Partitioning and Removal of Metals and Organic Substances in the Environment

DRAFT FINAL

Summary

Partitioning and precipitation of dissolved metal ions to particulate matter in the environment involves making new covalent bonds, which results in a change in speciation of the metal and in detoxification. Degradation of organic substances involves breaking covalent bonds, which also results in detoxification. As the end result is the same, metal partitioning to particulate matter and/or precipitation can be considered as analogous to degradation of organics.

Partitioning of organic substances to particulate matter occurs via non-specific van der Waals interactions. No covalent bonds are made or broken, and the nature of the substance (molecule) remains identical at the chemical level. Therefore, partitioning of organic substances cannot be considered as equivalent to metal binding and removal.

The extent of metal removal from the water column for many metals is correlated to an intrinsic property of the metal, the Irving-Rossotti slope. Laboratory/field observations have shown that sediment resuspension does not cause long-term remobilization of metals to the overlying water.

Questions addressed

This note clarifies the following issues related to the proposed T/DP-E method for measuring metal removal:

- The difference between inorganic versus organic substances regarding the nature and strength of binding.
- The intrinsic properties of metals related to the binding and speciation, and how these demonstrate that the Rapid Removal concept cannot be applied in the same way to organics.
- The speciation of metals in the partitioned phase and the irreversibility.

Metals are Fundamentally Different than Organic Chemicals

Compared to organic compounds, metals and metalloids exist in a wider range of physical and chemical forms, and can change reversibly or irreversibly from one form to another in the environment [1]. This is referred to as ***speciation*** [2]. Each form has unique physical, chemical, and toxicological properties. Conversely, most organics have limited, if any, speciation of note. A discussion of chemical bonding in metals and organics, metal intrinsic properties and their relation to removal from the water column, irreversibility of metal removal follows.

1. Chemical Bonding to Environmentally-Relevant Sorbents: Metals vs. Organics

In aquatic systems, metal ions partition to a variety of naturally-occurring particles including dissolved and particulate organic matter (DOM and POM, respectively) and oxides of iron, manganese, and aluminum oxides [3]. DOM and POM macromolecules serve as ligands

(from the Latin, to bind) for metal ions [4], forming coordination bonds between carboxylic acid and phenol functional groups with significant covalent character [5]. The interatomic distances between metals and environmental ligands can be determined very precisely, ranging from 1.9 to 2.4 Å (see Annex) [6]. The formation of metal precipitates with sulfides and carbonates in sediments is also typically covalent. Metal bonding to naturally-occurring ligands constitutes material changes in speciation, which lower the bioavailability of metals.

In contrast to metal bonding, non-polar, non-ionizable organic chemicals (e.g. PCBs) are attracted to hydrophobic centers of organic matter and hydrophobic mineral surfaces [7, 8]. This attraction is attributed to relatively weak van der Waals' forces and not covalent bonds [9]. The interatomic distance of these weak interactions ranges widely, but is at least 2.4 Å [9, 10] (see Annex), longer than bonding of metals to naturally-occurring ligands. The physical and chemical properties of the organic chemical are fundamentally unchanged during this process.

When organic molecules are degraded in the environment, covalent bonds are broken within the parent molecule. The parent molecule is thereby transformed into daughter products which are usually less toxic. In contrast, when dissolved metal ions undergo a change in speciation by binding to e.g. particles, new covalent bonds are formed. However, the result of both processes is the same: detoxification of the parent chemical.

2. Intrinsic properties of metal ions in aquatic systems

All metal ions possess preferences for bonding to different ligands [5]. This is a consequence of their unique electronic structure and is thus an intrinsic property of the metal. Carbonaro and Di Toro [11-13] have developed linear free energy relationships (LFERs) to describe bonding of metal ions to ligands containing oxygen donor atoms, the same groups responsible for metal partitioning in the water column. A single metal-specific parameter, α_O (the Irving–Rossotti slope), indicates the extent to which a given metal bonds preferentially to negatively-charged oxygen donor atoms relative to the proton [14]. The magnitude of metal removal from the water column is strongly correlated to the magnitude of Irving–Rossotti slope [15]. This is because metals bond with select components of particulate matter in lakes (e.g., humic acids, fulvic acids, and metal oxides) through negatively-charged oxygen donor atoms [4, 16, 17]. Additional details on the relationship between the Irving–Rossotti slope and removal from the water column is provided in the Annex.

3. Functionally irreversible removal of metals from environmental compartments

Metal speciation chemistry is usually presented first in terms of equilibrium reactions which, by definition, can proceed in both the forward and backward direction [1]. For metal and other inorganics, many speciation-changing reactions are fast enough that equilibrium between the forward and backward reactions is constantly maintained. However, slow reaction kinetics can often produce an apparent disequilibrium. Redox reactions and dissolution of minerals are often not at equilibrium [1, 3].

