

Metal Classification using a Unit World Model (TICKET-UWM) 5th DRAFT

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1. INTRODUCTION

European Union (EU) regulations pertaining to Classification, Labelling, and Packaging (CLP) of chemical substances follow the United Nations Globally Harmonized System (UN GHS). Annex 9 of the GHS document on classification and labelling recognizes speciation, partitioning, and precipitation as critical elements in metal hazard classification. It also provides an initial discussion on how transformation of metals to potentially less toxic forms (via partitioning and precipitation) and subsequent removal from the environment (i.e., the water column) can be analogous to degradation of organic chemicals in the context of classification (United Nations, 2011). Further practical guidance on environmental transformation of metals was provided in the EU CLP guidance document (ECHA, 2011). This guidance document includes a provision for demonstrating removal from the water column to assess the “persistence” or lack of degradation of metal ions, responsible for the toxicity of metals and metal compounds. In analogy to organic chemicals, “rapid degradation” for metals requires greater than 70% removal within 28 days. However, unlike organic chemicals, where removal from the water column occurs via degradation, metal removal occurs through changes in speciation (partitioning and precipitation) followed by sedimentation which transfers metal to the sediment. Therefore, in line with the GHS guidance, “rapid degradation” for metals requires one to demonstrate not only rapid loss from the water column, but also limited remobilization potential from sediment.

A unit world model for metals in lakes, TICKET-UWM, has been developed that considers key processes affecting metal transport, fate, and toxicity including complexation by aqueous inorganic and organic ligands (e.g., DOC), adsorption to particulate organic carbon (POC), binding to biological receptors (biotic ligands), and transport of dissolved metals and solids between the water column and sediment. The overarching goal of this work was to demonstrate that TICKET-UWM can be used to evaluate long-term effects and hazard classification for metals in line with the guidance in UN-GHS and EU-CLP. TICKET-UWM was used to assess the “degradation” of soluble metal salts in a generalized lake environment resulting from changes of speciation, subsequent precipitation, and sequestration in sediment. The two primary processes modeled include 1) Removal of soluble metal salts from the water column through speciation transformations and sedimentation of particulate metal, and 2) metal speciation transformations and remobilization potential in sediments (as indicated by sediment feedback and diffusive fluxes). Results from metal removal and remobilization potential assessments for copper (Cu), zinc (Zn), lead (Pb), nickel (Ni), cobalt (Co), cadmium (Cd), silver (Ag), and arsenic (As) are presented. Removal/remobilization behavior of select organic chemicals—including some persistent organic pollutants (POPs)—is compared to metals using model simulations paralleling those made for metals.

2. MODELING APPROACH

2.1. TICKET-UWM Background Information

A Unit World Model (UWM) is a screening level model used to assess the fate and effects of chemicals through simultaneous consideration of chemical partitioning, transport, reactivity, and bioavailability (MacKay 1979, MacKay 1991, MacKay et al., 1991). A UWM for metals has recently been developed that explicitly includes a description of the effect of metal speciation in assessing the long-term fate and effects of metals in the environment (Figure 2-1) (Farley et al., 2007 and Farley et al., 2011).

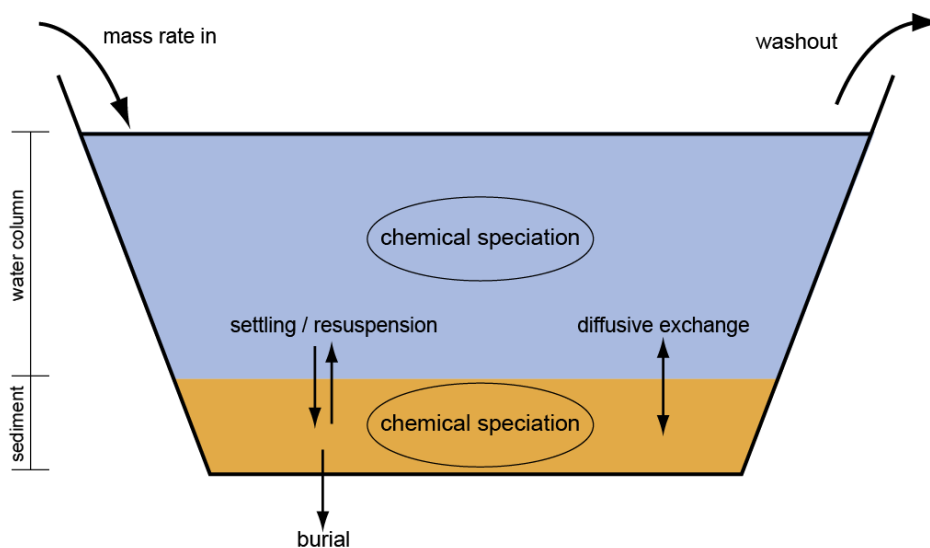


Figure 2-1. Conceptual model for the TICKET Unit World Model for Metals in Lakes (TICKET-UWM).

The model builds on previous screening-level calculations that have been developed for organic contaminants. Unlike previous models, however, the UWM for Metals in Lakes explicitly considers the effects of chemical speciation on metal partitioning, transport and bioavailability in the lake water column and underlying sediments. The numerical engine for the model calculations is the Tableau Input Coupled Kinetics Equilibrium Transport (TICKET) model (Farley et al., 2008). Specific processes considered in the UWM for Metals in Lakes (hereafter referred to as the TICKET-UWM) include:

1. dissolved and particulate phase transport between the overlying water and sediment;
2. metal binding to inorganic ligands, DOC and POC (using information from WHAM V (Tipping and Hurley, 1992; Tipping, 1993; Tipping, 1994), HFO (Dzombak and Morel, 1990), and HMO (Tonkin et al., 2004);
3. metal binding to biological receptors using information from the Biotic Ligand Model (Di Toro et al., 2001a; Santore et al., 2001);

4. metal precipitation as (hydr)oxides, carbonates and sulfides using information from MINEQL+ software (Schecher and McAvoy, 2003);
5. dissolution kinetics for metal powders, massives, etc.;
6. average-annual cycling of organic matter and sulfide production in the lake; and
7. simplified hydrous ferric oxide (HFO) and hydrous manganese oxide (HMO) cycles (HydroQual and Manhattan College, 2010)

During initial development, a simplified version of the model (i.e., no aqueous speciation, and simple linear solid-solution partitioning) was tested using data from Perch Lake (Diamond et al., 1990) and the MELIMEX enclosures in Lake Baldegg (Gächter, 1979; Farley et al., 2007). In these tests, $\log K_D$ values were adjusted to achieve optimal fits to the data. Calibrated $\log K_D$ values were subsequently compared to WHAM V-calculated values (obtained in separate calculations) to assess the applicability of WHAM V as a potential speciation engine for the TICKET-UWM.

Currently, the TICKET-UWM domain consists of a single oxic water column layer and a single sediment layer. The redox state of the sediment (oxic or anoxic) is specified by the user and refers to the set of metal binding phases included in the sediment compartment. For oxic sediment, sulfide production and metal sulfide precipitation are not considered. Metals sorb to POC, HFO, and HMO in the sediment and can precipitate as carbonates, hydroxides, and/or sulfates. For anoxic sediment, metal binding to HFO and HMO is not considered. Metals sorb to POC and can precipitate as sulfides, carbonates, hydroxides, and/or sulfates.

The TICKET-UWM algorithm was constructed as a general solver, with all information on chemical species, chemical equilibrium constants and kinetic rate coefficients stored in external databases. This allows for easy updating of model coefficients (e.g., the WHAM V and BLM binding constants).

The initial version of the TICKET-UWM was developed to perform steady-state calculations with a continuous load of metal(loid). The model was upgraded subsequently to perform time-variable simulations as well. The dynamic response of a lake to a continuous or instantaneous load of a metal(loid) can now be assessed. The metal(loid) source can be specified as a soluble salt subject to instantaneous dissolution or as a powder/massive which dissolves according to a user-specified kinetic expression and rate. The TICKET-UWM software is available free of charge at <http://unitworldmodel.net/>.

Concerning hazard assessment, the TICKET-UWM is capable of assessing removal of soluble metal(loid)s from the water column resulting from changes of speciation and subsequent precipitation. This entails simulation of two sets of processes:

- Removal of soluble metal(loid) salts from the water column through speciation transformations and sedimentation of particulate metal; and

- metal(loid) fate in sediments including metal speciation transformations and remobilization potential in sediments (as indicated by sediment feedback and diffusive fluxes)

As discussed below, model parameterization was standardized for use in hazard classification schemes based on GHS. Standard physico-chemical parameters were collected from several references discussed in detail in the following sections to develop a generalized lake environment, based on the EUSES model, with which to assess hazard.

2.2. Details of Water Column Removal Calculations

2.2.1. Physico-Chemical Parameters Associated with Water Column Removal Calculations

The water chemistries for 28-day TICKET-UWM simulations were based on directives in Annex IV of the Guidance on the Application of the CLP Criteria (ECHA, 2011) and Annex 10 of the *Globally Harmonized System of Classification and Labelling of Chemicals* (GHS) (United Nations, 2011):

- Suspended solids concentrations must be < 15 mg/L. Using the maximum suspended solids concentration of 15 mg/L and assuming $f_{OC} = 0.1$ from Technical Guidance Document on Risk Assessment (European Chemicals Bureau, 2003), the POC used was 1.5 mg/L
- Annex 10 reports a TOC limit of 2 mg/L. This annex describes a laboratory protocol for transformation/dissolution experiments in control solutions. Since the scope of these experiments does not include the introduction of POC, the TOC limit above is interpreted as a DOC value. Therefore, the DOC value of the generalized lake environment simulations was set at 2 mg/L.
- The solution composition (major cations/anions) for 3 different pH values was based upon data from Annex 10.

