

Critical Perspectives

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 the European Union have developed guidelines for the assessment of long-term (chronic) chemical environmental hazards. This approach recognizes that these hazards are often related to spillage of chemicals into freshwater environments. The goal of the present 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 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 nonavailable and nontoxic forms, and the potential for remobilization of metals from sediment. We developed a test method to quantify metal removal in aqueous systems: the extended transformation/dissolution protocol (T/DP-E). The method is based on that of the Organisation for Economic Co-operation and Development (OECD). The key element of the protocol extension is the addition of substrate particles (as found in nature), allowing the removal processes to occur. The present study focused on extending this test to support the assessment of metal removal from aqueous systems, equivalent to the concept of “degradability” for organic chemicals. Although 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 processes occurring during the T/DP-E method. Some metals, such as copper, rapidly decreased (within 96 h) under the 70% threshold criterion, whereas 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 interlaboratory variability. *Environ Toxicol Chem* 2019;38:1839–1849. © 2019 SETAC

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INTRODUCTION

Chemical substances may be classified and labeled based on their hazard, that is, the intrinsic property of a substance that has the potential to cause adverse effects in a living organism

(Organisation for Economic Co-operation and Development 2003). The United Nations (2017) developed the Globally Harmonized System (GHS) for classification, 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, among other factors, an assessment of its degradability.

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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.

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 because 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 1×10^9 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 Organisation for Economic Co-operation and Development (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 was adopted in the present study to assess the removal of metals from the water column. Skeaff et al. (2002) proposed such an approach to assessing metal "degradability" in the context of loss from the water column, using half-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 in the present 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 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 nonavailable and nontoxic 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 standardized test method to quantify metal removal in aqueous systems: the extended transformation/dissolution protocol (T/DP-E; Huntsman et al. 2019, this issue). This test method is based on the existing OECD 29 T/DP,

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. The present study 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.

APPROACH, RESULTS AND DISCUSSION

The weight-of-evidence approach can be subdivided into 4 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 1992). The formation of metal precipitates with sulfides and carbonates in sediments is also typically covalent. Adsorption of metals to naturally occurring ligands therefore constitutes material changes in metal speciation, which lower the bioavailability 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 (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 directions (Stumm and Morgan 1996). 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 and dissolution reactions of, for example, minerals can occur at slow rates (Stumm and Morgan 1996). The time required for a metal to desorb from a mineral surface or dissolve from a sulfide precipitate often exceeds 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 (Sigg et al. 1987; Mackay and Diamond 1989; Diamond et al. 1990a). Once in the sediment, the concentration of solids, and therefore potential ligands, is quite large, and the distribution of ligands is more 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 (Morse et al. 1987; Di Toro et al. 1990, 1992). 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 adsorbed to mineral surfaces, POM, or precipitate as amorphous oxides, hydroxides, and carbonates (Stumm and Morgan 1996). 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 has been shown to have minimal, if any, long-term impact on the quality of overlying water (Calmano et al. 1993; Caetano et al. 2003; 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, metals, based on their intrinsic properties, tend to sorb on suspended particulate matter. Because this particulate matter settles at appreciable rates, any associated metals are removed simultaneously. Di Toro et al. (2001b) demonstrated metal removal in oceans on a global scale in a simple dilution analysis in which sodium was used as a conservative tracer for metal weathering/transport from the lithosphere to the oceans. Concentrations of many metals (notably aluminum, iron, nickel, zinc, copper, cobalt, lead, and silver) predicted by dilution were orders of magnitude higher than the actual observed concentrations in the oceans (Figure 1). This nonconservative 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 (Thomann 1984; Mills et al. 1985) 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; Gächter 1979; Santschi et al. 1986; Diamond et al. 1990b; Hart et al. 1992; Hommen et al. 2016; Bird and Evenden 1996; Schäfers 2003; Smolyakov et al. 2010a, 2010b; Rand et al. 2011); and 3) removal of metals (including As, Co, Cs, Cu, Fe, Hg, Mn, Se, Sn, and Zn) in whole-lake field studies (Effler et al. 1980; Hesslein et al. 1980; Santschi et al. 1986; Bird et al. 1995; Haughey et al. 2000; van Hullebusch et al. 2002, 2003a, 2003b, 2003c; Liu et al. 2006). Studies on Cu are particularly plentiful given the use of Cu sulfate as an algacide in ponds, lakes, and reservoirs. In a recent review by Rader et al. (2019), which included many of the references just cited, the time required for 70% removal of Cu varied from 0.84 to 27 d, with one exception of 130 d. For the majority of studies, >70% of the added Cu was removed from the water column within 16 d of dosing. For other metals, the referenced

