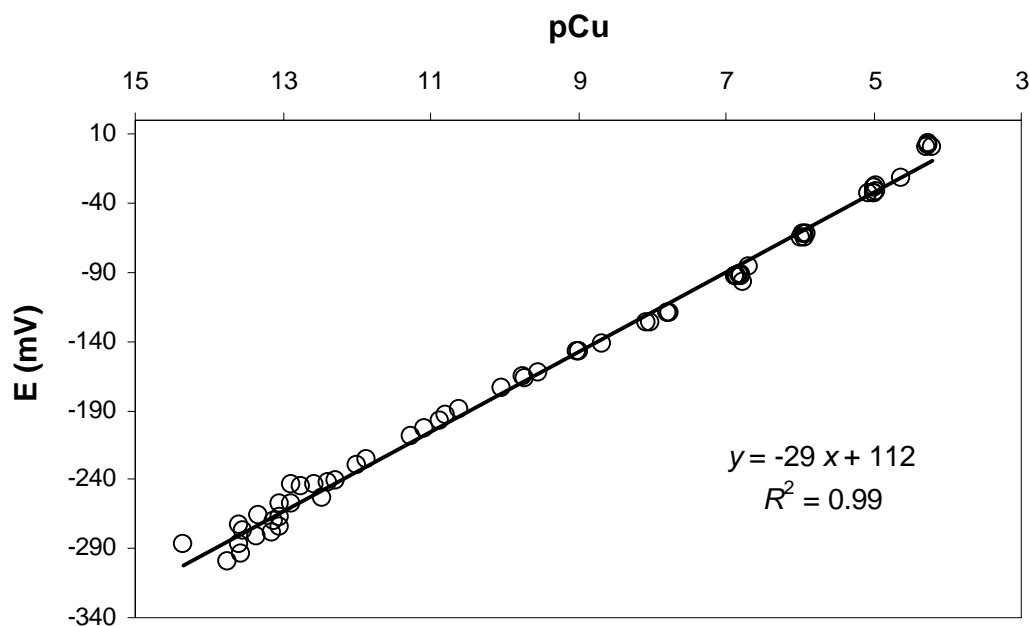


Fig. S2. ISE potential response as a function of Cu activity (pCu). $n = 66$.

Relationships between the percentage of free metal and pH and DOC concentrations

For all four metals (Cd, Cu, Ni and Zn), and in both the Rouyn-Noranda and Sudbury regions, the percentage of free metal as determined by the IET and ISE methods tended to decrease as the lake pH increased, pointing to complexation competition by protons as an important factor affecting metal speciation.

