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Running Head: Assessing Removal of Metals from the Water Column

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WEIGHT-OF-EVIDENCE APPROACH FOR ASSESSING REMOVAL OF METALS FROM THE WATER COLUMN FOR CHRONIC ENVIRONMENTAL HAZARD CLASSIFICATION

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ABSTRACT

The United Nations and European Union have developed guidelines for the assessment of long-term (chronic) chemical environmental hazards. This approach recognizes these hazards are often related to spillage of chemicals into freshwater environments. The goal of this study was to examine the concept of metal ion removal from the water column in the context of hazard assessment and classification. We propose a weight-of-evidence approach the assesses several aspects of metals including the intrinsic properties of metals, the rate at which metals bind to particles in the water column and settle, the transformation of metals to non-available, non-toxic forms, and the potential for remobilization of metals from sediment. We developed a new test method to quantify metal removal in aqueous systems: The Extended Transformation/Dissolution Protocol (T/DP-E). The method is based on the OECD 29 Transformation/Dissolution Protocol. The key element of the protocol extension is the addition of substrate particles (as found in nature), allowing the removal processes to occur. Our work focused on extending this test to support the assessment of metal removal from aqueous systems, equivalent to the concept of “degradability” for organic chemicals. While the technical aspects of our proposed method are different from the OECD method for organics, its use for hazard classification is equivalent. Models were developed providing mechanistic insight into

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processes occurring during the T/DP-E method. Some metals, such as copper, rapidly decreased (within 96 hours) under the 70% threshold criteria, while others such as strontium, did not. A variety of method variables were evaluated and optimized to allow for a reproducible, realistic hazard classification method that mimics reasonable worst-case scenarios. We propose that this method be standardized for OECD hazard classification via round robin (ring) testing to ascertain its intra- and inter-laboratory variability.

Keywords: aquatic metals, metal hazards in aquatic systems, metal classification, OECD environmental protocols

Introduction

Chemical substances may be classified and labeled based on their hazard, i.e. the intrinsic property of a substance that has the potential to cause adverse effects in a living organism (OECD, 2003). The United Nations developed the Globally Harmonized System (GHS) for classification (United Nations, 2017), and standardized test methods have been developed to allow consistency in the assessment of hazard. For example, the European Union implemented the GHS as Regulation (EC) No 1272/2008 on Classification, Labelling and Packaging of substances and mixtures (CLP).

Under the GHS and CLP, the classification of a substance for long-term (chronic) environmental hazards is based on, amongst others, an assessment of its degradability. This recognizes that, in the event of a spillage or accident, the effects of rapidly degraded substances are localized and of short duration, and there is a reduced potential for exposure.

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Metal chemistry has unique properties compared to organic chemicals, which complicates the assessment of degradability. Regarding environmental degradation, the GHS (section A9.7.1.5) indicates that, *"For inorganic compounds and metals, clearly the concept of degradability, as it has been considered and used for organic substances, has limited or no meaning. Rather, the substance may be transformed by normal environmental processes to either increase or decrease the bioavailability of the toxic species… Nevertheless, the concepts that a substance… may not be rapidly lost from the environment… are as applicable to metals and metal compounds as they are to organic substances"* (United Nations, 2017).

The GHS provides detailed guidance on the test methods to assess degradation of organic substances. For metals and inorganic substances, only preliminary guidance is available (section A9.7.1.7). As a result, applying the principle of organic chemical “degradability” to metals is challenging, since they do not degrade. The “intrinsic degradability” of organic chemicals can only occur in the presence of a critical microbial community, which is primarily associated with particles: a gram of sediment typically contains over 1 x 10^9 bacteria. Such particles exist in all aquatic ecosystems and are essential for promoting the degradation of some organic chemicals, and the removal of some metals and inorganic chemicals. The OECD screening test that assesses the degradability of organic substances includes a standardization of several conditions of the receiving water that are necessary for biodegradation (temperature, nutrient conditions, oxygenation, inoculation). A similar approach is adopted here to assess the removal for metals from the water column. Previously, Skeaff et al. (2002) have already proposed such approach to assessing metal "degradability" in the context of loss from the water column, using half-

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times (i.e., time required for metal concentration to decrease by 50%) as metrics of metal removal rates. They considered the permanence of the removal by looking at the extent of metal remobilization from sediment. Their work focused on field data, and they called for the development of a standard set of laboratory conditions to assess removal rates.

The overarching goal of the research described herein was to examine the concept of metal ion removal from the water column in the context of hazard assessment and classification. We propose a weight-of-evidence approach that assesses several aspects of metals including the intrinsic properties of metals, the rate at which metals bind to particles in the water column and settle, the transformation of metals to non-available, non-toxic forms, and the potential for remobilization of metals from sediment. As a pivotal element of the weight-of-evidence approach and building on the work by Skeaff et al. (2002), we developed a new standardized test method to quantify metal removal in aqueous systems: The Extended Transformation/Dissolution Protocol (T/DP-E) (Huntsman et al., this issue). This test method is based on the existing OECD 29 Transformation/Dissolution Protocol which is already well established and used for assessing the solubility of metals and metal compounds in the context of environmental hazard assessment. The key element of the protocol extension is the addition of substrate particles which allows removal processes to occur in a standardized setting. Our work focused on extending this test to support the assessment of metal removal from aqueous systems, equivalent to the concept of “degradability” for organic chemicals. Models were developed that provide mechanistic insight into the processes occurring during the T/DP-E method. Finally, the outcomes of the T/DP-E method are linked to the peer-reviewed literature on the fate of metals in aquatic systems.