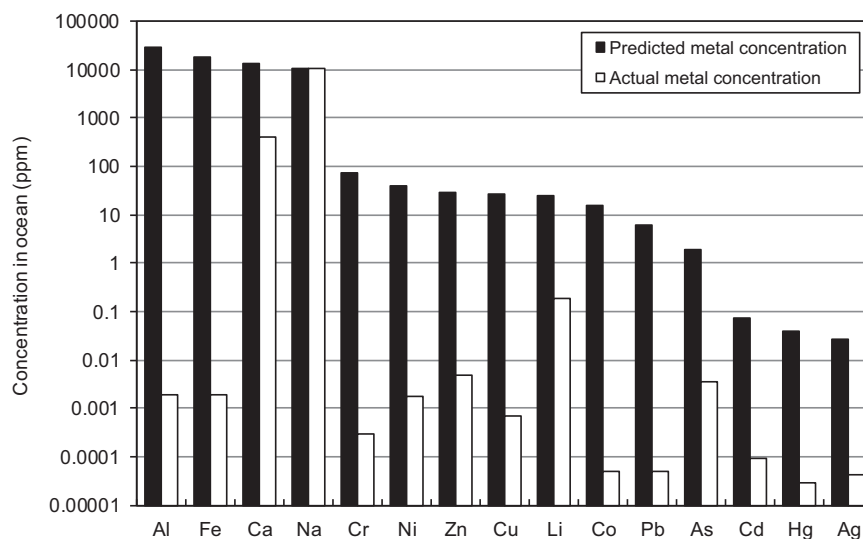


FIGURE 1: Predicted versus actual metal concentrations in the ocean (data from Di Toro et al. 2001).

literature supports substantial metal removal on timescales 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 2 mesocosms, in days): Co (4.35), Fe (10.8), Zn (17.6), As (19.2), Sn (9.45), Cs (22.65), and 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), and 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 porewater, 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 (Van den Berg et al. 2001; Burton et al. 2005; Costello et al. 2012, 2015, 2016; Mendonca et al. 2017), 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 (Van den Berg et al. 2001; Tonkin et al. 2004; Burton et al. 2005; Nguyen et al. 2011; Costello et al. 2012). Their role is important in virtually all freshwater sediments that are oxidized because that is where most benthic biota reside. Acid-volatile sulfides 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 permanent removal. Afterward, under settled conditions, AVS are regenerated (e.g., Costello et al. 2012, 2016; Fetters et al. 2016; 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 as a result of sorption, complexation, and transformation processes (Costello et al. 2015, 2016; Schlegel et al. 2016; Mendonca et al. 2017; Nedrich et al. 2017). All studied metals (Cu, Ni, and Zn) were strongly sorbed to sediments regardless of their 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., Chapman et al. 1998; Atkinson et al. 2007; Hong et al. 2011; Nguyen et al. 2011; Nedrich et al. 2017). Metal concentrations in the porewater of sediments declined through time as metals were transformed from the dissolved to particulate species causing a decreased solubility through time.

Because AVS was lost as a result of 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 be expected following a change in metal speciation to nonavailable forms (Flemming and Trevors 1989; Simpson et al. 1998; Stauber et al. 2000; Plach et al. 2011; Costello et al. 2011, 2012, 2015, 2016; De Jonge et al. 2012; Fetters et al. 2016).