The chemical composition associated with the three water chemistries in Table 2-1 is generally consistent with summary of environmental parameters prepared from EU monitoring databases (ARCHE, 2013).

Remaining TICKET-UWM input parameters with their basis/references were obtained from the ECHA REACH implementation guidance document summarizing EUSES model parameters (ECHA, 2010) and the RIVM EUSES report (RIVM, 2004). A summary of all TICKET-UWM parameters used for the generalized lake environment calculations is shown in Table 2-1. The sediment resuspension rate was calculated from a solid mass balance in the active sediment layer assuming steady-state conditions (no accumulation/depletion of sediment solids). The following equation was used:

$$v_r = v_s \frac{m}{m_a} - v_b \quad (2-1)$$

where v_s is the settling velocity (2.5 m/d), m is the water column suspended solids concentration (15 mg/L), m_a is the sediment solids concentration (0.5 kg/L), and v_b is the burial rate (0.3 cm/yr). To be consistent with laboratory/mesocosm/field removal tests, the diluting effect of flow into the system was

minimized by increasing the hydraulic residence time of the model lake system from the EUSES value of 40 days (0.11 year) to 300 years.

Table 2-1. TICKET Unit World Model Input Parameters for EUSES Model Lake

Parameter	Value		
Volume of water column, m ³	3.6 × 10 ⁹ ^a		
Surface area of water column, km ²	1200 ^a		
Depth of water column, m	3 ^a		
Active sediment depth, cm	3 ^a		
Residence time of water column, yr	0.110 ^a		
Settling rate, m/d	2.5 ^a		
Burial rate, cm/yr	0.3 ^a		
Resuspension rate, cm/yr	2.44 ^{a,b}		
Diffusive exchange, cm/day	0.24 ^{a,c}		
Suspended solids, mg/L	15		
POC, mg/L	1.5 ^d		
DOC, mg/L	2.0 ^e		
pH ^e	6.09	7.07	8.00
Alkalinity, mg/L as CaCO ₃ ^e	3.85	7.47	37.2
Calcium, mg/L ^e	8.0	32.1	80.1
Magnesium, mg/L ^e	1.2	4.9	12.1
Sodium, mg/L ^e	1.8	3.4	18.0
Potassium, mg/L ^e	0.3	1.2	3.02
Sulfate, mg/L as SO ₄ ^e	4.8	19.2	47.9
Chloride, mg/L ^e	14.5	57.8	145
Sediment solids conc., g/L	500 ^d		
Sediment <i>f</i> _{oc}	0.05 ^d		
AVS, μmol/g _{dry}	0.77 ^f		
Sediment pH, cations, and anions	Same as water column		

^a ECHA REACH implementation guidance document summarizing EUSES model parameters (ECHA, 2010)

^b Calculated using the settling velocity, suspended solids concentration, sediment bulk solid concentration, and the burial (net sedimentation) rate shown in table using a solids balance (Chapra, 1997).

^c EUSES pore water side mass transfer coefficient. Based on Di Toro et al. (1981) mass transfer resistance is all in the sediment.

^d From *Technical Guidance Document on Risk Assessment* (European Chemicals Bureau, 2003)

^e From Annex 10 of the *Globally Harmonized System of Classification and Labelling of Chemicals (GHS)* (United Nations, 2011)

^f 10th percentile value from the Flanders dataset (Vangheluwe, 2005; additional information from: <http://echa.europa.eu/copper-voluntary-risk-assessment-reports> [environment/Risk Characterization/Chapter 3.3.7.1.3.]])

2.2.2. Water Column Removal Modeling Approach

Metal addition was modeled in the TICKET-UWM simulations as a single instantaneous load of a soluble salt to the water column. Soluble salts dissolve instantaneously and completely in the water column. This is in contrast to metal powders/massives which may dissolve at slower rates, may be only sparingly soluble, and, depending on particle size and density, may be subject to rapid settling. Modeling metal addition as a salt, therefore, represents a worst-case scenario for metal release and persistence in the water column.

Initial total metal concentrations in the water column (i.e. the spiking concentration) were set at values listed in Table 2-2. For copper (Cu), the pH-specific acute and chronic ecotoxicity reference values (ERVs) were used as starting concentration in the simulations. For zinc (Zn) and nickel (Ni), acute and chronic ERVs are available at pH 6 and 8 and were used as starting concentrations in the simulations. At the pH 7 water chemistry, the more stringent of the pH 6 and 8 acute ERVs were used. For Pb, acute and chronic ecotoxicity reference values (ERVs) at pH 6, 7, 8 were used as starting calculations in the model simulations. For cobalt (Co), cadmium (Cd), and silver (Ag) the same acute and chronic ERVs were used for each of the three water chemistries. For all the trace metals and arsenic (Cu, Zn, Pb, Ni, Co, Cd and As), water column simulations were also performed with the initial concentration set at 1 mg/L. This is the higher of the two cutoff values for chronic classification as defined in the CLP guidance (ECHA, 2011).

Table 2-2. Summary of Initial Concentrations Used for TICKET-UWM Simulations.

Metal	pH 6		pH 7		pH 8	
	Chronic	Acute	Chronic	Acute	Chronic	Acute
Copper	20	25	7	35	11	30
Zinc	82	413	---	136	19	136
Lead	17.8	73.6	9	52	23.4	107
Nickel	2.4	120	---	68	2.4	68
Cobalt	4.9	90.1	4.9	90.1	4.9	90.1
Cadmium	0.21	18	0.21	18	0.21	18
Silver	0.120	0.220	0.120	0.220	0.120	0.220
Arsenic	40	480	40	480	40	480

Barium (Ba) simulations were run with concentrations ranging from 10 µg/L to 20 mg/L at each of the three pH water chemistries. Arsenic ERVs were provided by the arsenic consortium.

Two methods were used quantify the binding of metals on particles in the water column removal calculations: (1) the linear partitioning method and (2) the speciation model method. In the linear partitioning approach, metal binding to solids in the water column and sediment was described using a constant empirical distribution coefficient (K_D) value. The log K_D values used for each metal are indicated in Table 2-3. This same approach was used for the simulations with organic chemicals.

Table 2-3. Summary of Empirical Distribution Coefficient Values

Metal	Empirical log K_D Values		Source
	SPM	Sediment	
Copper	4.48	4.39	1
Zinc	5.04	4.86	2
Lead	5.47	5.19	3
Nickel	4.42	3.85	4
Cobalt	4.59	2.94	5
Cadmium	5.11	4.00	6
Silver	5.28	4.05	7
Barium	N/A	N/A	N/A

Sources:

1. Heijerick et al., 2005
2. TNO and RIVM, 2006
3. EURAS, ECOLAS and KUL, 2008
4. European Chemicals Bureau, 2008
5. Chemical Safety Report: Cobalt
6. 2005 Risk Assessment Report: Cadmium Oxide and Cadmium Metal
7. Ag Chemical Safety Report (CSR) http://apps.echa.europa.eu/registered/data/dossiers/DISS-9d92ea78-89c7-2334-e044-00144f67d249/DISS-9d92ea78-89c7-2334-e044-00144f67d249_DISS-9d92ea78-89c7-2334-e044-00144f67d249.html (Environmental Fate and Pathways/Transport and distribution/Absorption/desorption)

In the speciation model method, the speciation sub-model within the TICKET-UWM (WHAM V) was used to calculate trace metal log K_D values based on water chemistry (i.e., pH, DOC, cations, and anions) and the concentration of particulate binding phases (POC, HFO, HFO, and HMO) *at each time step in the simulation*. This method accounts for non-linear partitioning behavior associated with changes in total metal concentration in the water column as well as competition between metals, protons and hardness cations (Ca and Mg) for binding sites. Water column removal simulations utilizing the speciation model method were made at three pH water chemistries (Table 2-1). The following simulations considered organic carbon (DOC and POC) only and used the WHAM V speciation model within TICKET-UWM. Currently, the TICKET-UWM model considers POC to be 100% humic acid (50% carbon (w/w)). All of the humic acid constituting POC were considered to be active with respect to metal binding. To be consistent with practices used for copper and nickel, DOC was modeled as being 100% fulvic acid. The fraction of DOC fulvic acid that was considered to be active toward metal binding varied between 40% and 65% based upon previous approaches (Mutch Associates, 2010a, 2010b, 2011a, 2011b).

Both approaches of specifying metal binding have benefits and drawbacks. The linear partitioning method uses actual measured log K_D values. However the empirical log K_D values do not necessarily reflect the specific conditions present at a given site. The speciation model method accounts for the effect of site specific water chemistry and provides detailed information on the specific form of the metal in the system. However, speciation calculations possess uncertainties that can limit the accuracy of the log K_D

predictions. A more detailed discussion of the use of empirical $\log K_D$ values versus model-calculated $\log K_D$ values is provided in Appendix A. The upshot of this discussion is that it is important to consider *both* methods when using model calculations to determine hazard classification.