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Approach, Results and Discussion

The weight-of-evidence approach presented below can be subdivided into four main elements:

1. Consideration of metal intrinsic properties that determine their fate in aquatic systems;
2. Review of available field and laboratory studies that assess the fate of dissolved metal ions in aquatic systems;
3. Development and application of an extended OECD 29 T/DP (T/DP-E), a protocol for assessing metal removal and remobilization under standardized conditions; and
4. Development and application of a mechanistic numerical model describing metal removal in the T/DP-E method, to gain insight into the physicochemical processes that occur.

Intrinsic properties of metal ions in aquatic systems

In aquatic systems, metal ions bind to a variety of naturally-occurring particles. Adsorption of metals to dissolved and particulate organic matter (DOM and POM, respectively) involves formation of bonds with significant covalent character with various functional groups such as carboxylic acids, phenols, and amines (Tipping 2002). The same is true for metal adsorption to mineral surfaces which involves surface complex formation with hydroxide functional groups on iron, manganese, and aluminum oxides (Stumm 2001). The formation of metal precipitates with sulfides and carbonates in sediments is also typically covalent. Adsorption of metals to naturally occurring ligands therefore constitute material changes in metal speciation, which lower the bioavailability

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of metals in a way that can be predicted using speciation models. Such speciation models are a cornerstone of bioavailability models, such as the Biotic Ligand Model (BLM) (Di Toro et al. 2001a). This sets metals apart from most organic chemicals: adsorption of organic chemicals to DOM and POM occurs via relatively weak van der Waals attractive forces (Schwarzenbach et al. 1993). These interactions do not involve breaking or making of covalent bonds. The physical and chemical properties of the organic chemical are fundamentally unchanged during this process.

Metal speciation chemistry is usually presented first in terms of equilibrium reactions which, by definition, can proceed in both the forward and backward direction (Stumm and Morgan 1996a). For inorganics, speciation-changing reactions such as protonation occur fast enough that equilibrium is constantly maintained. This however, is not true for all ligand exchange reactions. Some ligand exchange reactions are known to be rapid for some metals (e.g., water exchange and chloro-complex formation) (Helm and Merbach 1999). However, in many cases, slow reaction kinetics can often produce an apparent disequilibrium. Redox reactions are notorious in this respect (Stumm & Morgan, 1996), and also dissolution reactions of e.g. minerals can occur at slow rates (Stumm 2001). The time required for a metal to desorb from a mineral surface or dissolve from a sulfide precipitate often exceed the duration of the conditions driving these reactions.

The tendency for metals to bond with functional groups on suspended particulate matter and be transported to the sediment is well-established (Diamond et al. 1990a; Mackay and Diamond 1989) (Sigg et al., 1987). Once in the sediment, the concentration of solids, and therefore potential ligands, is quite large, and the distribution of ligands is more

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diverse (Tessier and Campbell 1987). As a result, many soft and borderline metal ions exchange their oxygen ligand for sulfur and form metal sulfide precipitates (Di Toro et al., 1990; Di Toro et al., 1992) (Morse et al. 1987). Over time, these metals become incorporated into pyritic minerals via diagenesis (Morse and Luther 1999). Harder metal ions remain bonded to oxygen-containing ligands and remain adsorbed to mineral surfaces, particulate organic matter, or precipitate as amorphous oxides, hydroxides and carbonates (Stumm and Morgan 1996b). 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 (Cornell, 1988; Ford et al., 1997; Tebo et al., 2004). Remobilization of these sediments have been shown to have minimal, if any, long-term impact on the quality of overlying water (Caetano et al. 2003; Calmano et al. 1993; Cantwell et al. 2008; Fetters et al. 2016). These processes are “effectively irreversible” and provide an ultimate sink for metals in aquatic systems.

Field and laboratory studies on the fate of metal ions in aquatic systems

As mentioned above, metals, based on their intrinsic properties, tend to sorb on suspended particulate matter. Since this particulate matter settles at appreciable rates, any associated metals are removed simultaneously. Di Toro et (2001) demonstrated metal removal in oceans on a global scale in a simple dilution analysis in which sodium was used a conservative tracer for metal weathering/transport from the lithosphere to the oceans. Concentration of many metals (notably aluminum, iron, nickel, zinc, copper, cobalt, lead, and silver) predicted by dilution were orders of magnitude higher the actual

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observed concentration in the oceans (Figure 1). This non-conservative behavior can only be explained by metal removal.

