# Assessing Removal of Metals from the Water Column For Chronic Environmental Hazard Classification

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# Introduction

Under the GHS & CLP, classification chronic environmental hazards is based on degradability.

- Effects of rapidly degraded substances are localized/short-lived

Degradability of metals:

- Transformation instead of degradation
- Skeaff et al. (2002) proposed assessing metal "degradability" in the context of loss from water column, using half-times

GHS (section A9.7.1.5):
*"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 ).

# Goals

- Assess concept of **metal ion removal from the water column** in the context of hazard assessment and classification.

- Providing evidence of **metal degradability** in terms of removal from the water column via the following:
  - Adsorption to settling particles,
  - Transformation of metals to non-available, non-toxic forms, and
  - Sequestration in sediment that effectively irreversible (i.e. lack of remobilization)

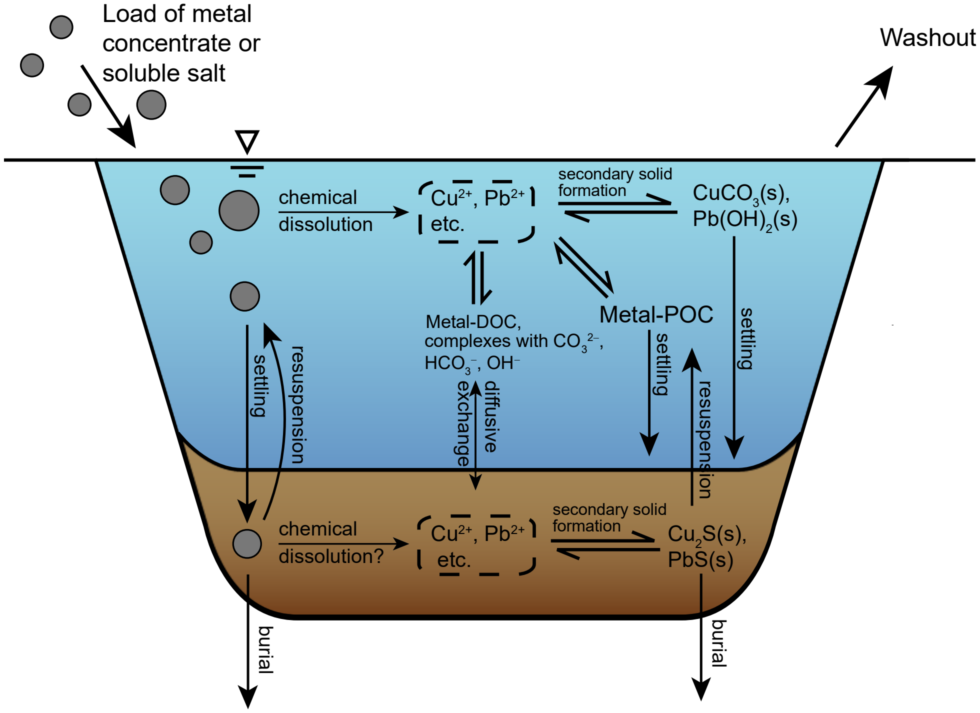
# Supporting Evidence

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

# WoE #1: Intrinsic Properties of Metals

**Important processes that dictate extent and time scale of metal removal from the water column:**

- Chemical (oxidative) dissolution
- Complex formation
- Adsorption
- Precipitation (aging)
- Diffusive exchange
- Settling/resuspension
- Burial



***Which of these processes can be related to the intrinsic properties of the metal that is being removed?***

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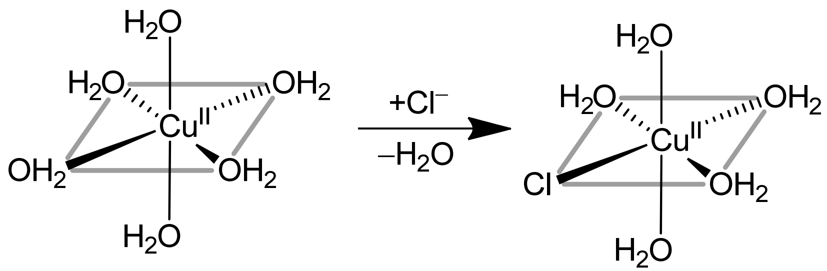
# #1: Intrinsic Properties of Metals