There exist three potential approaches for assessing metal removal:

1. Metal is added to the model water column as a soluble salt where dissolution is instantaneous (unlike powders or massives which take time to dissolve). The initial metal salt concentration (i.e. nominal or added concentration) is set equal to the reference value. Based upon the assumption of equilibrium speciation (partitioning), the added metal immediately partitions between the suspended particles and solution phase resulting in an initial dissolved metal concentration less than the initial metal added to the computational system according to the distribution coefficient (K_D) and the TSS value:

$$f_{\text{Part}} = \frac{K_D \text{ TSS}}{1 + K_D \text{ TSS}} \quad (2-2)$$

This initial instantaneous removal of metal from the soluble phase to the particles is counted toward the percent removal. After the initial removal, metal removal continues (non-instantaneously) as the finite amount of total metal added to the system maintains its equilibrium with suspended particles and these particles continually settle to the sediment bed. In essence, this approach includes two removal components: 1) removal of initially soluble metal associated with the immediate establishment of solid-solution equilibrium and 2) the removal associated with the settling of particles. According to this approach, the fraction remaining is calculated by dividing the dissolved metal concentration at time t , $C_{\text{Diss}}(t)$, by the initial total metal concentration, $C_{\text{Tot}}(0)$. Hereafter this will be referred to as Approach 1.

2. The initial total metal concentration is set equal to the appropriate reference value and the removal of total metal (particulate + dissolved) in the water column is tracked. According to this approach, the fraction remaining is calculated by dividing the total metal concentration at time t , $C_{\text{Tot}}(t)$, by the initial total metal concentration, $C_{\text{Tot}}(0)$. This approach is conservative in that it assumes that metal on particles is equally bioavailable to dissolved metal. Hereafter this will be referred to as Approach 2.
3. The initial total metal concentration is set at the reference values and the removal of dissolved metal is tracked. According to this approach, removal is calculated by dividing the dissolved metal concentration at time t , $C_{\text{Diss}}(t)$, by the initial dissolved metal concentration, $C_{\text{Diss}}(0)$. Hereafter this will be referred to as Approach 3.

Approaches 1 and 3 are more consistent with Annex IV language since they focus on soluble metal. Approach 3, however, can be problematic: In certain instances, precipitation precludes use of the reference value as the initial dissolved metal concentration. This is particularly true for calculations at the upper chronic cutoff value. This report focuses on simulation results from Approaches 1 and 2 but includes results from Approach 3 as well.

In the sections that follow, plots indicating the metal removal will have the fraction remaining, $C(t)/C_{Tot}(0)$, plotted on the y-axis. A fraction remaining of 0.3 corresponds to a percent removal value of 70%. By plotting the fraction remaining, all plots will have the same general appearance. The y-values range from zero to one and decrease with time. An example figure is shown below (Figure 2-2).

The plot in the left panel (Figure 2-2a) shows the time series of total metal concentration. The dashed line indicates a $C_{Tot}(t)/C_{Tot}(0)$ value of 0.3 or a removal of 70% according to Approach 2. The intersection of the blue and dashed line indicates the time required for 70% removal according to Approach 2.

The plot in the right panel (Figure 2-2b) shows the time series of dissolved metal concentration. This is plotted as $C_{Diss}(t)/C_{Tot}(0)$, which indicates removal according to Approach 1. As discussed above this includes some initial instantaneous removal (Figure 2-2b, gray bracket). The point at which the red line crosses a y-value of 0.3 indicates the time required for 70% removal according to Approach 1. The dashed line in this plot indicates a $C_{Diss}(t)/C_{Diss}(0)$ value of 0.3 or a removal of 70% according to Approach 3. The intersection of the red and dashed line indicates the time required for 70% removal according to Approach 3.

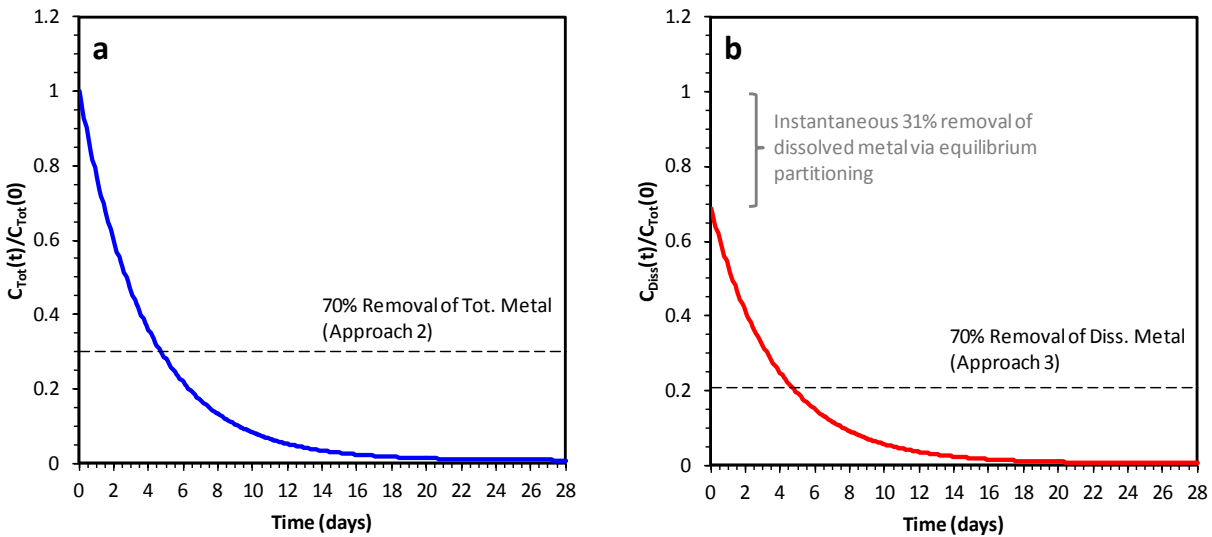


Figure 2-2. Example water column removal plot for a) total and b) dissolved metal.

2.2.3. Sensitivity Analyses

The following simplified mass balance equation for total metal in the water column provides an overview of the factors affecting removal:

$$\frac{dC}{dt} = -C \left(\frac{1}{\theta} + \frac{v_s}{H} f_{Part} \right) \quad (2-3)$$

The rate of change of total metal concentration in the water column (dC/dt) is related to the concentration in the water column (C) through the hydraulic residence time (θ), the settling velocity (v_s), the water depth (H), and the fraction of the total metal in the particulate form ($f_{\text{Part}} = 1 - f_{\text{Diss}}$, where f_{Diss} is the fraction dissolved). While each of these terms may change in time, for a simplified analysis they are treated as constants. The terms in parentheses have dimensions of $\{T^{-1}\}$ and can be thought of as a first-order rate constant describing the gross removal of metal from the water column through washout ($1/\theta$) and particle settling ($v_s f_{\text{Part}}/H$). The relationship between f_{Part} and distribution coefficient, K_D , is given by

$$K_D = \frac{f_{\text{Part}}}{(1 - f_{\text{Part}}) \text{TSS}} = \frac{f_{\text{Part}}}{f_{\text{Diss}} \text{TSS}} \quad (2-4a)$$

or, after rearranging to solve for f_{Part} ,

$$f_{\text{Part}} = \frac{K_D \text{TSS}}{1 + K_D \text{TSS}} \quad (2-4b)$$

where TSS is total suspended solids. Equations 2-3 and 2-4 indicate that the total metal loss rate increases with increasing settling velocity and f_{Part} (i.e., increasing K_D for a fixed TSS value or increasing TSS for a fixed K_D) and with decreasing hydraulic residence time and water column depth. The effect of depth and settling velocity were examined in sensitivity calculations. For these analyses, the following parameter modifications were made:

1. Depth was varied to determine the critical value at which dissolved metal removal (Approach 1) is exactly 70% at day 28.
2. The settling velocity was decreased from the EUSES value of 2.5 m/d to 0.24 m/d. This value (0.24 m/d) is at the lower end of the range of settling velocities for POC and corresponds to particles 1–10 μm in size (Burns and Rosa, 1980).

2.3. Details of Sediment Remobilization Potential Simulations

2.3.1. Rationale

As indicated in the rapid removal provision in Annex IV of the EU CLP guidance document, both rapid removal from the water column *and* limited remobilization potential (by virtue of a speciation changes) are requirements for demonstrating rapid “degradation” of a particular metal. The goal of the calculations described in this section was to assess the extent to which metal in sediment can re-enter the water column.

Important chemical processes in the sediment include complexation to inorganic ligands and organic ligands (including DOC) in the sediment porewater; sorption to metal-binding phases on sediment particles such as POC, HFO, and HMO; and precipitation as metal sulfide carbonate, hydroxide, and sulfate solids. Arsenic can precipitate as solids of S, O, Fe, Ca and Mg. Research has shown that the reaction of trace metals with sulfide (in the form of acid volatile sulfide, AVS) to form insoluble metal sulfide species is a key process that mitigates their bioavailability and toxicity in sediments and influences their fate in natural systems (Di Toro et al., 1990; Ankley et al., 1991; Di Toro et al., 1992; Berry et al.,

1996; Di Toro et al., 1996; Di Toro et al., 2001b). The reduction in trace metal bioavailability afforded by AVS has not been documented for As even though it forms sulfide solids (Nordstrom and Archer, 2003). There is evidence to suggest that the complexation of As by sulfide can reduce its bioavailability (Rader et al., 2004 and Planer-Friedrich et al., 2008); although analytical speciation of As-reduced sulfur species is problematic (Planer-Friedrich et al., 2010).