Numerous studies have demonstrated metal removal in surface waters. These include the following: (1) removal of Cd, Cu, and Zn, in riverine systems (Mills et al. 1985; Thomann 1984) and Cd, Zn, and Pb in estuaries (Di Toro et al. 2001b); (2) removal of various metals (including As, Co, Cs, Cu, Fe, Hg, Mn, Ni, Sn, and Zn) in laboratory, microcosm, and mesocosm studies representing lacustrine systems (Baccini et al. 1979; Bird and Evenden 1996; Diamond et al. 1990b; Gächter 1979; Hart et al. 1992; Hommen 2010; Hommen et al. 2016; Rand et al. 2011; Santschi et al. 1986; Schäfers 2003; Smolyakov et al. 2010a; Smolyakov et al. 2010b); and (3) removal of metals (including As, Co, Cs, Cu, Fe, Hg, Mn, Se, Sn, and Zn) in whole-lake field studies (Bird et al. 1995; Effler et al. 1980; Haughey et al. 2000; Hesslein et al. 1980; Liu et al. 2006; Santschi et al. 1986; van Hullebusch et al. 2003a; van Hullebusch et al. 2003b; van Hullebusch et al. 2002). Studies for copper are particularly plentiful given use of copper sulfate as an algaecide in ponds, lakes, and reservoirs. In a recent review by Rader et al., 2019, which included many of the references presented above, the time required for 70% removal of Cu varied from 0.84 to 27 days, with one exception of 130 days. For the majority of studies, more than 70% of the added copper was removed from the water column within 16 days of dosing. For other metals, the above-referenced literature supports substantial metal removal on time scales of days to weeks. For example, the mesocosm study of Diamond et al. (1990b), which assessed the behavior of several metals in the same mesocosms, observed the following half-times (i.e., time at which concentration has decreased by 50%, average of the two mesocosms, in days): Co (4.35), Fe (10.8), Zn

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(17.6), As (19.2), Sn (9.45), Cs (22.65), Hg (14.45). Hesslein et al. (1980) studied the fate of metals added to Lake 224 of the Experimental Lakes Area in northwestern Ontario. Observed half-times (in days) for this whole-lake study were as follows: Se (53), Cs (28), Zn (25), Hg (14), Fe (16), Co (19). Using estuary data from the Delft Hydraulics Laboratory, Di Toro et al. (2001b) demonstrated removal of Cd, Zn, and Pb in 12 European estuaries emptying into the North Sea. These estuaries have hydraulic residence times ranging from a few weeks to a few months. Removal efficiencies between 10% and 50% were noted for Cd. Removal efficiencies for 7 of the 12 estuaries were at or greater than approximately 75% for Pb.

An equally substantial body of literature exists on strong binding of metals to specific phases in sediment, metal removal from sediment pore water, and bioavailability changes in sediment. Acid-volatile sulfides (AVS) have clearly been shown to be important in near-surface sediments (within millimeters of the surface) where reducing conditions exist (Burton et al., 2005; Costello et al., 2012, 2015, 2016; Mendoca et al., 2017; Van den Berg et al., 2001), but the oxides and oxyhydroxides play a major role in oxidic sediments, in surficial sediment layers, and during resuspension events. Empirical evidence for the important role of iron and manganese oxides and oxyhydroxides in scavenging metals, such as Cu, Ni and Zn continues to grow (Burton et al., 2005; Costello et al., 2012; Nguyen et al. 2011; Tonkin et al., 2004; Van den Berg et al., 2001). Their role is important in virtually all freshwater sediments that are oxidized as that is where most benthic biota reside. AVS may be slowly oxidized during bioturbation or during resuspension events, but released metals are quickly bound by the Fe/Mn oxides and oxyhydroxides, and thereby returned to the sediment compartment ensuring

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permanent removal. Afterwards, under settled conditions, the AVS is regenerated (e.g., Costello et al., 2012, 2016; Fetters et al, 2015; Nedrich and Burton 2017; Nedrich et al., 2017).

Laboratory and field tests have been conducted with metal spiked or naturally contaminated sediment to understand how metal bioavailability and chronic toxicity in riverine systems change through time due to sorption, complexation, and transformation processes (Costello et al., 2015, 2016; Mondonca et al., 2017; Nedrich et al., 2017; Schlekat et al., 2016). All studied metals (Cu, Ni, and Zn) were strongly sorbed to sediments regardless of their acid volatile sulfide (AVS) and organic carbon contents. This is a key finding in that previous discussions have challenged the sufficiency of AVS and oxyhydroxides in sediments to provide sufficient binding phases to control metal bioavailability [e.g., Atkinson et al., 2007; Chapman et al 1998; Hong et al., 2011; Nedrich et al., 2017; Nguyen et al., 2011]. Metal concentrations in the pore water of sediments declined through time as metals were transformed from the dissolved to particulate species causing a decreased solubility through time. As AVS was lost due to surficial sediment oxidation, metals were increasingly associated with amorphous or crystalline Fe oxides. The chronic toxicity of metals to sediment dwelling organisms decreased with time and with decreasing metal solubility, as would expected following a change in metal speciation to non-available forms (Costello et al., 2011, 2012, 2015, 2016; De Jonge et al., 2012; Fetters et al., 2016; Fleming and Trevors 1989; Plach JM et al., 2011; Simpson et al., 1998; Stauber et al., 2000).

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The extended transformation-dissolution protocol (T/DP-E): assessing metal removal and remobilization using a standardized method

The OECD 29 Transformation/Dissolution Protocol (T/DP) determines the rate and extent at which a sample (a metal, sparingly soluble metal compound, or complex inorganic material) will release metal ions to an aqueous environmental medium with standardized composition. Under the U.N. GHS classification system, the measured metal concentrations are then compared with the acute or chronic Ecotoxicity Reference Values (ERVs). This, together with an assessment of degradability, allows to derive the environmental hazard classification. This approach has been successfully applied to derive environmental hazard classifications on metal concentrates, mattes, alloys, metal powders, massive metals and metal compounds (Huntsman et al., 2018; Skeaff et al., 2008, 2011 and 2012; Skeaff and Beaudoin 2014).