The tendency for metals to bond with functional groups on suspended particulate matter and be transported to the sediment is well-established in the literature [18-20]. The specific mechanisms responsible for metal sequestration in sediment depend upon the identity of the metal and the distribution of ligands present (covered in detail in the Annex).

Resuspension of sediment has been shown to have minimal, if any, long-term impact on the quality of overlying water at both the laboratory [21-23] and field-scale [24-26]. This because the water column residence time of sediment particles is relatively short following resuspension [26] and therefore metal-releasing redox and dissolution reactions do not have adequate time to reach equilibrium. Additionally, metals that are released due to oxidation or dissolution are rapidly scavenged by metal-sorbing phases present in the suspended solids. These two phenomena serve to make metal removal functionally irreversible. Over time, metals are buried in the deeper sediment layers where they become inaccessible to resuspension and biota.

Annex

1. Some reported interatomic distances for metals covalently bound to various environmental ligands, from EXAFS experiments.

	Ligand	First neighbor	Interatomic distance (Å)	Reference
Ni	Fulvic acid	Ni-O	2.03-2.04	[27]
Ni	Carboxylate ligands	Ni-O	2.03-2.05	[27]
Zn	Hydrous ferric oxide	Zn-O	1.94-1.97	[28]
Zn	Ferrihydrite and Biogenic iron oxyhydroxides	Zn-O	1.97-1.99	[29]
Cu	Ferrihydrite and Biogenic iron oxyhydroxides	Cu-O	1.93	[29]
Cu	Organic matter	Cu-O	1.92-1.95	[30]
Pb	Ferrihydrite and Biogenic iron oxyhydroxides	Pb-O	2.34-2.35	[29]
Ni	Hydrous ferric oxides	Ni-O	2.05-2.07	[31]

2. Relationship between Metal Removal and the Irving-Rossotti Slope

Metal removal from the water column is closely related to the magnitude of Irving–Rossotti slope, an intrinsic property of the metal (Figure A1).

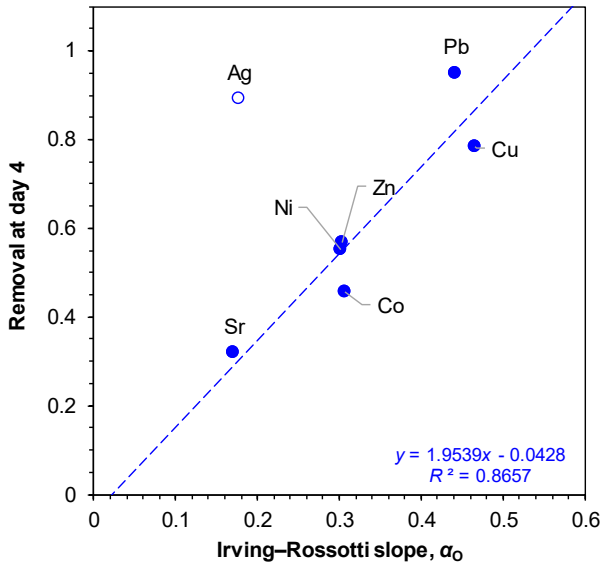

Figure A1. Relationship between removal of metal observed at day 4 of the CanmetMINING experiments and the Irving-Rossotti slope (α_O). Data point for Ag is excluded from the regression.

This is because metals bond with select components of particulate matter in lakes (e.g., humic acids, fulvic acids, and metal oxides) through negatively-charged oxygen donor atoms [4, 16, 17]. These solids, present either in the water column or in the sediment, play an important role in metal removal from the water column. Evidence to support this concept includes:

- Strong correlations have been developed between WHAM parameters for metal ions and the Irving–Rossotti slope [11]
- Use of Irving–Rossotti slope in the most recent formulation of WHAM (WHAM VII) [32]
- The Irving–Rossotti slope was an excellent predictor of % removal of various metals from the recent T/DP-E testing [15]

3. Details on Metal Sequestration in Sediment

"Soft" and "borderline" metal ions (e.g. Cu, Ni, Pb, Cd) exchange oxygen-containing ligands for sulfur [33-35] where they are sequestered via various mechanisms including adsorption, inclusion, metal-exchange and copreciptiaton [36]. Over time, these metals become incorporated into pyritic minerals [36-39] which are resistant to further transformation. "Hard" metal ions (e.g. Sr, Cr, Al) remain bonded to oxygen-containing ligands and remain adsorbed to mineral surfaces, particulate organic matter, or precipitate as amorphous oxides, hydroxides and carbonates[1]. Over time, these metals age into even more insoluble forms or become incorporated into the crystal structure and are frequently associated with insoluble iron and manganese oxyhydroxides or aluminum and iron silicates [40-42].