A systems diagram indicating key transport processes in the TICKET-UWM sediment layer is shown in Figure 2-3. Settling represents the primary metal source to the sediment layer. Resuspension and burial are two processes by which metal leaves the sediment layer. Resuspension re-introduces metal into the water column whereas burial transports metal to the deeper sediment layers. Since burial in the TICKET-UWM is an irreversible process, any metal lost to the deeper sediment permanently leaves the model lake domain. Soluble metal species are transported across the sediment interface via diffusion according to the concentration gradient and, accordingly, this process can serve either as a source to or sink from the sediment layer. Resuspension and diffusion are the transport processes associated with metal remobilization from the sediment to the water column. They comprise a feedback mechanism through which metal concentrations in the sediment influence metal concentrations in the water column. The TICKET-UWM, in its present state, includes an oxic water column with a negligible sulfide concentration. In accordance with the equilibrium mass action law, any metal sulfide solid resuspended from the anoxic sediment layer to the water column immediately dissolves, releasing metal to re-equilibrate between the settling particles the dissolved phase in the water column. Inasmuch as the immediate redistribution supplies dissolved metal in the water column, the model calculations are closer to a worst-case scenario for dissolved metal removal.

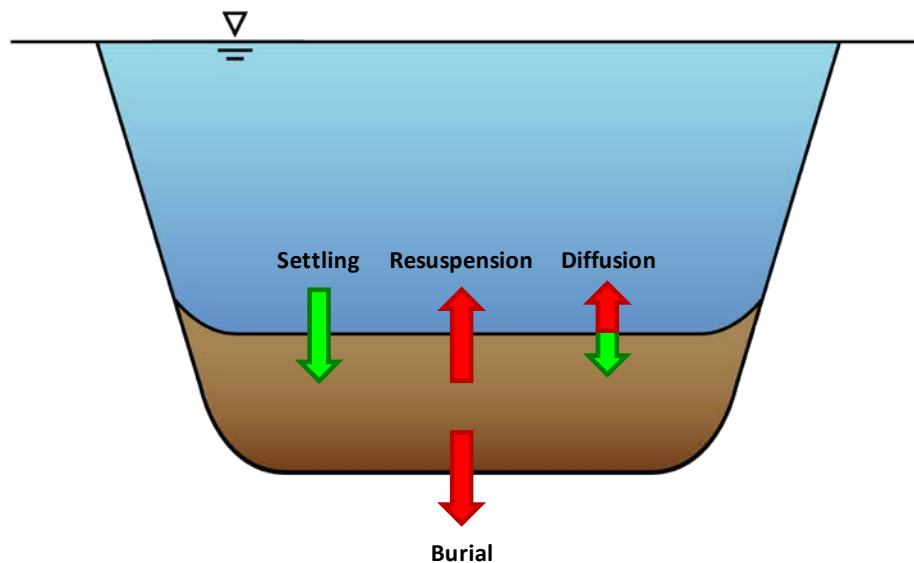


Figure 2-3. Systems diagram for the sediment layer of the TICKET-UWM. Green arrows indicate processes that transport metal(loid) into the sediment and red arrows indicate processes that transport metal(loid) out of the sediment.

Some additional comments on remobilization are required. Zero gross remobilization of metal from the sediment is only possible for a system with no resuspension and a diffusive flux permanently directed toward the sediment. The generalized lake used for the TICKET-UWM simulation includes average annual resuspension and this feedback process has been observed in the field (Diamond et al., 1990). However, the occurrence of resuspension alone does not necessarily imply significant remobilization since other transport processes are occurring (e.g. particle settling).

2.3.2. Physico-Chemical Parameters Associated with Sediment Remobilization Potential Simulations

The remobilization potential simulations were made with a single water column chemistry. The pH 7.07 water chemistry was used (Table 2-1). Starting metal concentrations used in the simulations ranged from the acute ERV to the higher chronic CLP cutoff concentration of 1000 µg/L. Simulations used bulk and porewater sediment chemistry from a number of field studies (Table 2-4).

Table 2-4. Bulk and Porewater Sediment Chemistry Parameters

Parameter	Value
pH	7.56 ^a
Ca ²⁺	144 ^a
Mg ²⁺	38.1 ^a
Na ⁺ , mg/L	141 ^b
K ⁺ , mg/L	6.19 ^b
Cl ⁻ , mg/L	79 ^a
SO ₄ ²⁻ , mg/L	65 ^a
Alkalinity, mg/L as CaCO ₃	478 ^c
DOC, mg/L	21 ^d
TOC, %	3.7 ^c
Iron, %	2.9 ^c
HFO, mg HFO/kg	18,600 ^e
Manganese, mg/kg	404 ^c
HMO, mg HMO/kg	154 ^e
AVS, µmol/g _{dry}	1.0 and 9.1 ^{c, f}
Porewater [Fe ²⁺], mg/L	0.912 ^g
Settling rate, m/d	2.5 ^h
Burial rate, cm/yr	0.3 ^h
Resuspension rate, cm/yr	2.44 ^h
Diffusive exchange, cm/day	0.24 ^h
Sediment solids conc., g/L	500 ^h
Active depth, cm	3 ^h

^a From a monitoring dataset on Flemish navigable waterways (de Deckere et al., 2000). For conversion of hardness to Ca²⁺ and Mg²⁺, a molar ratio of Ca:Mg = 2.20 was used based on average river water in Stumm

- and Morgan (1996).
- ^b Estimated using the SO_4^{2-} and Cl⁻ data from (de Deckere et al., 2000) and a seawater/river water mixing method similar to Di Toro et al. (2005)
 - ^c From USGS report to NiPERA (Besser et al., 2010) and personal communications with Chris Schlekot, John Besser, and William Brumbaugh
 - ^d From 1995 sediment monitoring program (AMINAL/AWZ, 1995)
 - ^e Determined using a relationship between total recoverable Fe/Mn and the Fe/Mn in a sequential extraction fraction most closely related to HFO/HMO as determined by HydroQual and Manhattan College (2010) using the following formula weights: 89 g HFO/mol Fe and 119 g HMO/mol Mn.
 - ^f 10th and 50th percentile from USGS report to NiPERA (Besser et al., 2010)
 - ^g An average dissolved Fe(II) in the porewater of 2.77 mg/L was calculated based on data from Wersin et al. (1991), Gallon et al. (2004), and Canavan et al. (2007). Using the porewater chemistry data in this table, WHAM6 calculations were used to determine the ferrous ion concentration, $[\text{Fe}^{2+}]$.
 - ^h ECHA REACH implementation guidance document summarizing EUSES model parameters (ECHA, 2010)
 - ⁱ From *Technical Guidance Document on Risk Assessment* (European Chemicals Bureau, 2003)

2.3.3. Sediment Remobilization Potential Modeling Approach

Similar to the water column removal simulations above, a single instantaneous addition of metal to the water column was used. For a system with sediment burial and a single instantaneous addition of metal as the only source, the ultimate steady-state metal concentration in both the water column and sediment is *zero*. Therefore, the TICKET-UWM simulations that follow evaluate the impact of sediment feedback (via resuspension and diffusion) on the water column metal concentration for a finite time interval of 1 year. Settling, resuspension, diffusion, and burial rates indicated in Table 2-4 represent average annual parameters taken or derived from the EUSES lake model. Short-term resuspension events, such as those due to dredging, propeller wash, and storms are beyond the scope of this investigation but remain a subject for future research.

For the water column, the pH 7.07 water chemistry was used (Table 2-1). The initial total concentration of metal ranged from the acute ERV to the upper chronic cutoff value of 1000 $\mu\text{g/L}$. Simulations used bulk and porewater sediment chemistry from a number of field studies (Table 2-4). Trace metal partitioning in the sediment was quantified using the speciation model method described in Section 2.2.2. For an oxic sediment, sulfide production and metal sulfide precipitation are not considered. Metals sorb to POC, HFO, and HMO in the sediment and can precipitate as carbonates, hydroxides, and/or sulfates. For an anoxic sediment, metal binding to HFO and HMO is not considered. Metals sorb to POC and can precipitate as sulfides, carbonates, hydroxides, and/or sulfates.

Four measures of remobilization were used to assess remobilization potential: 1) long-term maintenance of water column concentrations below 70% removal concentration, 2) relative magnitudes of water column and sediment K_D values, 3) prevailing direction of the sediment/water column diffusive flux, 4) and speciation changes. The first criterion indicates whether 70% removal is achieved and sustained during the 365 day simulations. This is the most intuitive indicator of remobilization potential. The second and third criteria are linked in that the relative magnitudes of the water column and sediment K_D values impacts the direction of the diffusive flux. The diffusive flux, when integrated over the simulation time, indicates whether dissolve metal is generally lost from the water column to the sediments or lost

from the sediments to the water column. If the water column $\log K_D$ is larger than that in the sediment, there is a greater tendency for the flux to be directed out of the sediment and vice versa.

2.4. TICKET-UWM Calculations with Organic Chemicals

TICKET-UWM simulations were made with six organic chemicals—mostly persistent organic pollutants (POPs)—to 1) demonstrate the broad applicability of the TICKET-UWM as a risk assessment and classification tool, and 2) address concerns that the “degradation” approach proposed for metals would indicate POPs are rapidly degraded. Water column removal and sediment remobilization simulations analogous to those performed for metals were performed for the selected organic chemicals.