**The Importance of Chemical Speciation**

- Metals undergo *changes in chemical speciation* which involve *breaking and forming of bonds with significant covalent character*
  - Complex formation (e.g. $CuCl_2^0$), partitioning to DOC, POC, HFO, HMO, etc.; precipitation with sulfide



$Cu^{2+}$ $CuCl^+$

- Degradation of organics also involves *covalent bond formation/breaking*
  - However interaction of organics with DOC/POC occurs via relatively weak van der Waals attractive forces
- Some *metal speciation* changes are rapid and reversible while others possess slow reaction kinetics, similar to degradation of organics

# #1: Intrinsic Properties of Metals

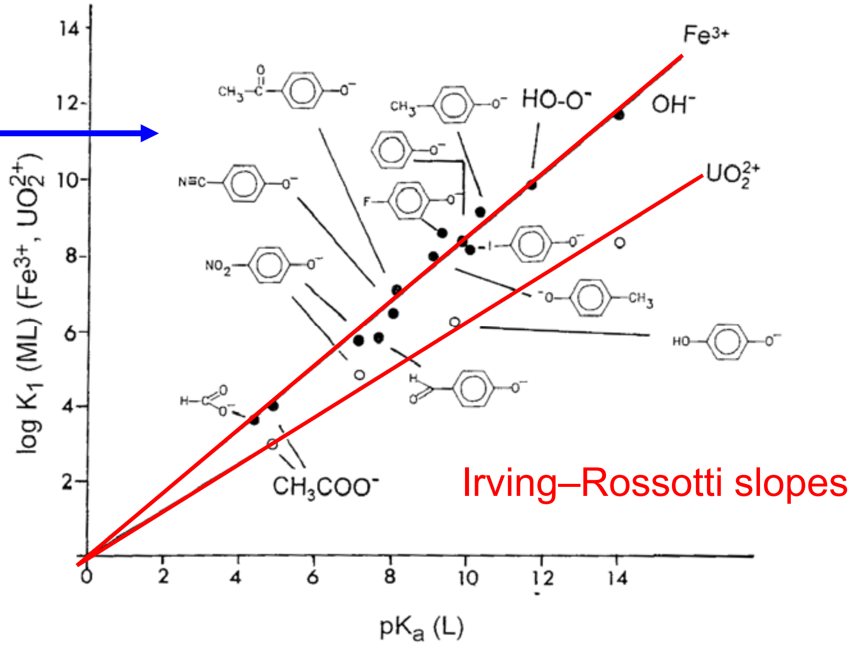
**Changes in Speciation are Predictable from Intrinsic Properties**

- Metal ions have a tendency to bond with functional groups (e.g., -COOH, -OH) on SPM and be transported to sediment
- Metal reactivity is relatable back to intrinsic properties:
  - Ligand Field Theory (Griffith & Orgel, 1957)
    - Describes the bonding, orbital arrangement, and other characteristics of coordination complexes.
  - Hard-Soft Acid Base Theory (Pearson, 1963)
    - Soft/borderline metals exchange O ligands for S and precipitate as metal sulfides
    - Harder metals remain bonded to O-containing ligands and remain adsorbed to mineral surfaces, POC, or precipitate as oxides, hydroxides and carbonates

# #1: Intrinsic Properties of Metals

**Changes in Speciation are Predictable from Intrinsic Properties**

- Linear Free Energy Relationships or “LFERs” (Martell & Hancock, 1980’s)
  - Bonding characteristics and stability of metal complexes with various ligands follow regular patterns
  - Irving-Rossotti allows for estimation of bonding from knowledge of molecular structure and binding of $H^+$