The research described in Huntsman et al. (this issue) extends the T/DP to provide additional information about metal removal from the water column. Substrate is added to assess the rate and extent of metal removal, and a resuspension event is mimicked to assess the potential for remobilization of metals. The rationale for this approach was to obtain an assessment of the fate of metal ions in aquatic systems under standardized conditions and based on an existing test method. The extension of the T/DP consists of the following additional steps:

1. A 28-day removal period where substrate is added, in order to measure metal removal rates, and
2. A one-hour resuspension event followed by an additional 4-day settling period, in order to assess the potential for remobilization of metals.

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It must be recognized that in the field, the processes driving metal exchange between the water and sediment compartments are complex. The rationale behind the T/DP-E was not to accurately represent each of these processes, but to work towards a standardized testing approach that includes the most relevant processes. The relative simplicity of the T/DP-E system facilitates better reproducibility. Furthermore, as was the intent of the original T/DP, this extension represents a standardized system within which to compare the behavior of different metals.

A series of proof-of-concept and method optimization experiments were performed as described in Huntsman et al., (this issue) on several metals, including Cu, Ni, Zn, Pb, Co, Sr, and Ag. The T/DP-E methodology (28-day removal period, a 1 h resuspension event, and a 4-day resettling period) was applied to several metals (Cu, Co, Sr) in order to confirm the reliability of the method to assess the long-term metal removal and potential for remobilization/irreversibility. The full results of the CANMETMining study and T/DP-E protocol development can be found in Huntsman et al., (this issue). Results of the study with Cu are presented in Figure 2. Cu is lost rapidly from the water column and is not remobilized following resuspension due to its high affinity for solids and oxyhydroxide surfaces. The concentrations of dissolved Fe were used as an indicator of substrate resuspension. It can be clearly seen that the resuspension triggers an increase in dissolved Fe; however, Cu was not released. The results from this testing confirm the T/DP-E can be used to empirically assess metal removal in a standardized way, forming one of the pillars of the weight of evidence to evaluate metal removal from the water column.

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T/DP-E Modeling

A numerical model was developed in R (R Core Team 2013) to provide mechanistic insight into important processes controlling dissolved metal removal from water column during the experiments performed using the T/DP-E 28-day removal period. Three state variables were defined in the model: the substrate concentration, dissolved metal concentration, and particulate metal concentration. The model considered kinetics of metal adsorption to substrate particles as well as transport of metal between the two model layers representing the overlying water and sediment. For a detailed description of the model, see the Supporting Information.

The 28-day datasets which employed cobalt, copper, and strontium provided a more complete description of the time-variable nature of metal removal and were fit using a single settling velocity and bulk exchange rate for dissolved transport between layers 1 and 2 and metal-specific adsorption rate constants and distribution coefficients. Experimental T/DP-E data and the model fit for copper are shown in Figure 3. Early in the experiment, the added substrate particles settled rapidly. Depending on the rate of adsorption (relative to the rate at which particles settle), some of the copper in the water column adsorbed to the particles and settled with them. The difference between measured total copper and dissolved copper in the early time data represents the amount of adsorbed copper. Once most of the particles had settled from the water column, the dissolved and total copper (measured and modeled data) merged indicating essentially all water column copper was dissolved. Copper removal from the water column continued via transport to and direct adsorption by the settled substrate particles which form the sediment layer. Direct adsorption of metal by sediment as a sole removal process has

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been noted (Bird and Evenden 1996; Nyffeler et al. 1986). It is the combination of the two removal mechanisms described above that causes the total copper line in Figure 3 to exhibit two distinct regions of decreasing concentration. The first ends around day 0.3 when all particles have settled out of the water column and particle-associated copper removal ceases. The concentration decrease in the second region slows after approximately 5 days as dissolve copper in the water column and pore water approach equilibrium. The model was able to fit the data for the 4-day experiments with silver, lead, nickel, and zinc with the same settling velocity and bulk exchange rate determined from the 28-day datasets. Metal-specific parameters (adsorption rate constant and distribution coefficient) were the only parameters that were adjusted to fit to the data. This outcome indicates that the overall amount of removal is related to the individual metal's affinity for particles, which is a unique and intrinsic property of the metal.

Relating Removal from the Water Column to Intrinsic Properties

As discussed in the rationale and summary of results section, metal partitioning to suspended solids plays a critical role in their removal from the water column. Metals that partition well to suspended solids are carried more effectivity to the sediment compartment via settling. The extent of metal removal can be linked quantitatively to intrinsic properties of metal ions by considering mass balance equation for a lake where a simple, first-order model is used to describe metal loss from the water column. This type of model is commonly applied to metals and other non-volatile substances (Thomann and Mueller 1987). A convenient metric for understanding removal timescales is the half-time (t_{50}). This was discussed in Skeaff et al. (2002) and is analogous to a half-life in that it represents the time required for concentration to decrease by 50%. It can be shown (see

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Supporting Information for details), that for a lake where wash-out is negligible compared to metal loss via sedimentation, the half-time is related to the fraction of metal sorbed to particles by the following:

$$t_{50} = \frac{\text{In}(2)H}{v_s}\left(\frac{1}{f_{part}}\right) \quad (1)$$

where v_s is the settling velocity, H is the average water depth, and f_{Part} is the fraction of the total metal in the particulate form. Equation 1 indicates that the half-time, is inversely-related to the to the fraction of the total metal in the particulate form. This model assumes uniform particle size and density among other simplifications. This relationship is evident in the Diamond et al. (1990b) mesocosm data as plotted by (Di Toro et al. 2001b) (Figure 4a). It can also be shown that the relationship between the half-time and the distribution coefficient is

$$t_{50} = \frac{\ln(2)H}{v_s}\left(1+\frac{1}{K_D SPM}\right) \quad (2)$$

where K_D is the distribution coefficient and SPM is the suspended particulate matter concentration.