For these simulations, the chemical loss from the system via degradation reaction and/or volatilization was precluded so as to focus on sorption processes. Partitioning of the organic contaminant between dissolved and particulate phases was described using a linear K_D model. The K_D values in the water column and underlying sediment layer were specified as a function of the fraction organic carbon (f_{OC}) and the octanol–water partition coefficient (K_{OW}) according to the following equation:

$$K_D = 0.41f_{OC}K_{OW} \quad (2-5)$$

In TICKET-UWM simulations with organics, the starting water column concentration of each organic chemical was 1 $\mu\text{g/L}$.

Table 2-5. Chemical and Parameters Used in Organic Chemical Simulations.

Name	Molecular Weight (g/mol)	$\log K_{OW}$	Water column $\log K_D$	Sediment $\log K_D^a$	Source
4,4'-DDT *	354.4	6.0	4.61	4.31, 4.18	1
Hexachlorobenzene *	284.8	5.5	4.11	3.81, 3.68	2
Heptachlor *	373.3	5.27	3.88	3.58, 3.45	3
Endrin *	380.9	4.5	3.11	2.81, 2.68	4
Acenaphthene	154.2	3.93	2.54	2.24, 2.11	1
Lindane *	290.8	3.7	2.31	2.01, 1.88	1

Notes:

* On persistent organic pollutant list

^a First value is for water column analysis ($f_{OC} = 0.05$) and the second is for the remobilization potential analysis ($f_{OC} = 0.037$)

Sources:

- 1 MacKay et al., 1992
- 2 Niimi, 1987
- 3 Schüürmann and Klein, 1988
- 4 Eadsforth, 1986

3. RESULTS AND DISCUSSION

3.1. Copper

3.1.1. Copper Water Column Results – Linear Partitioning Method

Preliminary model calculations confirmed that for linear partitioning in the generalized lake system, metal removal rates were independent of initial copper (Cu) concentration used. Therefore, linear partitioning method results for only one initial Cu concentration are presented. TICKET-UWM output for total and dissolved Cu remaining versus time for the linear partitioning method is shown in Figure 3-1. Based on the suspended solids concentration of 15 mg/L and the empirical log K_D (Table 2-3), approximately 31% of the Cu added to the water column was bound to suspended particles. After this initial removal, dissolved Cu continued to decline as equilibrium between the dissolved and particulate Cu was maintained and particulate Cu settled from the water column (Figure 3-1b, red line). Dissolved Cu removal was rapid: 70% dissolved Cu removal was reached 3.3 days after addition (Approach 1). Under the more conservative approach where removal is based on total Cu (Approach 2), the rapid removal benchmark was met 4.7 days after Cu addition (Figure 3-1a, blue line). The time for rapid removal using Approach 3 was essentially equal to that for Approach 2.

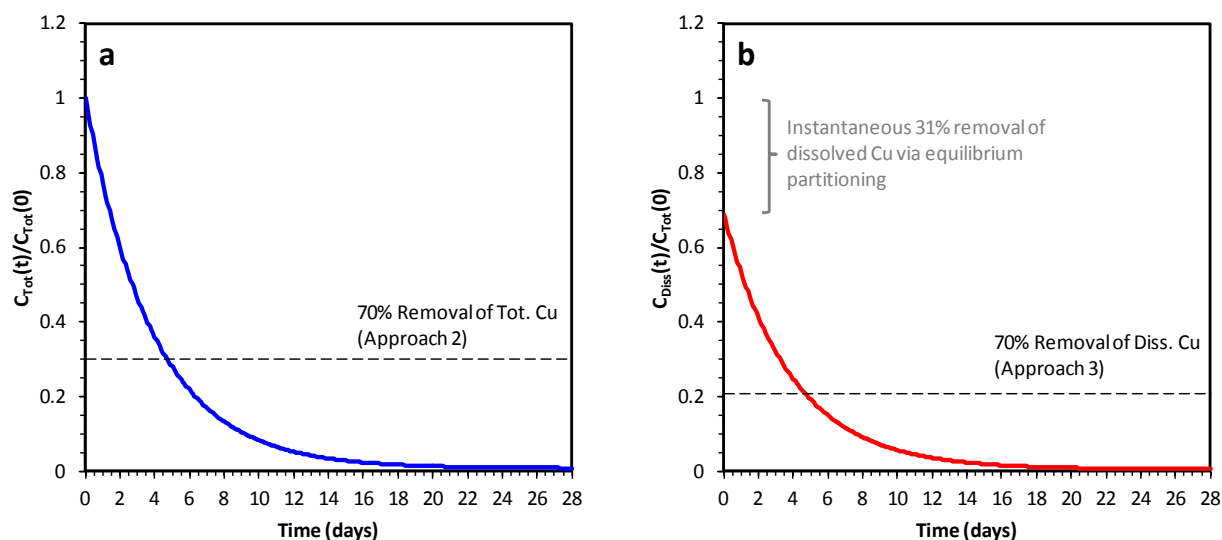


Figure 3-1. a) Total and b) dissolved copper (Cu) removal from the water column using EUSES model parameters and the linear partitioning method. The initial total Cu concentration in the water column, $C_{Tot}(0)$, was specified at the acute ERV of 35 $\mu\text{g/L}$. The horizontal dashed lines represents a) $C_{Tot}(t)/C_{Tot}(0) = 0.3$ (70% removal of total Cu) and b) $C_{Diss}(t)/C_{Diss}(0) = 0.3$ (70% removal of dissolved Cu).

3.1.2. Copper Water Column Results – Speciation Model Method

Table 3-1 and Table B-1 (Appendix B) summarize results of the various model Cu simulations made using the speciation model method. For all concentrations considered (Table 2-2), removal was rapid. Times required to achieve 70% removal ranged from instantaneous to 3.2 days depending on the method for calculating removal.

Table 3-1. Water Column Removal Results for Copper

Scenario	Water Chemistry		
	pH 6	pH 7	pH 8
Empirical K_D Approach			
Acute/Chronic ERV and Upper Chronic Cutoff ^a		●	
Speciation Model Method			
Acute/Chronic ERV and Upper Chronic Cutoff	●	●	●

Legend:

- Greater than 70% removal achieved in 28 days for Approaches 1, 2, and 3
- ◐ Greater than 70% removal achieved in 28 days for a subset of approaches
- Less than 70% removal achieved in 28 days for none of the three approaches

Footnotes:

^a ERV Values:

Scenario	Initial Cu Concentration, µg/L		
	pH = 6	pH = 7	pH = 8
Acute	25	35	30
Chronic	20	7	11

Upper Chronic Cutoff = 1 mg/L

Table B-1 indicates that the predicted water column log K_D values from the speciation model method simulations were generally greater than the empirical value of 4.48. An investigation of competitive effects indicated that removal of hardness cation (Ca and Mg) competition only increased the discrepancy between the predicted and empirical log K_D value.

3.1.3. Copper Water Column Sensitivity Analysis Results

A sensitivity analysis was conducted to evaluate the critical depth at which exactly 70% removal was achieved in 28 days using Approach 1 for a system with an initial Cu at the pH-specific acute ERV values. Results are shown in Table 3-2. For the linear partitioning method, 70% removal can be attained in 28 days at a depth that is more than eight times greater than the default generalized lake depth of 3 meters. For the speciation model method simulations, the model-predicted strong binding between Cu and POC resulted in relatively large critical depth. According to the model predictions, rapid removal is still possible in systems more than fifteen times deeper than the generalized lake system.

Table 3-2. Maximum Depth to Achieve 70% Removal of Copper in 28 Days ^a

Simulation Description	Depth (m)
Linear Partitioning	25.2
pH 6.09	53.1
pH 7.07	52.4
pH 8.00	47.1

^a Initial Cu concentration was set at the pH-specific acute ERV (Table 2-2)

Another sensitivity analysis was conducted to assess removal with settling velocity decreased from the EUSES value of 2.5 m/d to 0.24 m/d. A settling rate of 0.24 m/d represents the lower end of the POC range from Burns and Rosa, (1980). The results are shown in Table 3-3. Rapid removal was not achieved for the linear partitioning method simulation. For the speciation model method, the relatively high predicted log K_D values, facilitated rapid removal even at the lower settling velocity.

Table 3-3. Water Column Removal Results for Copper with Decreased Settling Velocity ^{a,b}

Simulation Description	Removal Result
Linear Partitioning	○
pH 6.09	●
pH 7.07	●
pH 8.00	●

Legend:

- Greater than 70% removal achieved in 28 days for Approaches 1, 2, and 3
- Greater than 70% removal achieved in 28 days for a subset of approaches
- Less than 70% removal achieved in 28 days for none of the three approaches

Footnotes:

^a Settling velocity = 0.24 m/d

^b Initial Cu concentration was set at the pH-specific acute ERV (Table 2-2)

3.1.4. Preliminary Assessment of Copper Remobilization Potential from Sediments

With AVS at the 10th percentile value of 1 $\mu\text{mol/g}$ and the initial concentration set at the L(E)C₅₀ and 100 $\mu\text{g/L}$, there was sufficient AVS available to bind all Cu in the sediment. The additional Cu binding afforded by the AVS resulted in very large sediment log K_D values (16.1 and 16.6, Table B-3) which are significantly greater than the values calculated for the water column. As a result, the integrated dissolved Cu flux was directed into the sediment. Therefore, with AVS = 1 $\mu\text{mol/g}$, all three sequestration criteria were met for Cu loadings at the at the L(E)C₅₀ and 100 $\mu\text{g/L}$ (Table 3-4). However, with the Cu loading increased to the upper chronic CLP cutoff value, available AVS in the sediment was exhausted. As indicated by the table below, the sediment Cu was divided between AVS and POC. There was limited enhancement of Cu binding in the sediment, the water column log K_D was larger than the sediment value (Table B-3), and the integrated diffusive flux was directed *out* of the sediment (Table 3-4).