The T/DP-E: Assessing metal removal and remobilization using a standardized method

The OECD 29 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 GHS classification system, the measured metal concentrations are then compared with the acute or chronic ecotoxicity reference values. This, together with an assessment of degradability, allows us 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 (Skeaff et al. 2008, 2011, 2012; Skeaff and Beaudoin 2014; Huntsman et al. 2018).

The research described in Huntsman et al. 2019 (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-d removal period where substrate is added, to measure metal removal rates, and 2) a 1-h resuspension event followed by an additional 4-d settling period, to assess the potential for remobilization of metals.

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 toward 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 was performed as described in Huntsman et al. 2019 (this issue) on several metals, including Cu, Ni, Zn, Pb, Co, Sr, and Ag. The T/DP-E methodology (28-d removal period, 1-h resuspension event, and 4-d resettling period) was applied to several metals (Cu, Co, Sr) to confirm the reliability of the method to assess the long-term metal removal and potential for remobilization/irreversibility. The full results of the

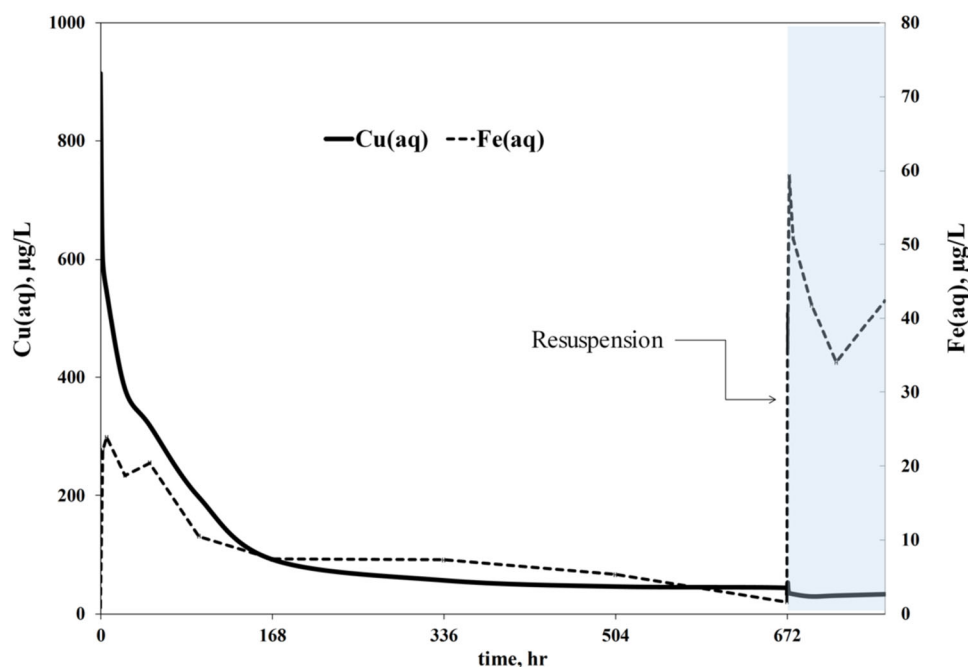


FIGURE 2: Dissolved (<math><0.2\ \mu\text{m}</math>) Cu concentrations during application of the extended transformation-dissolution protocol to measure Cu removal and remobilization. Dissolved Fe concentrations were monitored as an indicator for remobilization of the substrate (see Huntsman et al. 2019, this issue).

CANMETMining study and T/DP-E protocol development can be found in Huntsman et al. 2019 (this issue). Results of the study with Cu are presented in Figure 2. Copper is lost rapidly from the water column and is not remobilized following resuspension because of 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 that 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.

T/DP-E modeling

A numerical model was developed in R (R Development Core Team 2013) to provide mechanistic insight into important processes controlling dissolved metal removal from the water column during the experiments performed using the T/DP-E 28-d removal period. Three state variables were defined in the model: 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 2 model layers representing the overlying water and sediment. For a detailed description of the model, see the Supplemental Data.