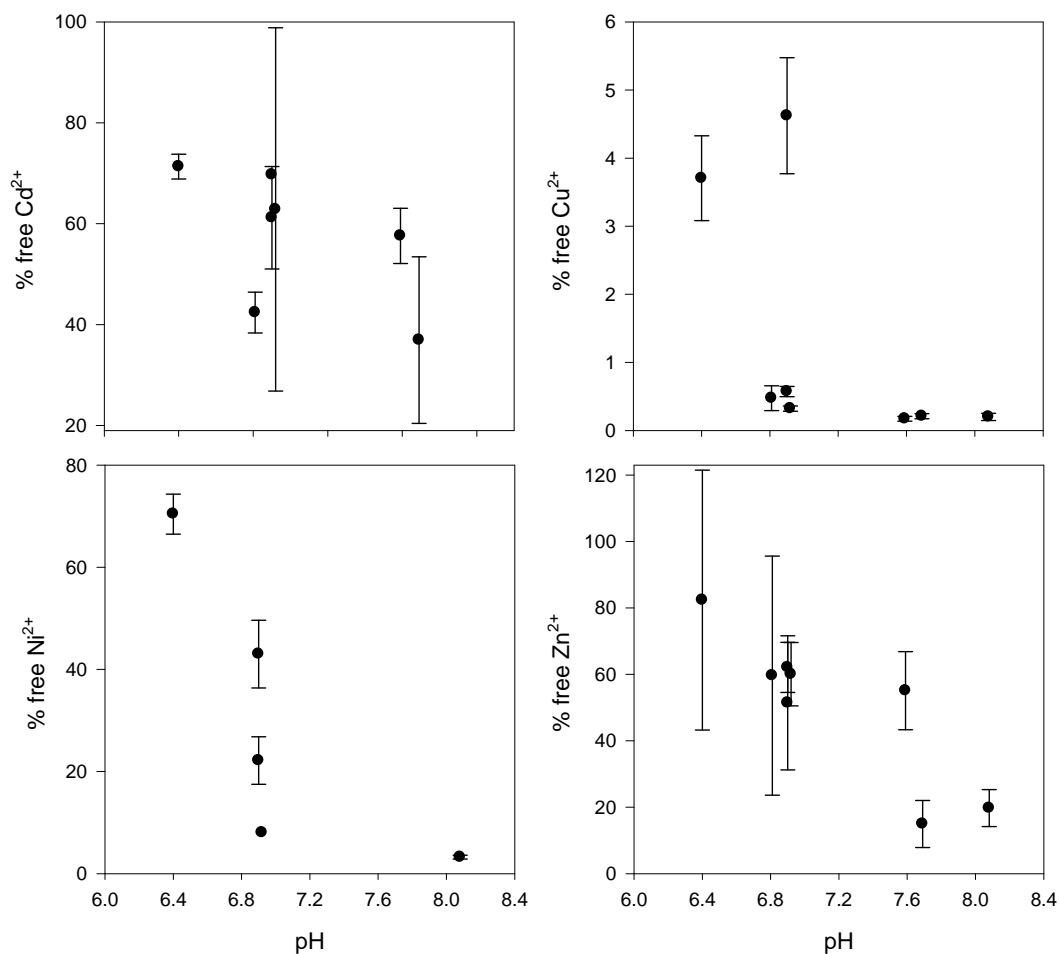


Fig. S3. Measured percentage free metal (\pm s.d., $n = 3$) as a function of lake pH.

A general decline in the measured percentage of free metal was also observed for Cd, Cu and Ni as the DOC concentration increased, presumably reflecting an increase in available metal binding sites on the DOM with an increase in the ligand-to-metal ratio.