Consequently, one would expect the relationship between half-time and K_D to be similar to the relationship between half-time and f_{Part}. As discussed previously, Diamond et al. (1990b), measured half-times for metal radioisotope loss from the water column in lake enclosures. They also calculated f_{Part} and K_D from measured total and particle-sorbed isotope concentrations. These data indicate a similar relationship between half-time and K_D and half-time and f_{Part} (Figure 4b).”

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Equations 1 and 2 and the mesocosm data in Figure 4 demonstrate that removal rate—expressed as a half-time—is inversely related to the extent to which metals binding to particles as determined by f_{Part} or K_D. Figure 4 indicates that Co in the mesocosms binds very strongly to the suspended particles (Diamond et al. 1990b). This may be due Co binding to manganese oxides which involves oxidation from Co(II) to Co(III) (Balistrieri and Murray 1986; Balistrieri et al. 1992; Murray and Dillard 1979).

A similar relation between removal and particulate fraction was observed for European estuaries by Di Toro et al. (2001b). They found that for the 12 estuaries examined, metal removal efficiency increased in the order Cd < Zn < Pb, and that this ordering is consistent with the metals' respective partition coefficients. As discussed in the intrinsic properties section, the affinity of a given metal for the functional groups on suspended particulate matter is an intrinsic property of the metal. This demonstrates that removal rate is related to intrinsic properties of metals.

Of the seven metals assessed in the CANMETMining T/DP-E experiments, six (Ag, Co, Co, Ni, Pb, Zn) reached 50% removal within the timeframe of the experiments and one (Sr) did not. The half-times and K_D values associated with the T/DP-E modeling analysis are plotted in Figure 5. This figure shows a qualitatively similar relationship to that in Figure 4b. The T/DP-E protocol is able to discern variations in removal rates related to varying particle affinity of different metals. Highly particle-reactive metals such as Pb have very short half-times whereas the less-particle reactive Sr achieve less than removal in the T/DP-E experiments. The change in half-time ordering of Co in the T/DP-E experiment relative to that in the mesocosm experiments (compare Figures 4 and 5) may

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be due to a lack of manganese oxides in the low binding substrate used in the T/DP-E experiments.

On a more fundamental level, metal ions, by virtue of their electronic structure, possess preferences for binding to different atoms present within ligands. These atoms donate electrons to the central metal and are referred to as Lewis acids. The tendency for metals to bond with various Lewis acids is, therefore, an intrinsic property of the metal. Carbonaro and Di Toro (2007) review and explore various qualitative and quantitative descriptions of metal coordination tendencies. A linear free energy relationship (LFER) was developed to describe monodentate binding of 24 metal ions to negatively-charged oxygen donor atoms (e.g., such as those that exist in phenolic, carboxylic or inorganic hydroxide functional groups). The slope of this linear relationship, α_O (termed the Irving–Rossotti slope), indicates the extent to which a given metal binds preferentially to negatively-charged oxygen donor atoms relative to the proton (Irving and Rossotti, 1956). The Irving–Rossotti slope is an intrinsic parameter of all metals. Each metal has a unique Irving–Rossotti slope.

Select components of particulate matter in lakes (e.g., humic acids, fulvic acids, and metal oxides) bind metals through negatively-charged oxygen donor atoms (Dzombak and Morel 1990; Tipping 2002; Tonkin et al. 2004). These solids—either in the water column or in the sediment—play an important role in metal removal from the water column. Therefore, one would intuitively expect metal removal from the water column to be related to the intrinsic propensity of the metal to oxygen donor atoms associated with particulate matter as expressed by the Irving–Rossotti slope (α_O).

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This relationship was assessed using CanmetMINING OECD 29 T/DP-E experimental data from day 4 of the tests (Figure 6). Day 4 was only used because that was the period of time selected for the majority of the metal removal studies. The regression line in the figure is passed through all data except silver, which appears to be an outlier. The substantial silver partitioning and removal observed in the experiments is likely the result of strong binding to ligands other than oxygen on the substrate used possibly including ligands with reduced sulfur groups (Bell and Kramer 1999; Smith et al. 2002), ligands with carbon-to-carbon double bonds (Hepner et al. 1952; Kasai et al. 1980; Trueblood and Lucas 1952) and ligands with conjugated π-electrons systems (e.g., aromatic chemicals) (Zhu et al. 2004) Equilibrium speciation calculations were used to eliminate silver precipitation as a possible explanation of the observed partitioning and removal behavior. Setting silver aside as an outlier, the relationship in Figure 6 suggests that metal ion removal is indeed related to the relative preference of a metal for oxygen donor atoms (i.e. the Irving-Rossotti slope). This further supports the idea that removal is related to an intrinsic property of metals, and that the T/DP-E allows to distinguish between metals on this basis.