The 28-d data sets which employed Co, Cu, and Sr 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 Cu 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 Cu in the water column adsorbed to the particles and settled with them. The difference between measured total Cu and dissolved Cu in the early time data represents the amount of adsorbed Cu. Once most of the particles had settled from the water column, the dissolved and total Cu (measured and modeled data) merged, indicating that essentially all water column Cu was dissolved. Removal of Cu 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 been noted (Nyffeler et al. 1986; Bird and Evenden 1996). It is the combination of the 2 removal mechanisms that causes the total Cu line in Figure 3 to exhibit 2 distinct regions of decreasing concentration. The first ends at approximately day 0.3 when all particles have settled out of the water column and particle-associated Cu removal ceases. The concentration decrease in the second region slows after approximately 5 d as dissolved Cu in the water column and porewater approach equilibrium. The model was able to fit the data for the 4-d experiments with Ag, Pb, Ni, and Zn with the same settling velocity and bulk exchange rate determined from the 28-d data sets. 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.

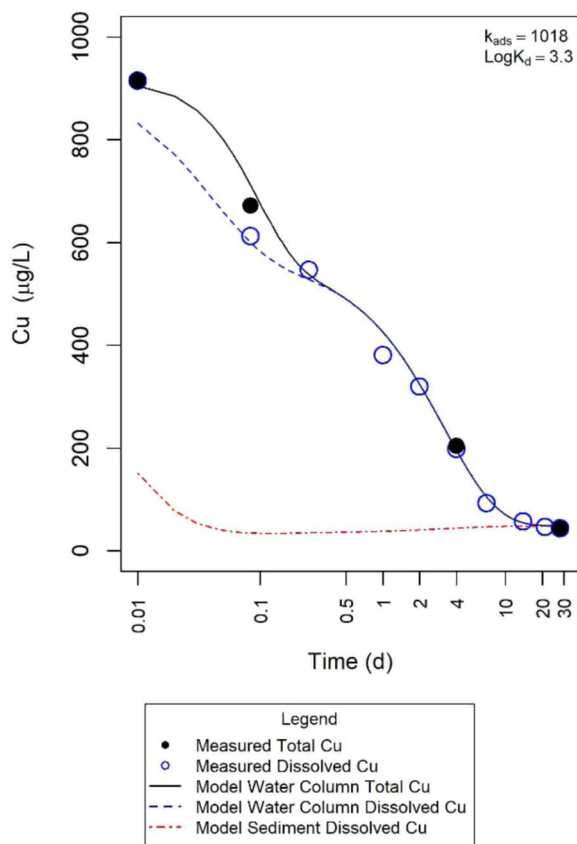


FIGURE 3: Experimental data and 2-layer model fits for Cu from the CANMETMining extended transformation-dissolution protocol experiments (Huntsman et al. 2019, this issue). The time scale (x-axis) is logarithmic. The units of the adsorption rate constant are liters per kilogram per day, and the units of distribution coefficient are liters per kilogram. Data points are the measured values. Filled circles are total metal in the water column, and hollow circles are dissolved Cu in the water column. The lines are the model output. The solid black line is total Cu in the water column (layer 1). The dashed blue line is the dissolved Cu in the water column. The dashed red line is dissolved Cu in the sediment layer (layer 2), which is comprised of settled substrate particles. k_{ads} = adsorption rate constant; K_d = distribution coefficient.

Relating removal from the water column to intrinsic properties

As discussed in the *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 effectively to the sediment compartment via settling. The extent of metal removal can be linked quantitatively to intrinsic properties of metal ions by considering a 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 nonvolatile 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 the concentration to decrease by 50%. It can be shown (see Supplemental Data for details) that for a lake where washout is negligible compared to metal loss via

sedimentation, the half-time is related to the fraction of metal sorbed to particles by

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

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 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, 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).

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 bind 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 attributable to Co binding to manganese oxides which involves oxidation from Co(II) to Co(III) (Murray and Dillard 1979; Balistrieri and Murray 1986; Balistrieri et al. 1992).

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 $\text{Cd} < \text{Zn} < \text{Pb}$ and that this ordering is consistent with the metals' respective partition coefficients. As discussed previously, 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 the intrinsic properties of metals.