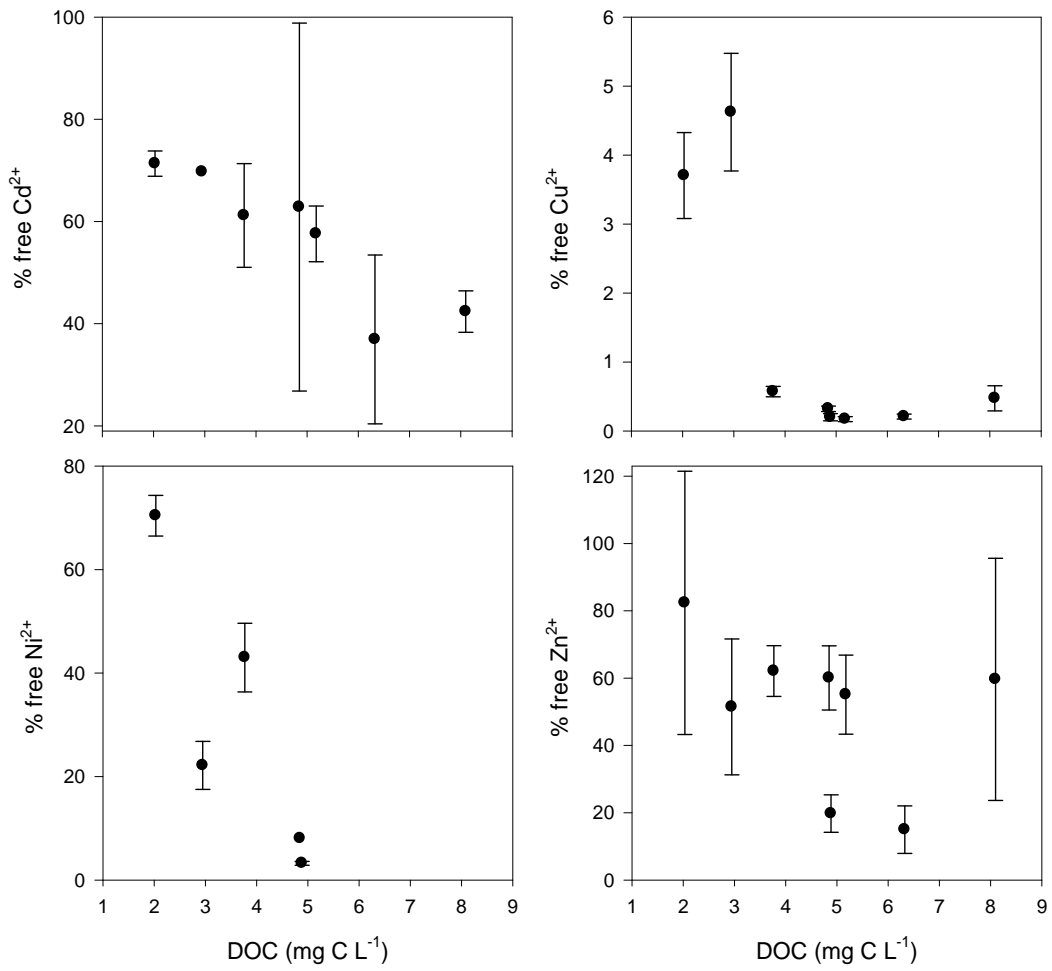


Fig. S4. Measured percentage free metal (\pm s.d., $n = 3$) as a function of lake DOC concentration.

Relationships between the optimised %aFA_{opt} and DOM optical properties

The measured optical quality of the DOM in the lakes sampled for this study is presented below (Table S1) and is described in detail elsewhere.^[3]

Table S1. Measured (\pm s.d., $n = 3$) DOM optical quality (SUVA₂₅₄, Fluorescence Index (FI) and the relative proportion of PARAFAC fluorescence components 1 to 4) for lakes sampled from Rouyn-Noranda (QC) and Sudbury (ON) in 2008

Lake	SUVA ₂₅₄ (L m ⁻¹ mg ⁻¹ C)	FI	C1/C _T	C2/C _T	C3/C _T	C4/C _T
Dasserat	7.8 ± 0.3	1.33 ± 0.02	0.287 ± 0.001	0.384 ± 0.002	0.216 ± 0.004	0.114 ± 0.003
Dufault	7.3 ± 0.4	1.301 ± 0.003	0.28 ± 0.01	0.34 ± 0.01	0.25 ± 0.03	0.133 ± 0.006
Opasatica	7.5 ± 0.4	1.361 ± 0.008	0.271 ± 0.005	0.325 ± 0.003	0.29 ± 0.01	0.116 ± 0.004
Vaudray	10.0 ± 0.3	1.27 ± 0.01	0.28 ± 0.02	0.254 ± 0.001	0.40 ± 0.02	0.068 ± 0.006
Bethel	5.0 ± 0.3	1.51 ± 0.04	0.246 ± 0.005	0.380 ± 0.002	0.167 ± 0.007	0.206 ± 0.004
Geneva	5.3 ± 0.2	1.30 ^A	0.30 ^A	0.39 ^A	0.14 ^A	0.17 ^A
Raft	5.8 ± 0.8	1.30 ± 0.09	0.321 ± 0.004	0.384 ± 0.009	0.08 ± 0.01	0.218 ± 0.008
Whitson	7.3 ± 0.5	1.36 ± 0.03	0.310 ± 0.004	0.385 ± 0.003	0.161 ± 0.005	0.144 ± 0.002

^AOnly one replicate sample measured.

We explored possible relationships between the optimal percentage of FA actively involved in metal complexation (%aFA_{opt}) and the optical properties of the DOM in the lake water samples, in order to estimate the proportion of DOM that is active in metal complexation. The most statistically significant relationships with %aFA_{opt} for the four metals emerged for C1/C_T and C3/C_T (see Fig. 3 in the manuscript). Figs S5–S8 show the lack of significant bivariate relationships between %aFA_{opt} and the other optical properties.