CONCLUSIONS

In addition to the metal-removal processes that occur in the T/DP-E test, other mechanisms further reduce metal availability in natural systems. Primarily, in contrast to natural systems, the T/DP-E test does not have a bedded sediment layer initially. This can impact metal removal in two ways. Preexisting bedded sediment provides an abundance of suspended solids which increases capacity for metal uptake, and exchange of dissolved

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metals across the sediment-water interface is an important removal mechanism that has been demonstrated (Bird and Evenden 1996; Nyffeler et al. 1986).

Another important factor not considered in the T/DP-E is that rapid scavenging of many metals from the water-column in natural systems is followed by slower irreversible change in speciation to more insoluble and non-available forms. As discussed previously in the intrinsic properties section, hard metals ions become incorporated into iron and manganese oxides, while borderline and soft metal ions become incorporated into sulfidic and pyritic solids which exhibit low solubility. Field monitoring has documented that acid volatile sulfide (AVS) is widely found in the sediments of European surface waters, as it is in most depositional sediments (Burton et al., 2007). These solids represent an ultimate sink for these metals in that they exhibit extremely low solubility and are gradually buried by deposition of fresh solids at the sediment water interface.

These metal removal mechanisms collectively allow benthic biological communities to thrive and be exposed only to recently deposited metals. Indeed, this has been well-studied for decades by assessing vertical gradients via sediment cores. Vertical sediment cores taken from the bottom of oceans and lakes reveal a continuous input of metals from natural processes and allows one to discern when metal concentration gradients change due to anthropogenic or natural activities.

Resuspension and remobilization

Huntsman et al., (*this issue – Helen – we need to insert the relevant citation here and elsewhere*) show Cu is not remobilized after settling in the T/DP-E. There are a number of excellent studies demonstrating, in the first instance, the principle of irreversibility of

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metals in sediments and, second, a lack of toxicity when metals are resuspended into the water column due to anthropogenic activities or natural disturbances such as bioturbation (Fetters et al., 2016; Simpson et al. 1998; Van den Berg et al., 2001). For this to happen there must be a change in local conditions where some intervention changes the pH of the aqueous system or, water column concentrations of metal are significantly reduced, by source reduction, such that there is a dis-equilibrium between the water and sediment for a short period of time. This latter phenomenon has been observed in the Salmon River drainage (Idaho, USA) where large amounts of As, Cu and Co were released, with subsequent stream recovery (Mebane et al, 2014).

Surficial sediments are often resuspended via bioturbation, currents, dredging or boat propellers. There are two factors to consider in regard to resuspension and the possible release of dissolved metals: i) oxidative dissolution rates for metal sulfides and ii) scavenging of mobilized metal by binding phases on suspended solids. An experimental study has shown that a small fraction of the total metal present, labeled “easily exchangeable metals” may be released into the dissolved phase. However, this metal is scavenged within minutes to hours by the suspended solids in the water column and quickly resettle, so biotic exposures are negligible (Fetters et al., 2016). A recent review supported that the remobilization potential of Cu from sediments was limited (Rader et al., 2019 in review).

Detoxification of settled metals for benthic organisms

Once metals settle out from the water column, they may then be ingested benthic organisms; however, a large body of literature has failed to show this dietary exposure route results in adverse benthic community responses (DeForest et al., 2007; Meyer et al.,

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2005; Schlekat et al., 2016). Resuspended surficial sediments are frequently resuspended again and again, resulting in a "scrubbing" of easily exchangeable sediment metals and metals from the water column (Simpson et al., 1998; Van den Berg et al., 1986). Several resuspension studies in the peer-reviewed literature only measure total metals, and do not measure speciation changes or document exposure times to biota. Such studies are of limited use, because it is well established that exposure to "total" metals does not correlate with adverse effects or toxicity.

Studies using caged *Hyalella azteca* and indigenous benthic macroinvertebrate colonization of metal spiked sediments showed benthic macroinvertebrates were unaffected as metals quickly partitioned out, unless concentrations exceeded AVS and Fe oxide binding thresholds (Burton et al., 2005; Costello and Burton 2014; Costello et al, 2011, 2012; Custer et al, 2016ab; Mendoca et al., 2017; Nguyen et al., 2011).

This overview provides a weight of evidence-based approach to assess the removal of metals from the water column in the context of hazard classification. Ample literature data is available to show that metals are removed from aquatic systems by naturally occurring processes. This is related to the affinity of metal ions for various ligands that occur in the environment – a reflection of the intrinsic properties of metal ions. The Extended OECD29 Transformation-Dissolution protocol (T/DP-E) was successfully developed to assess and quantify the removal of metals from the water column (Huntsman et al., this issue). This test method allows for a uniform, standardized, and reproducible way to assess the removal rates for various metals under representative environmental conditions. The validity of the proposed T/DP-E method was demonstrated with data on Cu, Ni, Pb, Co, Ag, Zn, and Sr. The modeling analysis of the CanmetMINING T/DP-E experiments indicated multiple phenomena were responsible for removal of metals including (1) kinetically-controlled adsorption to rapidly-settling substrate particles and (2) transport to and direct adsorption by the settled substrate particles. Furthermore, the overall amount of metal removal is related to the individual metal's affinity for particles. Therefore, while this standardized approach does not reproduce the full complexity of metal transformations in real sediments, the dominant processes are effectively mimicked. Taken together, historical and recent peer-reviewed literature, along with recent studies and T/DP-E data, can be used in a substantial weight

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of evidence-based assessment to assess the removal and remobilization potential for metals in the context of environmental hazard classification under GHS

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Figures

Figure 1. Predicted vs. actual metal concentrations in the ocean (data from Di Toro et al., 2001).