With AVS at the 50th percentile value of 9.1 $\mu\text{mol/g}$, AVS dominates sediment Cu speciation. The additional Cu binding afforded by AVS resulted in the sediment $\log K_D$ being larger than the water column $\log K_D$. The integrated diffusive flux was directed into the sediment (Table 3-4 and Table B-3).

The model predicted relatively weak binding of Cu to HFO. For the three loadings only the first sequestration criterion was met.

Table 3-4. Sediment Remobilization Results for Copper

Scenario		Sequestration Criteria			Solid-Phase Speciation
		Sustained 70% removal	$K_{D, \text{sed}} > K_{D, \text{wc}}$	Diffusive Flux into Sediment	
Anoxic, AVS = 1 $\mu\text{mol/g}$	Acute ERV and Lower Chronic Cutoff	●	●	●	100% AVS
	Upper Chronic Cutoff	●	○	○	66.4% POC; 33.6% AVS
Anoxic, AVS = 9.1 $\mu\text{mol/g}$	Acute ERV, Lower and Upper Chronic Cutoff	●	●	●	100% AVS
Oxic	Acute ERV	●	○	○	98.2% POC; 1.7% HFO 0.1% HMO
	Lower Chronic Cutoff	●	○	○	98.1% POC; 1.7% HFO 0.1% HMO
	Upper Chronic Cutoff	●	○	○	98.0% POC; 1.8% HFO 0.1% HMO

- Sequestration criterion is met
- Sequestration criterion is not met

Footnotes:

^a Acute ERV = 35 $\mu\text{g/L}$; Lower Chronic Cutoff = 0.1 mg/L ; Upper Chronic Cutoff = 1 mg/L

Additional analysis where performed in which the TICKET-UWM simulation output was compared to measured metal removal data from whole lake and microcosm experiments. These are documented in the full TICKET-UWM report for Cu (Mutch Associates, 2011a).

A remobilization potential analysis was also made using the linear partitioning method and the empirical $\log K_D$ values listed in Table 2-3. Results indicate that there was sustained 70% removal. Despite the fact that the water column $\log K_D$ was greater than the sediment $\log K_D$, the integrated diffusive flux was directed *into* the sediment. The first and third sequestration metrics are met, but not the second. Although the relative magnitude of the water column and sediment $\log K_D$ values supports diffusion out of the sediment during the pseudo steady-state, enough mass of Cu diffuses into the sediment early in the simulation (prior to the establishment of pseudo steady-state conditions) to produce an *integrated* diffusive flux directed into the sediment.

3.2. Zinc

3.2.1. Zinc Water Column Results – Linear Partitioning Method

TICKET-UWM output for total and dissolved zinc (Zn) remaining versus time for the linear partitioning method is shown in Figure 3-2. Based on the suspended solids concentration of 15 mg/L and the empirical log K_D (Table 2-3), approximately 62% of the Zn added to the water column was bound to suspended particles. Thus, according to Approach 1 for calculating removal, the rapid removal benchmark was met almost immediately by virtue of equilibrium partitioning. The benchmark was met 0.45 days after addition (Figure 3-2b, red line). Under the more conservative approach where removal is based on total Zn (Approach 2), the rapid removal benchmark was met 2.4 days after Zn addition (Figure 3-2a, blue line). The time for rapid removal using Approach 3 was essentially equal to that for Approach 2.

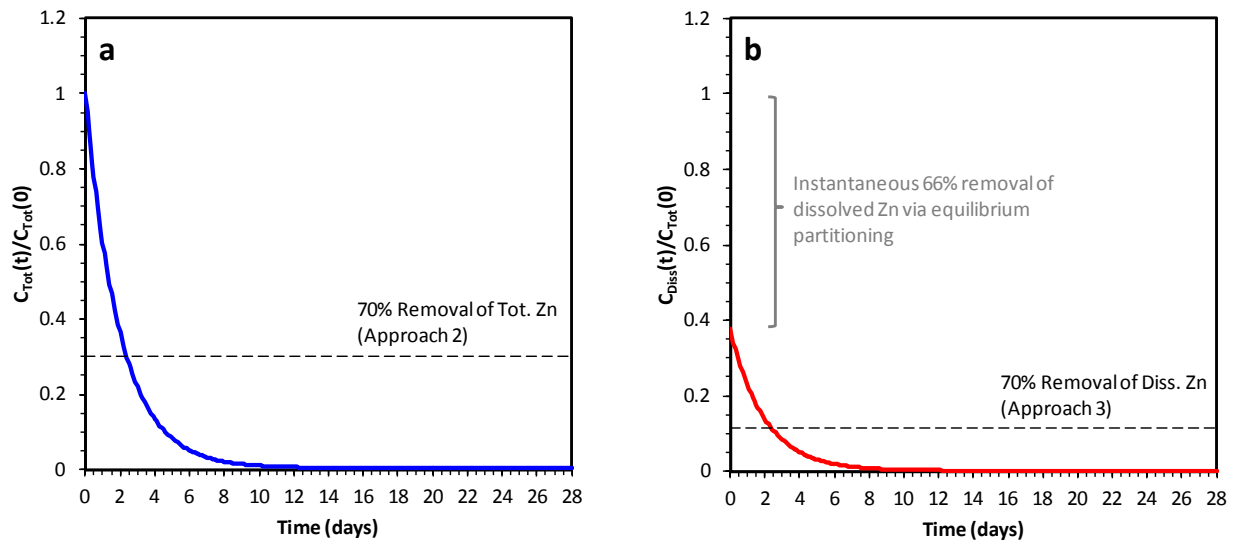


Figure 3-2. a) Total and b) dissolved zinc (Zn) removal from the water column using EUSES model parameters and the linear partitioning method. The initial total Zn concentration in the water column, $C_{Tot}(0)$, was specified at the pH 8 acute ecotoxicity reference value (ERV) of 136 $\mu\text{g/L}$. The horizontal dashed lines represents a) $C_{Tot}(t)/C_{Tot}(0) = 0.3$ (70% removal of total Zn) and b) $C_{Diss}(t)/C_{Diss}(0) = 0.3$ (70% removal of dissolved Zn).

3.2.2. Zinc Water Column Results – Speciation Model Method

Table 3-5 and Table C-1 (Appendix C) summarize the results of the various model simulations made using the speciation model method. For all water chemistries and loading concentrations considered, greater than 70% removal was achieved within 28 days.

Table 3-5. Water Column Removal Results for Zinc

Scenario	Water Chemistry		
	pH 6	pH 7	pH 8

Empirical K_D Approach			
Acute/Chronic ERV and Upper Chronic Cutoff ^a	●		
Model Speciation Approach			
Acute/Chronic ERV and Upper Chronic Cutoff	●	●	●

Legend:

- Greater than 70% removal achieved in 28 days for Approaches 1, 2, and 3
- ◐ Greater than 70% removal achieved in 28 days for a subset of approaches
- Less than 70% removal achieved in 28 days for none of the three approaches

Footnotes:

^a ERV Values:

Scenario	Initial Zn Concentration, $\mu\text{g/L}$	
	pH = 6	pH = 8
Acute	413	136
Chronic	82	19

Upper Chronic Cutoff = 1 mg/L; pH 7 calculation was made using 136 $\mu\text{g/L}$

The calculated log K_D values (range = 4.08 – 4.77) are all lower than the empirical value of 5.04 (Table 2-3). This deviation can be caused by a number of factors including the following:

1. The set of reactions and sorptive processes considered in the TICKET-UWM speciation model may not include all Zn-particle interactions occurring in field samples that generated the empirical log K_D . As mentioned in Section 2.2.2, POC was the primary particulate metal binding phase considered in the TICKET-UWM simulations. It is possible that other processes such as adsorption to hydrous ferric oxides (HFOs) and hydrous manganese oxides (HMOs) influence Zn speciation. Furthermore, depending on the nature of the extraction methods used to quantify particle bound metal, field-measured distribution coefficients can include refractory metal (metal in mineral lattices). These phenomena were not included in TICKET-UWM simulations.
2. The specific water chemistries in Table 2-1 may not be inconsistent with the water chemistry from the data sets used to derive the empirical value.
3. WHAM V may not reproduce accurately the binding of metals to POC in natural waters. Studies examining the prediction of Zn solid-solution log K_D values in surface waters are limited. A general underestimation of Zn log K_D value was noted by Lofts and Tipping (2000) when applying WHAM V to Humber rivers. A marked improvement in log K_D prediction was noted when the effect of the hardness cation (Ca and Mg) competition for binding sites on organic matter was excluded. Rader (2009) reported similar findings for WHAM6.