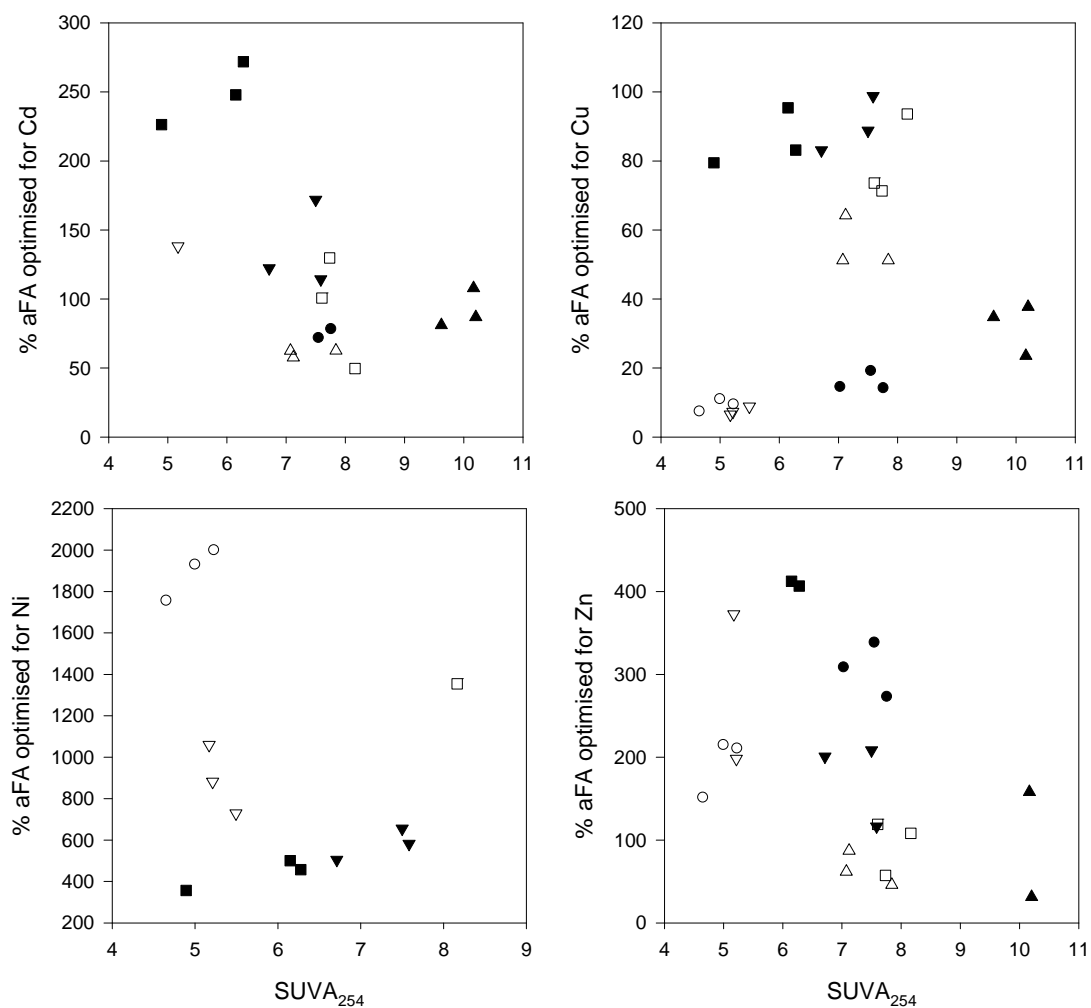


Fig. S5. Relationship between the WHAM calculated percentage of fulvic acid active in complexation (%aFA_{opt}) for Cd, Cu, Ni and Zn and the specific UV absorbance (SUVA₂₅₄) of lake DOM. Points of the same shape and fill represent replicate samples.