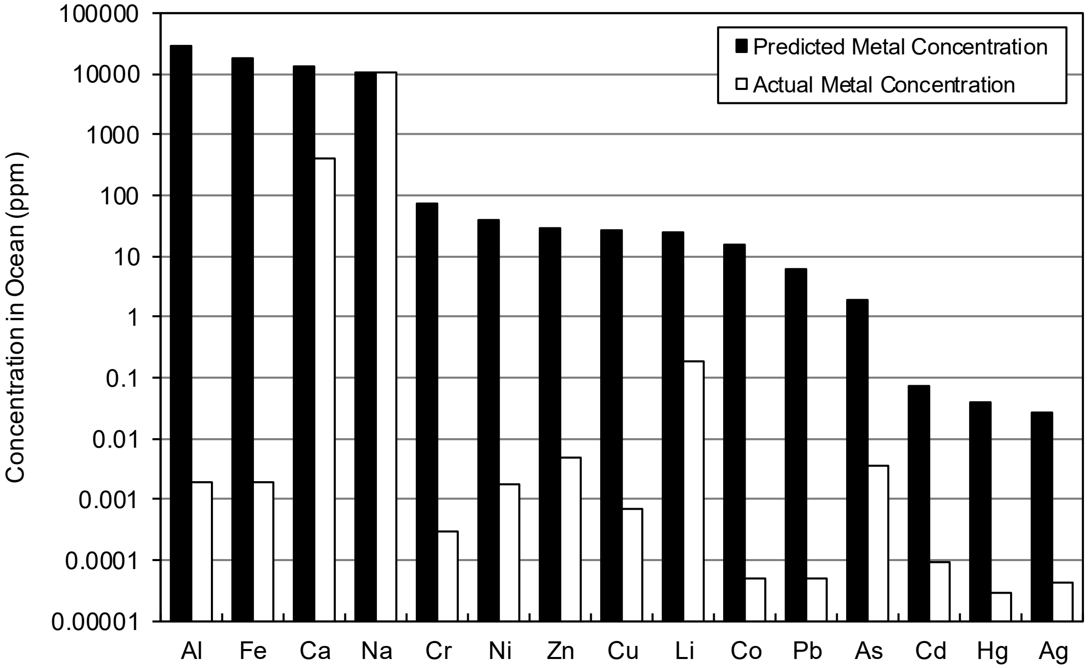


Irving–Rossotti slopes

# #2: Field/Laboratory Studies on Metal Fate

**Numerous studies have demonstrated metal removal in surface waters**

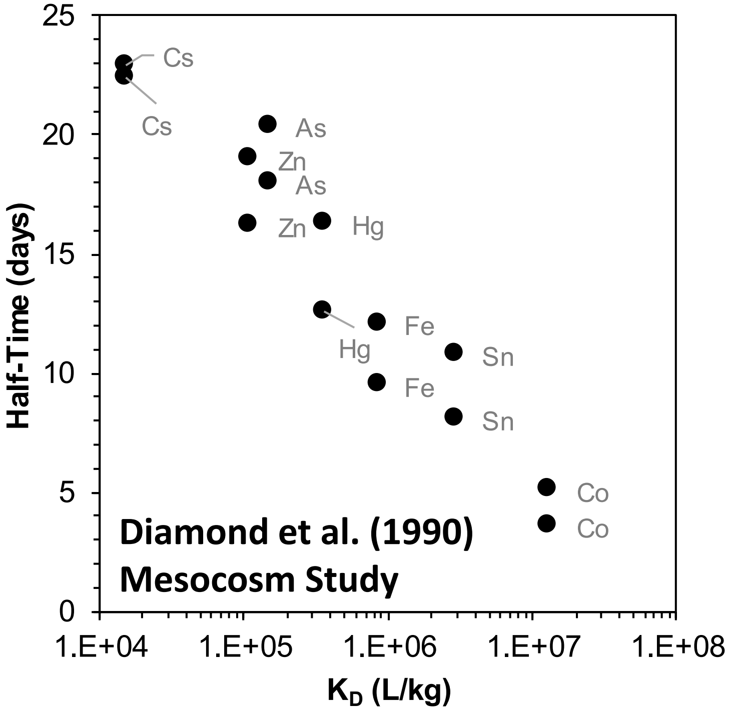
- In near-shore ocean waters, concentration of many metals *predicted* by dilution were orders of magnitude *higher* than observed concentration
- This non-conservative behavior can only be explained by metal removal



# #2: Field/Laboratory Studies on Metal Fate

**Numerous studies have demonstrated metal removal in surface waters**

- Review by Rader et al. (2019), > 70% of added Cu was removed from water column within 2 weeks of dosing for majority of studies
- For 12 estuaries examined by Di Toro et al. (2001), metal removal efficiency increased Cd < Zn < Pb
    - Ordering is consistent w/ metal $K_d$ values