A sensitivity analysis was conducted to assess the impact of HFO and HMO on the calculated log K_D . For this analysis, the iron and manganese content of natural suspended particulate matter in surface water (Table 3-6) was used to estimate HFO and HMO concentrations. The data in Table 3-6 indicate average iron and manganese contents in suspended particulate matter of 37.5 and 2.2 mg/g, respectively. Research indicates that approximately 40% and 18% of the particulate Fe and Mn are HFO and HMO,

respectively (HydroQual and Manhattan College, 2010). Based on these percentages and a suspended solids concentration of 15 mg/L, the estimated concentrations of HFO and HMO are 0.226 mg/L as Fe and 5.76 µg/L as Mn, respectively. At the high pH water chemistry (pH = 8), where sorption to oxides is expected to be strongest for cationic species, there is only a modest increase in log K_D with HFO and HMO binding included. In the simulation with initial Zn at 19 µg/L, the log K_D increased from 4.66 to approximately 4.74.

Table 3-6. Iron and Manganese Content of Natural Particulate Matter.

Waterbody	Type	Country	Fe, mg/g	Mn, mg/g	Source
Lake Courtille	Lake	France	31.0	1.79	1
Haringvliet Lake	Lake	Netherlands	39.0	2.49	2
Aire at Beal Bridge	River	United Kingdom	39.3	2.99	3
Sudbury Lakes	Lake	Canada	23.5	---	4
Czech Rivers	River	Czechoslovakia	46.6	2.8	5
Scheldt estuary	Estuary	Netherlands	45.7	0.866	6

Sources:

- 1 Hullebusch et al., 2003
- 2 Canavan et al., 2007
- 3 Leeks et al., 1997
- 4 Nriagu et al., 1998
- 5 Vesely et al., 2001
- 6 Zwolsman and van Eck, 1999

3.2.3. Zinc Water Column Sensitivity Analysis Results

A sensitivity analysis was conducted to evaluate the critical depth at which exactly 70% removal was achieved in 28 days using Approach 1 for a system with an initial Zn at the pH-specific acute value (Table 2-2). The results are shown in Table 3-7. For the linear partitioning method, 70% removal can be attained in 28 days at a depth that is more than sixty times greater than the default generalized lake depth of 3 meters. For the speciation model method simulations, critical depths were more moderate. However, according to the model predictions, rapid removal is still possible in systems more than six times deeper than the generalized lake system.

Table 3-7. Critical Depth to Achieve 70% Removal of Zinc in 28 Days ^a

Simulation Description	Depth (m)
Linear Partitioning	182
pH 6.09	19.7
pH 7.07	52.3
pH 8.00	38.5

^a Initial Zn concentration was set at the pH-specific acute ERV (Table 2-2)

Another sensitivity analysis was conducted to assess removal with settling velocity decreased from the EUSES value of 2.5 m/d to 0.24 m/d. A settling rate of 0.24 m/d represents the lower end of the POC range from Burns and Rosa, (1980). The results are shown in Table 3-8. Rapid removal was achieved for the linear partitioning method simulation. For the speciation model method, rapid removal was not achieved at pH 6 for any of the approaches. For the remaining water chemistries, greater than 70%

removal within 28 days was achieved for Approach 1 but not for the more conservative Approach 2. For Approach 3, rapid removal was achieved only at pH 7.

Table 3-8. Water Column Removal Results for Zinc with Decreased Settling Velocity ^{a,b}

Simulation Description	Removal Result
Linear Partitioning	●
pH 6.09	○
pH 7.07	◐
pH 8.00	◐

Legend:

- Greater than 70% removal achieved in 28 days for Approaches 1, 2, and 3
- ◐ Greater than 70% removal achieved in 28 days for a subset of approaches
- Less than 70% removal achieved in 28 days for none of the three approaches

Footnotes:

^a Settling velocity = 0.24 m/d

^b Initial Zn concentration was set at the pH-specific acute ERV (Table 2-2)

3.2.4. Preliminary Assessment of Zinc Remobilization Potential from Sediments

This assessment makes use of the thermodynamic data for the Zn-S system as determined by Daskalakis and Helz (1993). This group of research determined stability constants for several Zn-S soluble complexes as well as a solubility product for sphalerite, ZnS(s). Sphalerite is one of two ZnS polymorphs. It was selected for using in this analysis since it is the stable form at room temperature (Daskalakis and Helz, 1993).

For all sediment scenarios tested, Zn concentrations decreased to less than 70% of the initial value and were maintained there during the 365 day simulation (Tables 3-9 and Table C-3). Pseudo steady-state water column concentrations were more than 60 times below the 70% removal concentrations (Table C-3). Thus, the first sequestration criterion was met in all cases tested.

Attainment of the two remaining sequestration criteria depended on the amount of Zn added to the system and the strength of the binding phase. With AVS at the 10th percentile value of 1 μmol/g and the initial Zn concentration set at the lower chronic cutoff value and the acute ERV, there was sufficient AVS available to bind all Zn in the sediment. The Zn binding afforded by the AVS resulted in sediment log K_D values ranging from 7.12 - 7.26 (Table C-3) which is significantly greater than the values calculated for the water column. As a result, the integrated dissolved Zn flux is directed into the sediment. Therefore, with AVS = 1 μmol/g, all three sequestration criteria were met for simulations with the Zn loading at the lower chronic cutoff and the acute ERV (Table 3-9). However, with the Zn loading increased to the upper chronic cutoff value, available AVS in the sediment was exhausted. Sediment Zn was divided between AVS and POC (Table 3-9) which limited the extent to which Zn binding was enhanced in the sediment relative to Zn binding in the water column. The water column log K_D was larger than the sediment value (Table C-3), and the integrated diffusive flux was directed out of the sediment (Table 3-9).

Table 3-9. Sediment Remobilization Results for Zinc

Scenario		Sequestration Criteria			Solid-Phase Speciation
		Sustained 70% removal	$K_{D, \text{sed}} > K_{D, \text{wc}}$	Diffusive Flux into Sediment	
Anoxic, AVS = 1 $\mu\text{mol/g}$	Lower Chronic Cutoff and Acute ERV	●	●	●	100% AVS
	Upper Chronic Cutoff	●	○	○	65.3% POC; 34.7% AVS
Anoxic, AVS = 9.1 $\mu\text{mol/g}$	Lower Chronic Cutoff, Acute ERV and Upper Chronic Cutoff	●	●	●	100% AVS
Oxic	Lower Chronic Cutoff	●	○	○	81.8% POC; 15.7% HFO 2.5% HMO
	Acute ERV	●	○	○	82.0% POC; 15.6% HFO 2.5% HMO
	Chronic Cutoff	●	○	○	84.1% POC; 14.1% HFO 1.8% HMO

● Sequestration criterion is met

○ Sequestration criterion is not met

Footnotes:

^a Acute ERV = 136 $\mu\text{g/L}$ (pH 7); Lower Chronic Cutoff = 0.1 mg/L; Upper Chronic Cutoff = 1 mg/L

With AVS at the 50th percentile value of 9.1 $\mu\text{mol/g}$, AVS dominated Zn speciation in the sediment for all loadings considered. The additional Zn binding afforded by AVS resulted in a sediment log K_D that was larger than the water column log K_D . The integrated diffusive flux was directed into the sediment (Table 3-9 and Table C-3). The three sequestration criteria are met for all three loadings.

The model predicted moderate binding of Zn to HFO and HMO. Only approximately 16-18% of the particulate Zn was associated with oxides with the remainder bound to POC. For the three loadings in the oxic simulations, only the first sequestration criterion was met.

A remobilization potential analysis was also made using the linear partitioning method and the empirical log K_D values listed in Table 2-3. Results indicate that there was sustained 70% removal. Despite the fact that the water column log K_D was greater than the sediment log K_D , the integrated diffusive flux was directed *into* the sediment. The first and third sequestration metrics are met, but not the second. Although the relative magnitude of the water column and sediment log K_D values supports diffusion out of the sediment during the pseudo steady-state, enough mass of Zn diffuses into the sediment early in the simulation (prior to the establishment of pseudo steady-state conditions) to produce an *integrated* diffusive flux directed into the sediment.

3.3. Lead

3.3.1. Lead Water Column Results – Linear Partitioning Method

TICKET-UWM output for total and dissolved lead (Pb) remaining versus time for the linear partitioning method is shown in Figure 3-3. Based on the suspended solids concentration of 15 mg/L and the empirical log K_D (Table 2-3), approximately 82% of the Pb added to the water column was bound to suspended particles. Thus, according to Approach 1 for calculating removal, the rapid removal benchmark was met immediately by virtue of equilibrium partitioning (Figure 3-3b). Under the more conservative approach where removal is based on total Pb (Approach 2), the rapid removal benchmark was met 1.8 days after Pb addition (Figure 3-3a, blue line). The time for rapid removal using Approach 3 was essentially equal to that for Approach 2.