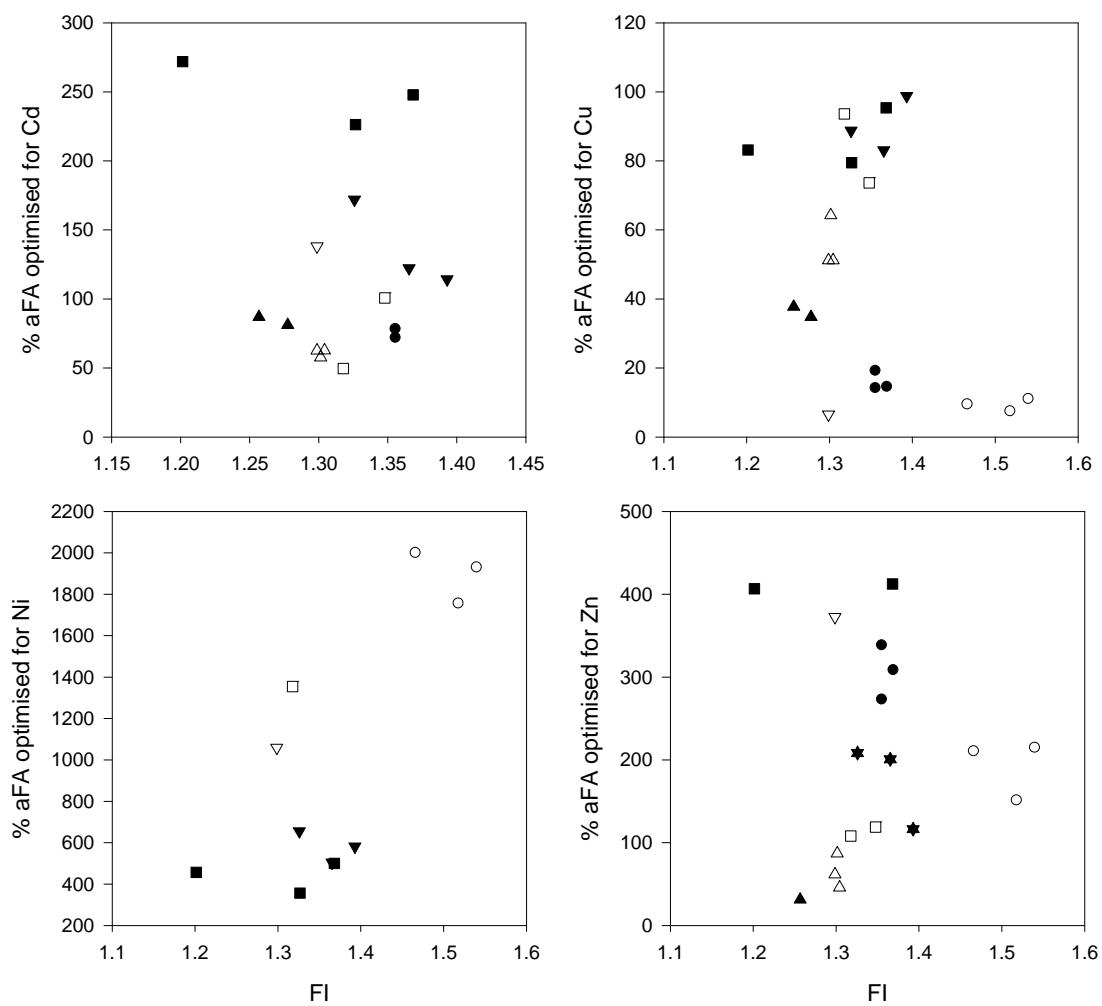


Fig. S6. Relationship between the WHAM calculated percentage of fulvic acid active in complexation (%aFA_{opt}) for Cd, Cu, Ni and Zn and the fluorescence index (FI) of lake DOM. Points of the same shape and fill represent replicate samples.