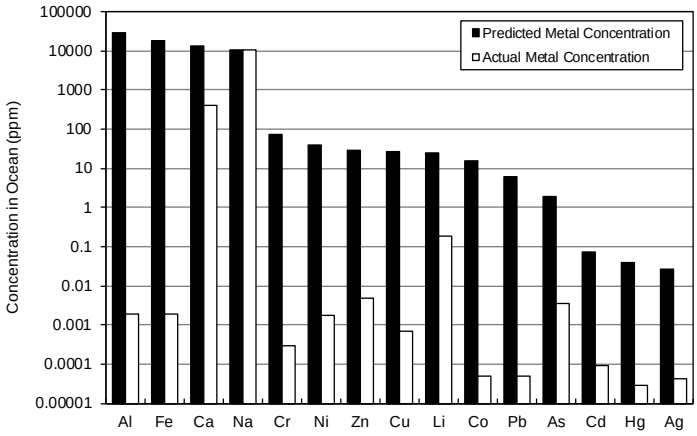

Figure 2. Dissolved (<0.2 µm) Cu concentrations during application of the Extended Transformation-Dissolution protocol (T/DP-E) to measure Cu removal and remobilization. Dissolved Fe concentrations were monitored as an indicator for remobilization of the substrate (see Huntsman et al., this issue).

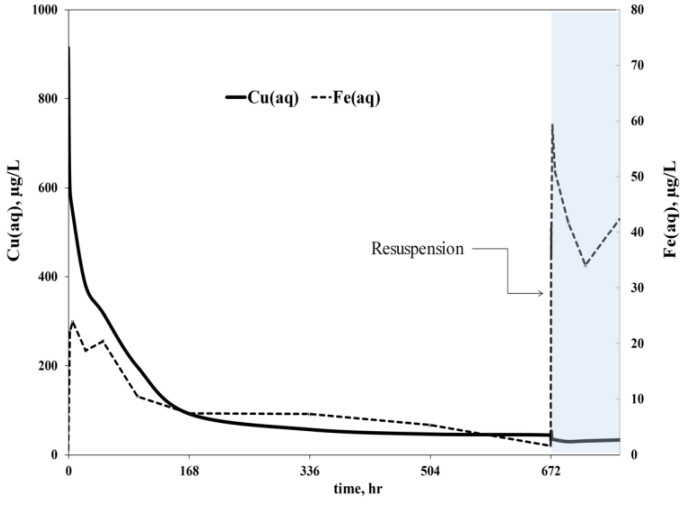

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Figure 3. Experimental data and two-layer model fits for copper (Cu) from the CANMETMining T/DP-E experiments (Huntsman et al., this issue). The time scale (x-axis) is logarithmic. The units of the adsorption rate constant (kads) are L kg−1 d−1 and the units of distribution coefficient (Kd) are L/kg. Data points are the measured values. Filled circles are total metal in the water column and hollow circles are dissolved copper in the water column. The lines are the model output. The solid black line is total copper in the water column (layer 1). The dashed blue line is the dissolved copper in the water column. The dashed red line is dissolved copper in the sediment layer (layer 2) which is comprised of settled substrate particles.