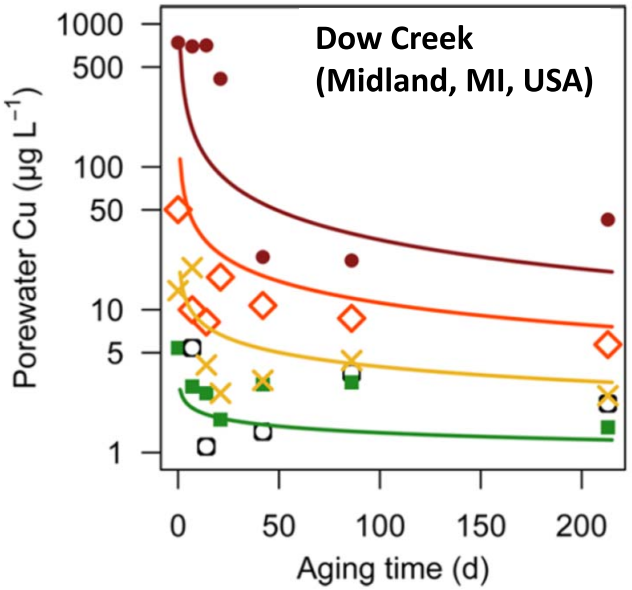


# #2: Field/Laboratory Studies on Metal Fate

**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.**

- Relevant summary of sediment study findings:
  - Sulfides and oxides are the predominant phases responsible for removal
  - Cu, Ni, and Zn are strongly partitioned to sediments regardless of their acid volatile sulfide (AVS) and OC contents.
  - As AVS is lost due to surficial sediment oxidation, metals are increasingly associated with amorphous or crystalline Fe oxides

**Costello et al. (2015) Flow-Through Study**



# #3: Development of Extended OECD 29 T/DP

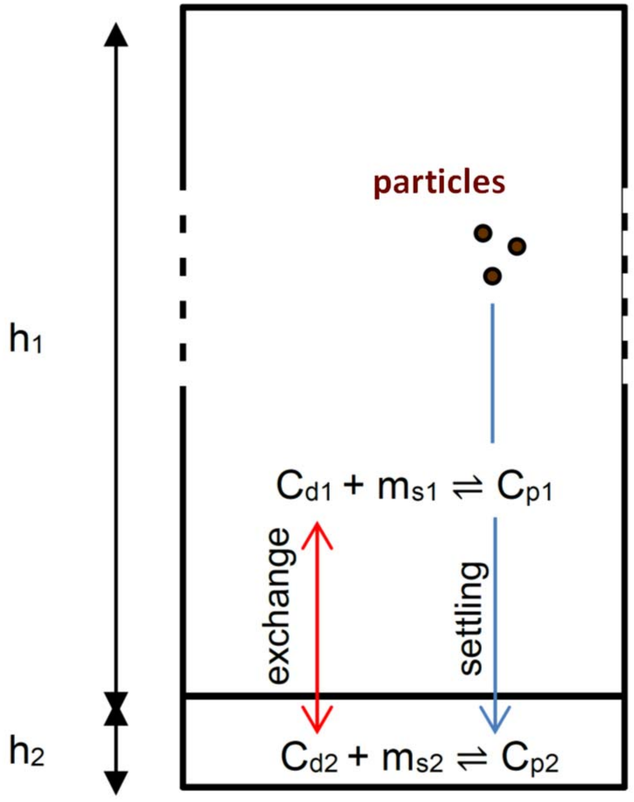
**Existing Protocols are not Sufficient for Assessing Metal Removal from the Water Column**

- 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
- **A T/DP extension (T/DP-E) is proposed** to provide additional information about metal removal from the water column.
  - Substrate and metal are both added to the water to assess the rate and extent of metal removal
  - 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.

# #4: T/DP-E Mechanistic Model

**Models Provide Mechanistic Insight into Metal Removal Mechanisms and Processes**

- A numerical model was developed 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.
  - Metal-specific parameters included: adsorption rate constant and distribution coefficient (these 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.