Of the 7 metals assessed in the CANMETMining T/DP-E experiments, 6 (Ag, Co, Cu, Ni, Pb, Zn) reached 50% removal within the time frame 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 the varying particle affinities of different metals. Highly particle-reactive metals such as Pb have very short half-times, whereas the less particle-reactive Sr achieves less

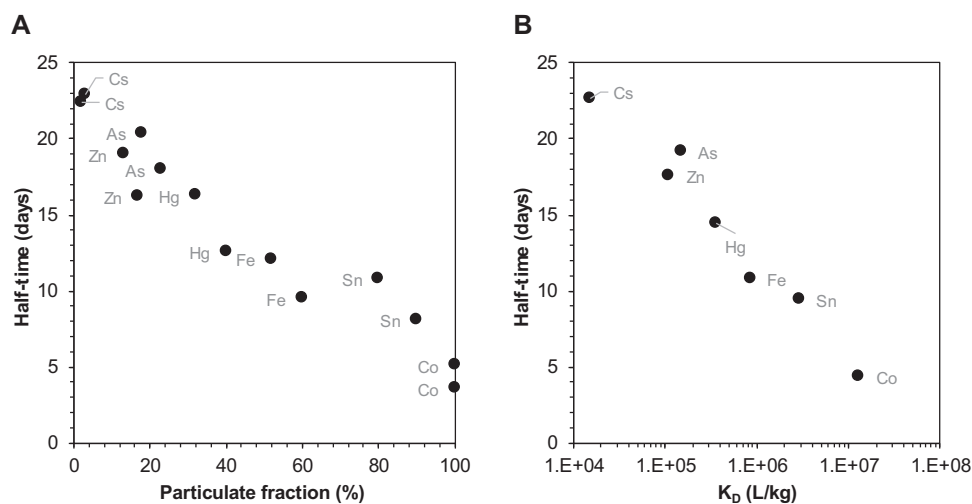


FIGURE 4: Relationship between removal time and metal partitioning to solids. Data from Diamond et al. (1990b). Plot in (A) from Di Toro et al. (2001b). Diamond et al. (1990) provided measured half-times and particulate fraction values for both enclosures (C-1 and C-2). They, however, only provided an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

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 be attributable 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 was developed to describe monodentate binding of 24 metal ions to negatively charged oxygen donor atoms (e.g., those that exist in phenolic, carboxylic, or inorganic hydroxide functional groups). The slope of this linear relationship, α_O (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).

This relationship was assessed using CanmetMINING OECD 29 T/DP-E experimental data from day 4 of the tests (Figure 6). Day 4 was used because that was the period of time selected for the majority of the metal removal studies. The regression line in the figure passes through all data except Ag, which appears to be an outlier. The substantial Ag 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; Trueblood and Lucas 1952; Kasai et al. 1980), and ligands with conjugated π -electrons systems (e.g., aromatic chemicals; Zhu et al. 2004). Equilibrium speciation calculations were used to eliminate Ag

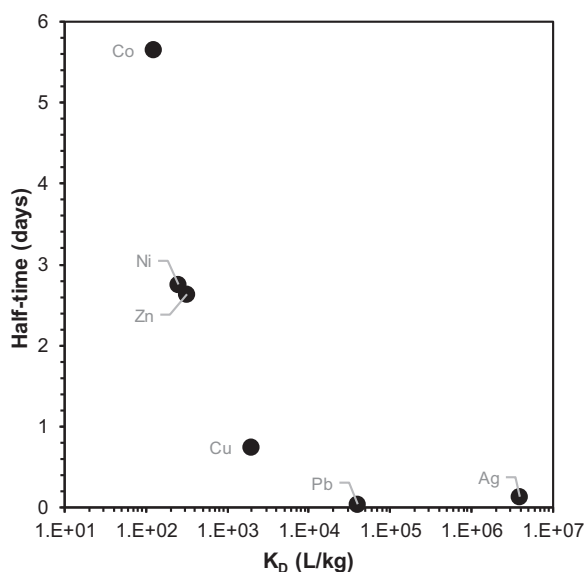


FIGURE 5: Relationship between removal time and metal partitioning to solids for the CANMETMining extended transformation-dissolution protocol (T/DP-E) experiments. Half-times and distribution coefficient values are those associated with the CANMETMining T/DP-E modeling analysis. Strontium is not plotted because 50% removal was not attained during the experiments. K_D = distribution coefficient.