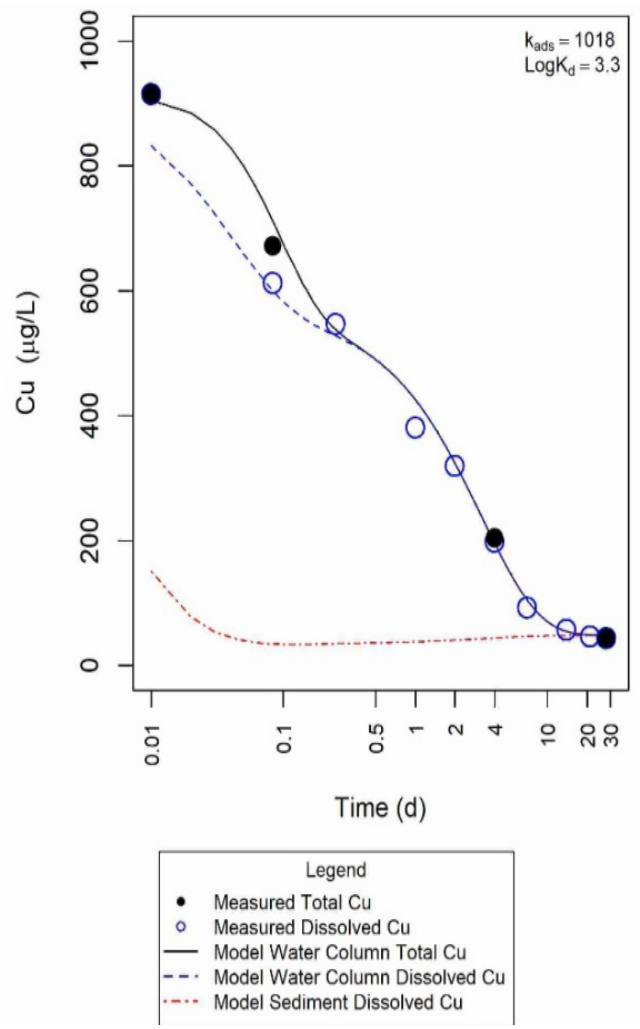

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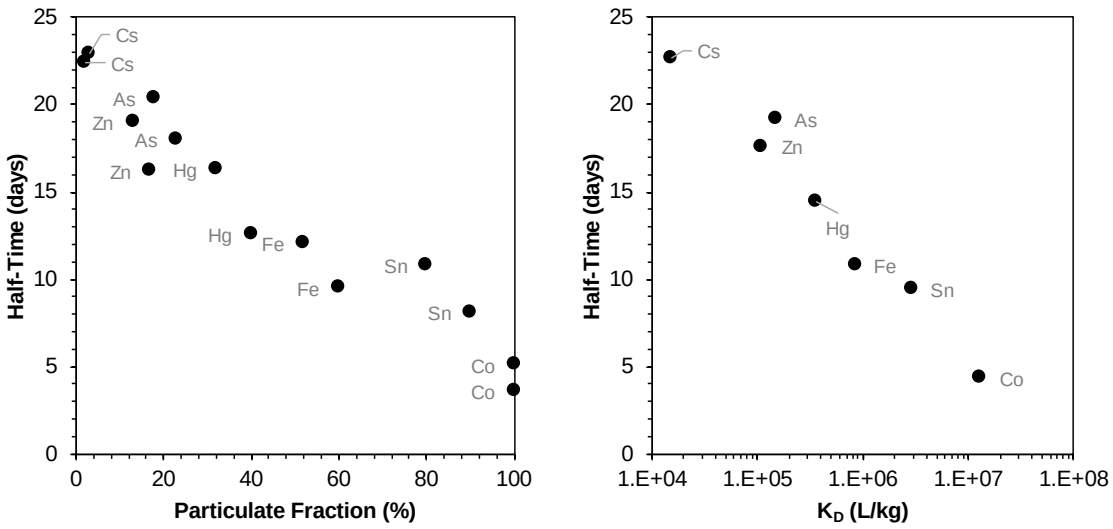
Figure 4. Relationship between removal time and metal partitioning to solids. Data from Diamond et al. (1990b). Plot in panel a from Di Toro et al. (2001b). Note: Diamond et al. (1990) provided measured half-times and particulate fraction values for both enclosures (C-1 and C-2). They, however, only provided an average of measured K_D values from the two enclosures. Therefore, the average half-time for the two enclosures is plotted versus the average K_D in the plot in panel b.



a. **b.**

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Figure 5. Relationship between removal time and metal partitioning to solids for the CANMETMining T/DP-E experiments. Half-times and KD values are those associated with the CANMETMining T/DP-E modeling analysis. Sr is not plotted since 50% removal was not attained during the experiments.

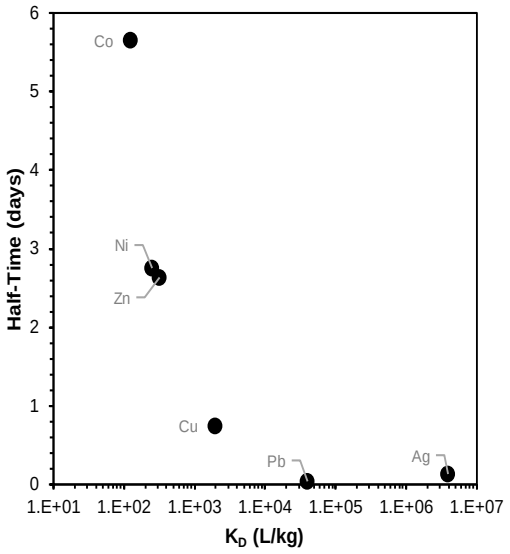
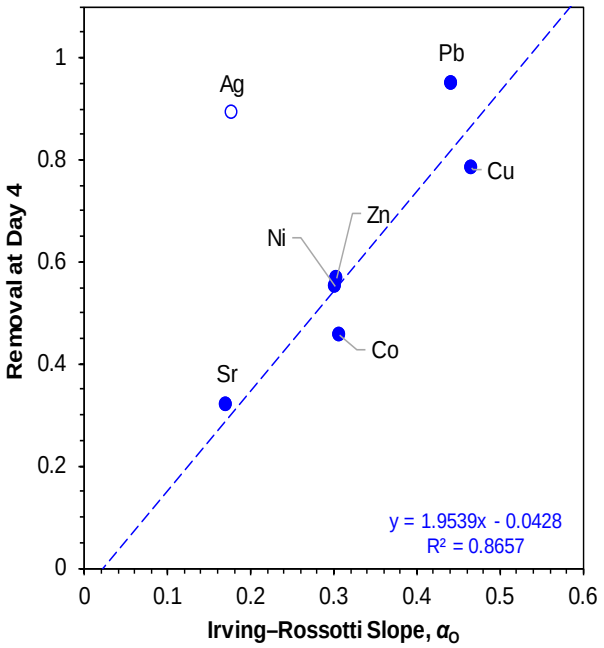


Figure 6. Relationship between removal of metal observed at day 4 of the CanmetMINING experiments (Huntsman et al., this issue) and the Irving-Rossotti slope (αO). The data point for Ag is excluded from the regression.



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