References

1. Stumm W, Morgan JJ. 1996. *Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters*. New York, NY, John Wiley and Sons, Inc.
2. Templeton DM, Ariese F, Cornelis R, Danielsson L, Muntau H, van Leeuwen HP, Lobinski R. 2000. Guidelines for terms related to chemical speciation and fractionation of elements. Definitions, structural aspects, and methodological approaches (IUPAC Recommendations 2000). *Pure Appl Chem* 72:1453-1470.
3. Stumm W. 2001. *Chemistry of the Solid-Water Interface: Processes at the Mineral-Water and Particle-Water Interface in Natural Systems*, John Wiley & Sons.
4. Tipping E. 2002. *Cation Binding by Humic Substances*. Cambridge, UK, Cambridge University Press.
5. Schalfer HL, Gliemann G. 1969. *Basic Principles of Ligand Field Theory*. New York, Wiley-Interscience.
6. Korshin GV, Frenkel AI, Stern EA. 1998. EXAFS Study of the Inner Shell Structure in Copper(II) Complexes with Humic Substances. *Environ Sci Technol* 32:2699-2705.
7. Schwarzenbach RP, Gschwend PM, Imboden DM. 2002. *Environmental Organic Chemistry, Second Edition*. New York, NY, Wiley-Intersceince.
8. Dunnivant FM, Anders E. 2019. *Pollutant Fate and Transport in Environmental Multimedia*, Wiley.
9. Carey FA. 2007. *Organic Chemistry*, Seventh Edition ed, McGraw Hill.
10. Grimme S. 2004. Accurate description of van der Waals complexes by density functional theory including empirical corrections. *J Comp Chem* 25:1463-1473.
11. Carbonaro RF, Di Toro DM. 2007. Linear free energy relationships for metal–ligand complexation: Monodentate binding to negatively-charged oxygen donor atoms. *Geochim Cosmochim Acta* 71:3958-3968.
12. Atalay YB, Di Toro DM, Carbonaro RF. 2013. Estimation of stability constants for metal–ligand complexes containing neutral nitrogen donor atoms with applications to natural organic matter. *Geochim Cosmochim Acta* 122:464-477.
13. Carbonaro RF, Atalay YB, Di Toro DM. 2011. Linear free energy relationships for metal–ligand complexation: Bidentate binding to negatively-charged oxygen donor atoms. *Geochim Cosmochim Acta* 75:2499-2511.
14. Irving H, Rossotti H. 1956. Some relationships among the stabilities of metal complexes. *Acta Chem Scand* 10:72-93.
15. Burton GA, Hudson M, Huntsman P, Carbonaro RF, Rader KJ, Waeterschoot H, Baken S, Garman ER. 2019. Weight-of-evidence approach for assessing removal of metals from the water column for chronic environmental hazard classification. *Environ Toxicol Chem* Accepted for publication.
16. Dzombak DA, Morel FM. 1990. *Surface Complexation Modeling. Hydrous Ferric Oxide*, Wiley-Interscience.
17. Tonkin JW, Balistrieri LS, Murray JW. 2004. Modeling sorption of divalent metal cations on hydrous manganese oxide using the diffuse double layer model. *Appl Geochem* 19:29-53.
18. Diamond ML, Mackay D, Cornett RJ, Chant LA. 1990. A model of the exchange of inorganic chemicals between water and sediments. *Environ Sci Technol* 24:713-722.
19. Mackay D, Diamond M. 1989. Application of the QWASI (Quantitative Water Air Sediment Interaction) fugacity model to the dynamics of organic and inorganic chemicals in lakes. *Chemosphere* 18:1343-1365.
20. Sigg L, Sturm M, Kistler D. 1987. Vertical transport of heavy metals by settling particles in Lake Zurich. *Limnol Oceanogr* 32:112-130.
21. Huntsman P, Beaudoin R, Rader K, Carbonaro R, Burton Jr. GA, Hudson M, Baken S, Garman E, Waeterschoot H. 2019. Method Development for Determining the Removal of Metals from the Water Column under Transformation/Dissolution Conditions for Chronic Hazard Classification. *Environ Toxicol Chem* 0.