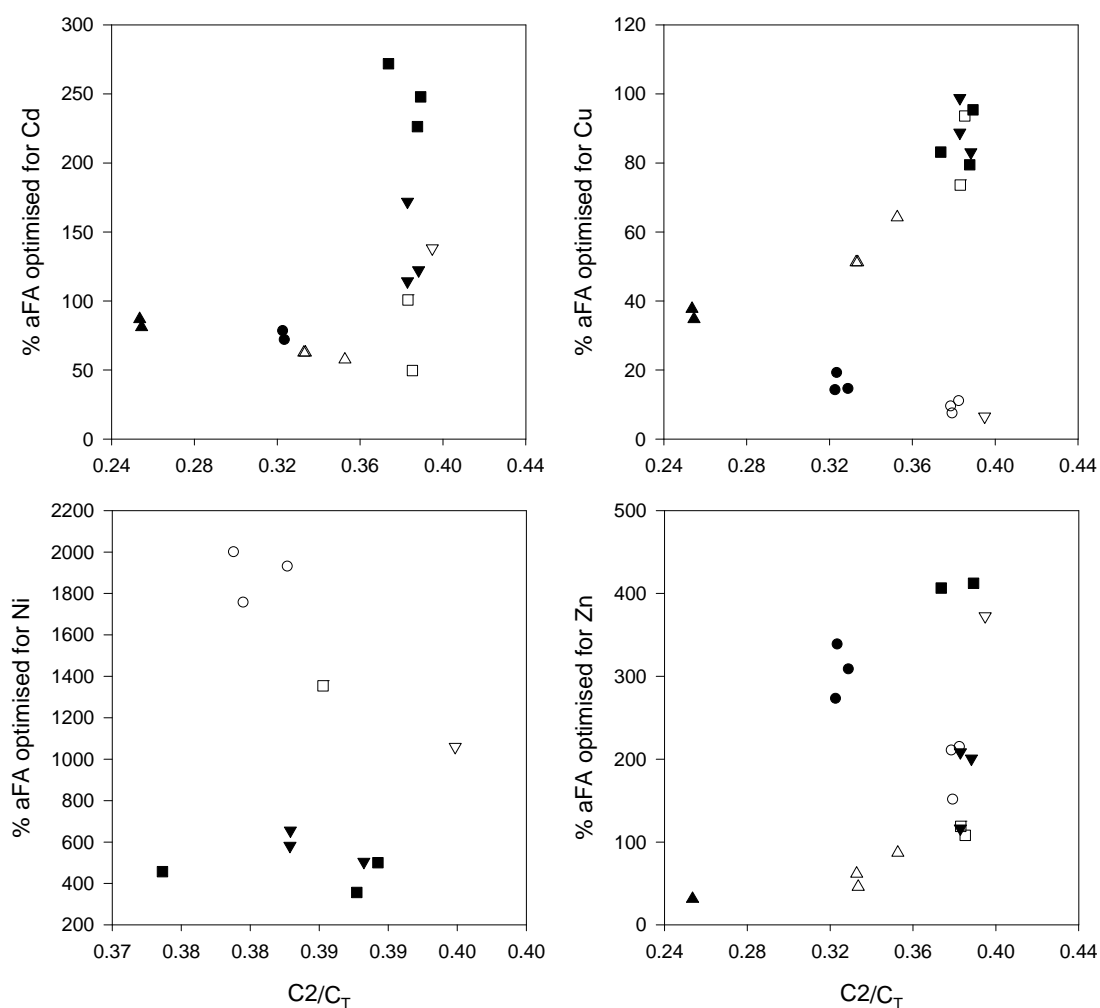


Fig. S7. Relationship between the WHAM calculated percentage of fulvic acid active in complexation (%aFA_{opt}) for Cd, Cu, Ni and Zn and the relative contribution of PARAFAC fluorescence component 2 to the overall fluorescence spectrum of lakewater DOM. Points of the same shape and fill represent replicate samples.