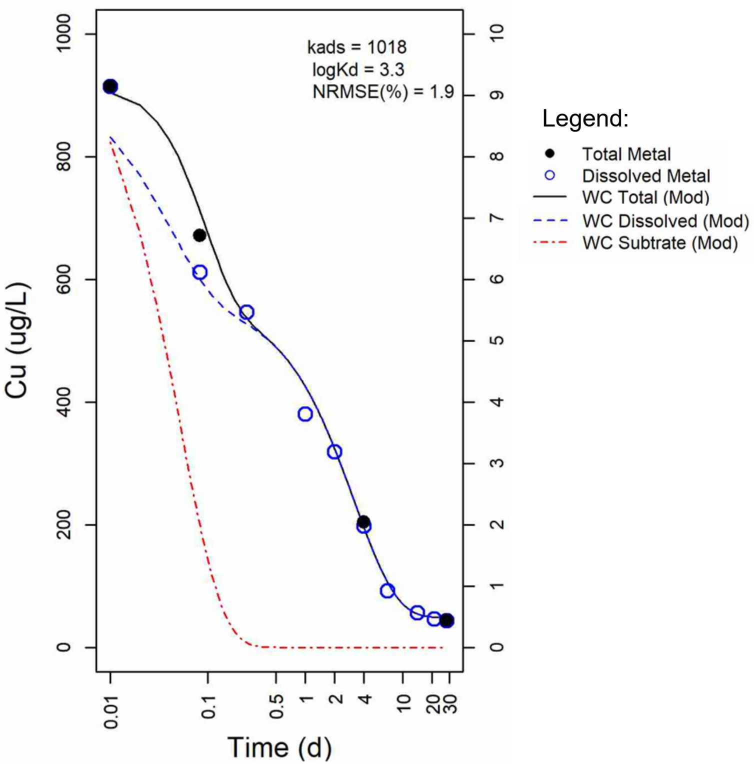


# #4: Model Results: Copper

## Models Provide Mechanistic Insight into Metal Removal Mechanisms and Processes

Insight provided by TD/P-E model results:

- Added substrate particles settle rapidly
- Some metal in water column adsorbs to particles, settles w/ the particles
- Once particles have settled from water column, dissolved and total metal concentrations are the same
- Metal removal from water column continues via transport to/direct adsorption by settled substrate particles
- Model fit the data for 4-day experiments with Ag, Pb, Ni, and Zn w/ the same settling velocity and bulk exchange rate determined from 28-day datasets for Cu, Co, and Sr.



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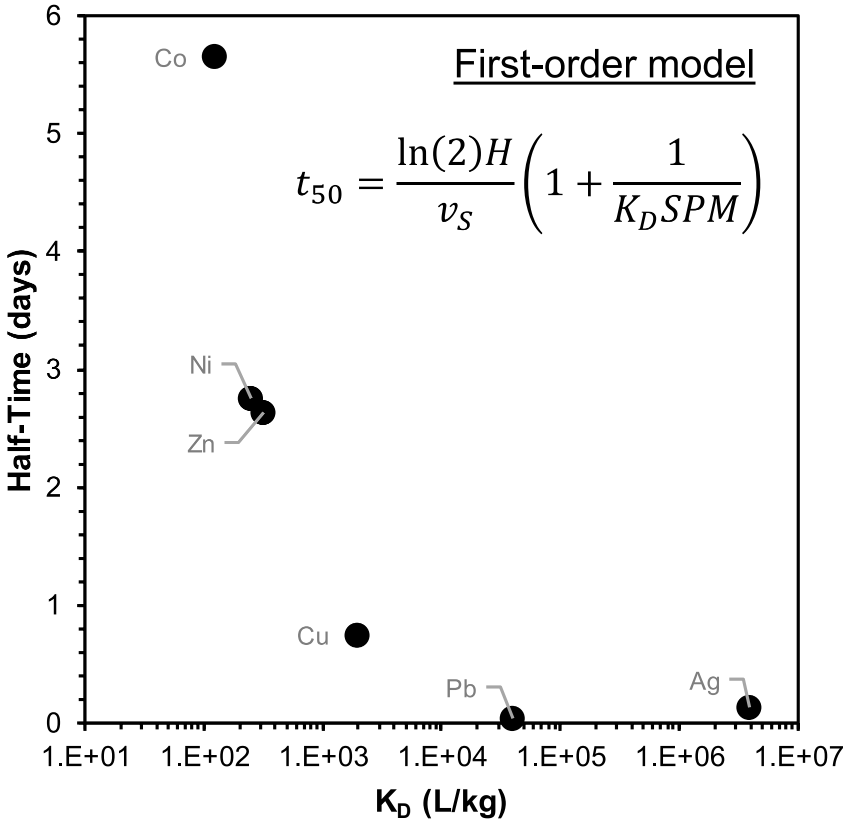
# Relating Water Column Removal to Intrinsic Properties