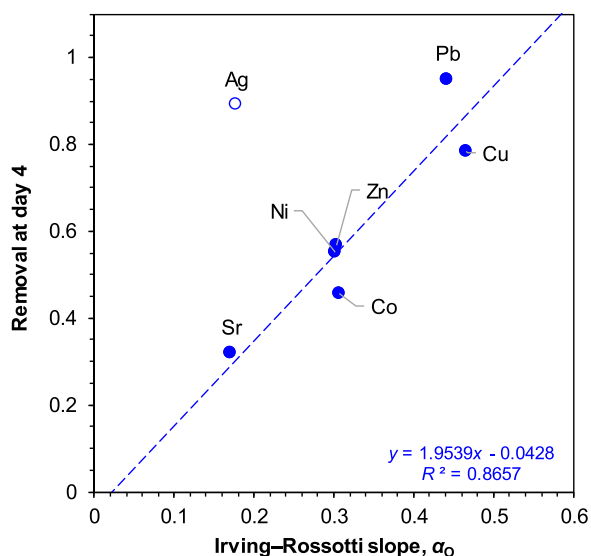


FIGURE 6: Relationship between removal of metal observed at day 4 of the CanmetMINING experiments (Huntsman et al. this issue) and the Irving-Rossotti slope (α_0). The data point for Ag is excluded from the regression.

precipitation as a possible explanation of the observed partitioning and removal behavior. Setting Ag 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 one 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 2 ways. Preexisting bedded sediment provides an abundance of suspended solids, which increases capacity for metal uptake; and exchange of dissolved metals across the sediment–water interface is an important removal mechanism that has been demonstrated (Nyffeler et al. 1986; Bird and Evenden 1996).

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 nonavailable forms. As discussed in the section *Intrinsic properties of metal ions in aquatic systems*, hard metal ions become incorporated into iron and manganese oxides, whereas borderline and soft metal ions become incorporated into sulfidic and pyritic solids which exhibit low solubility. Field monitoring has documented that AVS is widely found in the sediments of European surface waters, as it is in most depositional sediments (Burton et al. 2005). 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 allow one to discern when metal concentration gradients change as a result of anthropogenic or natural activities.

Resuspension and remobilization

Huntsman et al. 2019 (this issue) show that 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 metals in sediments and, second, a lack of toxicity when metals are resuspended into the water column because of anthropogenic activities or natural disturbances such as bioturbation (Simpson et al. 1998; Van den Berg et al. 2001; Fetters et al. 2016). 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 disequilibrium 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. 2015).

Surficial sediments are often resuspended via bioturbation, currents, dredging, or boat propellers. There are 2 factors to consider in regard to resuspension and the possible release of dissolved metals: 1) oxidative dissolution rates for metal sulfides, and 2) 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).

Detoxification of settled metals for benthic organisms

Once metals settle out from the water column, they may be ingested by benthic organisms; however, a large body of literature has failed to show that this dietary exposure route results in adverse benthic community responses (DeForest et al. 2007; Schlekot 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 (Van den Berg et al. 2001; Simpson et al. 1998). 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 that benthic macroinvertebrates were unaffected as metals quickly partitioned out, unless concentrations exceeded AVS and Fe oxide binding thresholds (Burton et al. 2005; Nguyen et al. 2011; Costello et al. 2011, 2012; Costello and Burton 2014; Custer et al. 2016a, 2016b; Mendonca et al. 2017).

The present study 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 are 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 T/DP-E was successfully developed to assess and quantify the removal of metals from the water column (Huntsman et al. 2019, 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 that 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, although 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 of evidence–based assessment to assess the removal and remobilization potential for metals in the context of environmental hazard classification under GHS.

Supplemental Data—The Supplemental Data are available on the Wiley Online Library at DOI: 10.1002/etc.4470.

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