22. Caetano M, Madureira M-J, Vale C. 2003. Metal Remobilisation during Resuspension of Anoxic Contaminated Sediment: Short-Term Laboratory Study. *Water, Air, & Soil Pollution* 143:23-40.
23. Cantwell MG, Burgess RM, King JW. 2008. Resuspension of contaminated field and formulated reference sediments Part I: Evaluation of metal release under controlled laboratory conditions. *Chemosphere* 73:1824-1831.
24. Rader KJ, Carbonaro RF, van Hullebusch ED, Baken S, Delbeke K. 2019. The Fate of Copper Added To Surface Water: Field, Laboratory, and Modeling Studies. *Environ Toxicol Chem* 0.
25. Calmano W, Förstner U, Hong J. 1993. Mobilization and Scavenging of Heavy Metals Following Resuspension of Anoxic Sediments from the Elbe River. Environmental Geochemistry of Sulfide Oxidation. Vol 550-ACS Symposium Series. American Chemical Society, p. 298-321.
26. Fetters KJ, Costello DM, Hammerschmidt CR, Burton GA. 2016. Toxicological effects of short-term resuspension of metal-contaminated freshwater and marine sediments. *Environ Toxicol Chem* 35:676-686.
27. Strathmann TJ, Myneni SCB. 2004. Speciation of aqueous Ni(II)-carboxylate and Ni(II)-fulvic acid solutions: Combined ATR-FTIR and XAFS analysis 11Associate editor: G. Sposito. *Geochim Cosmochim Acta* 68:3441-3458.
28. Lee S, Anderson PR. 2005. EXAFS study of Zn sorption mechanisms on hydrous ferric oxide over extended reaction time. *J Colloid Interf Sci* 286:82-89.
29. Whitaker AH, Duckworth OW. 2018. Cu, Pb, and Zn Sorption to Biogenic Iron (Oxyhydr)Oxides Formed in Circumneutral Environments. *Soil Systems* 2:18.
30. Karlsson T, Persson P, Skyllberg U. 2006. Complexation of Copper(II) in Organic Soils and in Dissolved Organic Matter − EXAFS Evidence for Chelate Ring Structures. *Environ Sci Technol* 40:2623-2628.
31. Xu Y, Axe L, Boonfueng T, Tyson TA, Trivedi P, Pandya K. 2007. Ni(II) complexation to amorphous hydrous ferric oxide: An X-ray absorption spectroscopy study. *J Colloid Interf Sci* 314:10-17.
32. Tipping E, Lofts S, Sonke JE. 2011. Humic Ion-Binding Model VII: a revised parameterisation of cation-binding by humic substances. *Environ Chem* 8:225-235.
33. Di Toro DM, Mahony JD, Hansen DJ, Scott KJ, Carlson AR, Ankley GT. 1992. Acid Volatile Sulfide Predicts the Acute Toxicity of Cadmium and Nickel in Sediments. *Environ Sci Technol* 26:96-101.
34. Di Toro DM, Mahony JD, Hansen DJ, Scott KJ, Hicks MB, Mayr SM, Redmond MS. 1990. Toxicity of Cadmium in Sediments - the Role of Acid Volatile Sulfide. *Environ Toxicol Chem* 9:1487-1502.
35. Morse JW. 1993. Release of Toxic Metals via Oxidation of Authigenic Pyrite in Resuspended Sediments. Environmental Geochemistry of Sulfide Oxidation. Vol 550-ACS Symposium Series. American Chemical Society, p. 289-297.
36. Rickard D. 2012. *Sulfidic Sediments and Sedimentary Rocks*, Elsevier.
37. Morse JW, Luther GW. 1999. Chemical influences on trace metal-sulfide interactions in anoxic sediments. *Geochim Cosmochim Acta* 63:3373-3378.
38. Huerta-Diaz MA, Carignan R, Tessier A. 1993. Measurement of trace metals associated with acid volatile sulfides and pyrite in organic fresh water sediments. *Environ Sci Technol* 27:2367-2372.
39. Huerta-Diaz MA, Tessier A, Carignan R. 1998. Geochemistry of trace metals associated with reduced sulfur in freshwater sediments. *Appl Geochem* 13:213-233.
40. Cornell RM. 1988. The Influence of Some Divalent Cations on the Transformation of Ferrihydrite to More Crystalline Products. *Clay Minerals* 23:329-332.
41. Ford RG, Bertsch PM, Farley KJ. 1997. Changes in transition and heavy metal partitioning during hydrous iron oxide aging. *Environ Sci Technol* 31:2028-2033.
42. Tebo BM, Bargar JR, Clement BG, Dick GJ, Murray KJ, Parker D, Verity R, Webb SM. 2004. Biogenic manganese oxides: Properties and mechanisms of formation. *Annual Review of Earth and Planetary Sciences* 32:287-328.