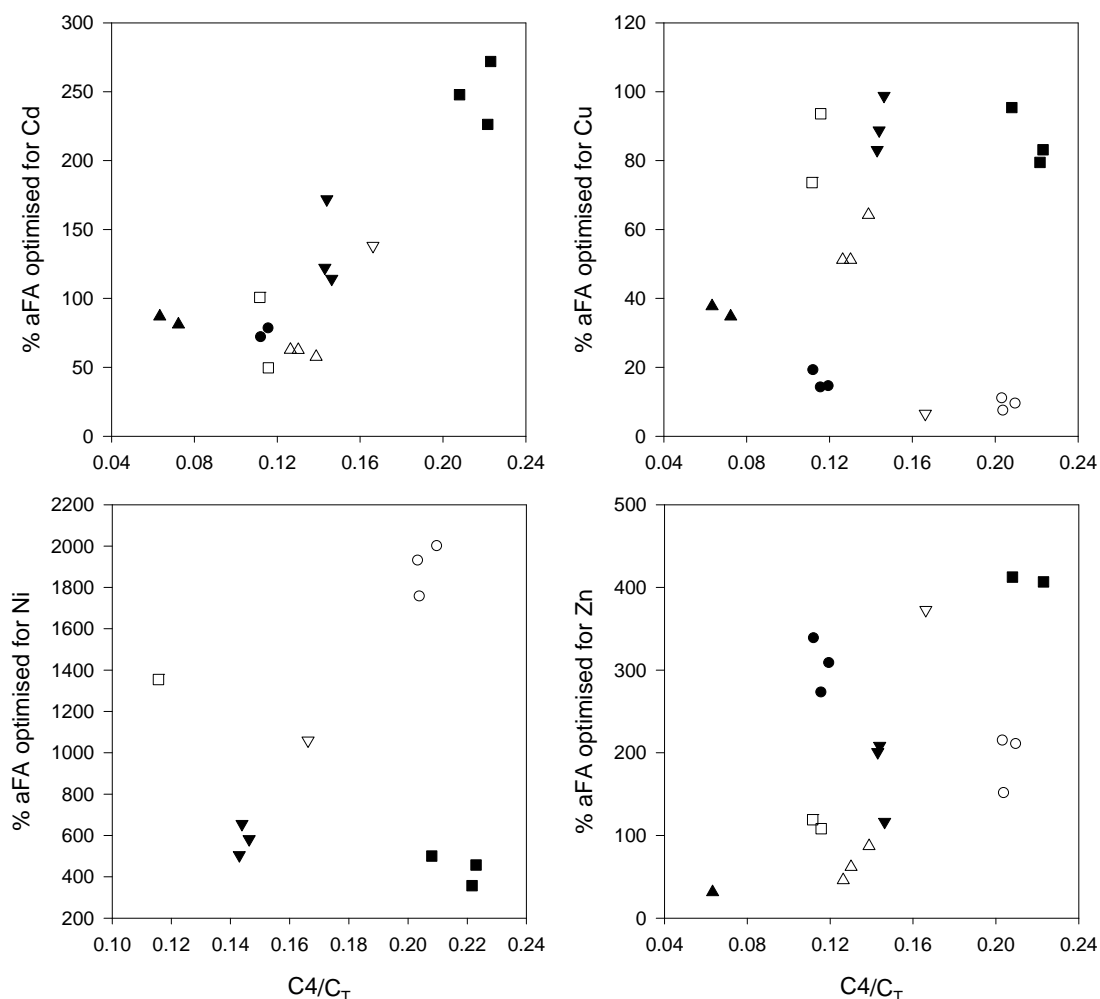


Fig. S8. Relationship between the WHAM calculated percentage of fulvic acid active in complexation (%aFA_{opt}) for Cd, Cu, Ni and Zn and the relative contribution of PARAFAC fluorescence component 4 to the overall fluorescence spectrum of lakewater DOM. Points of the same shape and fill represent replicate samples.

References

- [1] C. Fortin, Y. Couillard, B. Vigneault, P. G. C. Campbell, Determination of free Cd, Cu and Zn concentrations in lake waters by in situ diffusion followed by column equilibration ion-exchange. *Aquat. Geochem.* **2010**, *16*, 151–72. doi:10.1007/s10498-009-9074-3
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- [3] K. K. Mueller, C. Fortin, P. G. C. Campbell, Spatial variation in the optical properties of dissolved organic matter (DOM) in lakes on the Canadian Precambrian shield and links to watershed characteristics. *Aquat. Geochem.* **2012**, *18*, 21–44. doi:10.1007/s10498-011-9147-y