T/DP-E protocol is able to discern variations in removal rates related to varying particle affinity of different metals.

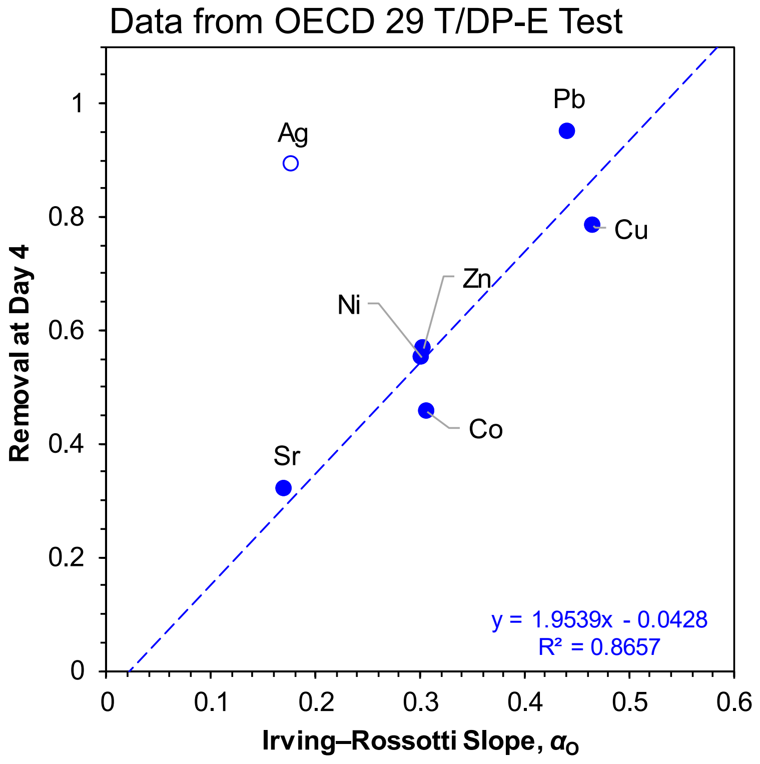
- Highly particle-reactive metals such as Pb have very short half-times
- Less-particle reactive Sr achieve less removal in the T/DP-E experiments.



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

# Relating Water Column Removal to Intrinsic Properties

- The tendency for metals to bond with functional groups on POC and oxides can be quantified using Irving–Rossotti slopes
- The Irving–Rossotti slope is an intrinsic parameter of all metals - each metal has a unique value
  - The outlier (Ag) is likely the result of strong binding to ligands other than oxygen on the substrate (e.g. sulfur atoms)



# Additional Removal Mechanisms

**Additional metal-removal processes that are not represented in the T/DP-E test:**

- The T/DP-E test does not have an initial substrate loading
  - An initial substrate loading would provides an abundance of suspended solids which increases capacity for metal uptake
  - Exchange of dissolved metals across the sediment-water interface is an important removal mechanism that has been demonstrated in several studies
- In natural systems, the rapid scavenging of many metals from the water column is followed by slower irreversible change in speciation to more insoluble and non-available forms.
  - Borderline and soft metal ions become incorporated into sulfidic and pyritic solids which exhibit low solubility.
  - Hard metals become incorporated into hydroxides and oxides

# Concluding Remarks

- Ample literature data is available to show that **metals are removed from aquatic systems** by naturally occurring processes.
- **Removal results from a change in metal speciation** which can be quantitatively 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 proposed **T/DP-E** is a uniform, standardized, and reproducible method 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 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.