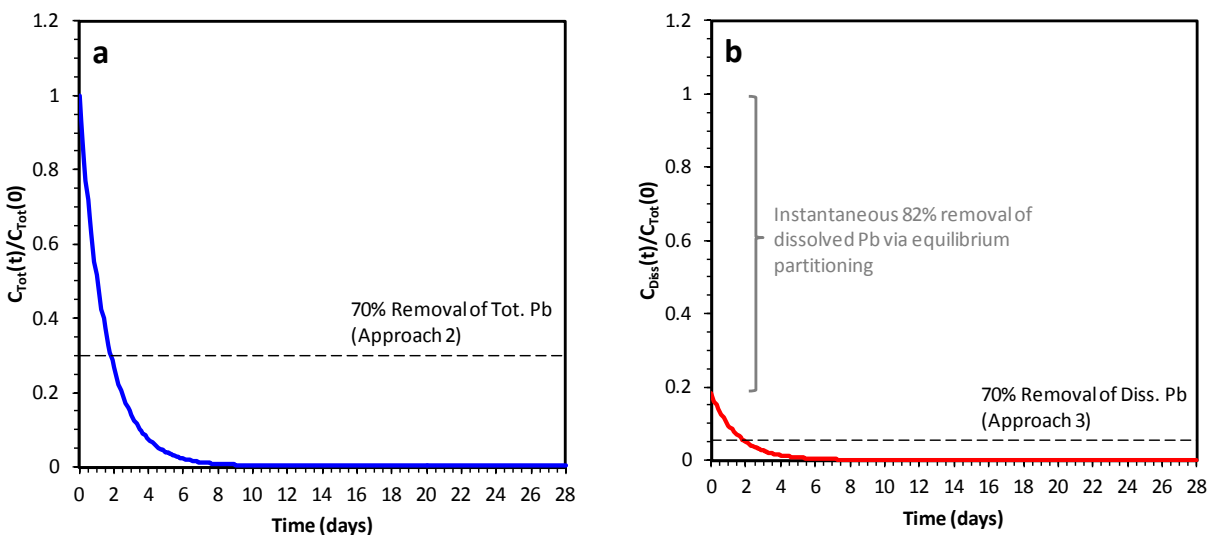


Figure 3-3. a) Total and b) dissolved lead (Pb) removal from the water column using EUSES model parameters and the linear partitioning method. The initial total Pb concentration in the water column, $C_{Tot}(0)$, was specified at the pH 6 acute ecotoxicity reference value (ERV) of 73.6 $\mu\text{g/L}$. The horizontal dashed lines represents a) $C_{Tot}(t)/C_{Tot}(0) = 0.3$ (70% removal of total Pb) and b) $C_{Diss}(t)/C_{Diss}(0) = 0.3$ (70% removal of dissolved Pb).

3.3.2. Lead Water Column Results – Speciation Model Method

Table 3-10 and Table D-1 (Appendix D) summarize the results of the various Pb model simulations made using the speciation model method. For all water chemistries and loading concentrations considered, greater than 70% removal was achieved within 28 days. It is worthwhile to note that the range of model-predicted log K_D values (Table D-1) (5.02 – 5.95) brackets the empirical value of 5.47 (Table 2-3).

Table 3-10. Water Column Removal Results for Lead

Scenario	Water Chemistry		
	pH 6	pH 7	pH 8
Empirical K_D Approach			
Acute/Chronic ERV and Upper Chronic Cutoff ^a		●	
Model Speciation Approach			

Acute/Chronic ERV and Upper Chronic Cutoff	●	●	●
--	---	---	---

Legend:

- Greater than 70% removal achieved in 28 days for Approaches 1, 2, and 3
- ◐ Greater than 70% removal achieved in 28 days for a subset of approaches
- Less than 70% removal achieved in 28 days for none of the three approaches

Footnotes:

^a ERV Values:

Scenario	Initial Pb Concentration, µg/L		
	pH = 6	pH = 7	pH = 8
Acute	73.6	52	107
Chronic	17.8	9	23.4

Upper Chronic Cutoff = 1 mg/L

3.3.3. Lead Water Column Sensitivity Analysis Results

A sensitivity analysis was conducted to evaluate the critical depth at which exactly 70% removal was achieved in 28 days for a system with an initial Pb at the pH-specific acute value (Table 2-2). The results are shown in Table 3-11. Based on Approach 1, removal occurred instantly for the linear partitioning method and all three water chemistries. Therefore, critical depth was also evaluated based on total concentrations (Approach 2). For the linear partitioning method, 70% removal can be attained in 28 days at a depth that is more than fifteen times greater than the default generalized lake depth of 3 meters. For the speciation model method simulations, rapid removal is still possible in systems more than ten times deeper than the generalized lake system.

Table 3-11. Critical Depth to Achieve 70% Removal of Lead in 28 Days ^a

Simulation Description	Depth (m)
Linear Partitioning	45.2 ^b
pH 6.09	51.0 ^b
pH 7.07	50.6 ^b
pH 8.00	41.0 ^b

^a Initial Pb concentration was set at the pH-specific acute ERV (Table 2-2)

^b Under Approach 1 70% removal occurs instantly via initial solid-solution equilibrium partitioning. The depth quoted refers to 70% removal of *total* Pb (Approach 2)

Another sensitivity analysis was conducted to assess removal with settling velocity decreased from the EUSES value of 2.5 m/d to 0.24 m/d. A settling rate of 0.24 m/d represents the lower end of the POC range from Burns and Rosa (1980). The results are shown in Table 3-12 and D-2. Rapid removal was achieved for the linear partitioning method and speciation model method simulations (all 3 water chemistries).

Table 3-12. Water Column Removal Results for Lead with Decreased Settling Velocity^{a,b}

Simulation Description	Removal Result
Linear Partitioning	●
pH 6.09	●
pH 7.07	●
pH 8.00	●

Legend:

- Greater than 70% removal achieved in 28 days for Approaches 1, 2, and 3
- Greater than 70% removal achieved in 28 days for a subset of approaches
- Less than 70% removal achieved in 28 days for none of the three approaches

Footnotes:

- ^a Settling velocity = 0.24 m/d
- ^b Initial Pb concentration was set at the pH-specific acute ERV (Table 2-2)

3.3.4. Preliminary Assessment of Lead Remobilization Potential from Sediments

For an anoxic sediment with AVS at the 10th and 50th percentile values, the TICKET-UMW results indicate that all three sequestration criteria were met with initial concentrations up to and including the upper chronic cutoff value (Tables 3-13 and Table D-3).

Table 3-13. Sediment Remobilization Results for Lead

Scenario		Sequestration Criteria			Solid-Phase Speciation
		Sustained 70% removal	$K_{D, sed} > K_{D, wc}$	Diffusive Flux into Sediment	
Anoxic, AVS = 1 μmol/g	Acute ERV, Lower and Upper Chronic Cutoff	●	●	●	100% AVS
Anoxic, AVS = 9.1 μmol/g	Acute ERV, Lower and Upper Chronic Cutoff	●	●	●	100% AVS
Oxic	Acute ERV	●	○	●	94.1% HMO; 4.1% HFO 1.8% POC
	Lower Chronic Cutoff	●	○	○	87.4% HMO; 8.8% HFO 3.8% POC
	Upper Chronic Cutoff	●	○	○	49.5% HFO; 36.3% POC 14.2% HMO

- Sequestration criterion is met
- Sequestration criterion is not met

Footnotes:

^a Acute ERV = 52 µg/L (pH 7); Lower Chronic Cutoff = 0.1 mg/L; Upper Chronic Cutoff = 1 mg/L

Lead binds strongly to oxides (Dzombak and Morel, 1990; Tonkin et al., 2004). At the acute ERV, most of the Pb was bound to HMO and the first and third sequestration criteria were met. At higher loadings, the amount of Pb on HMO decreased, the amount bound to POC and HFO increased and the third criterion was no longer met. This suggests that HMO binding sites became saturated at the higher Pb loadings.

A remobilization potential analysis was also made using the linear partitioning method and the empirical log K_D values listed in Table 2-3. Results indicate that there was sustained 70% removal. Despite the fact that the water column log K_D was greater than the sediment log K_D , the integrated diffusive flux was directed *into* the sediment. The first and third sequestration metrics are met, but not the second. Although the relative magnitude of the water column and sediment log K_D values supports diffusion out of the sediment during the pseudo steady-state, enough mass of Pb diffuses into the sediment early in the simulation (prior to the establishment of pseudo steady-state conditions) to produce an *integrated* diffusive flux directed into the sediment.

3.4. Nickel

Like most of the metals discussed in this report, water column simulations for Ni were made using both the Linear Partitioning Method and the Speciation Model Method. However, as discussed below, use of WHAM V in Speciation Model Method simulations resulted in significant under-estimation of surface water log K_D values as compared to empirical values. Newer versions of the WHAM model are available which 1) incorporate new and emerging chemical insight into the interaction of metals with natural organic matter and 2) were calibrated using a larger number of datasets. These newer models were recently added to the TICKET-UWM. Additional TICKET-UWM water column and sediment Ni simulations were made with the revised WHAM models. The results and discussion for these simulations immediately follow those associated with the default WHAM V simulations.

3.4.1. Nickel Water Column Results – Linear Partitioning Method

TICKET-UWM output for total and dissolved Ni remaining versus time for the linear partitioning method is shown in Figure 3-4. Based on the suspended solids concentration of 15 mg/L and the empirical log K_D (Table 2-3), approximately 28% of the Ni added to the water column was bound to suspended particles. According to Approach 1 for calculating removal, the rapid removal benchmark was met 3.8 days after addition (Figure 3-4b, red line). Under the more conservative approach where removal is based on total Ni (Approach 2), the rapid removal benchmark was met 5.2 days after Ni addition (Figure 3-4a, blue line). The time for rapid removal using Approach 3 was essentially equal to that for Approach 2.

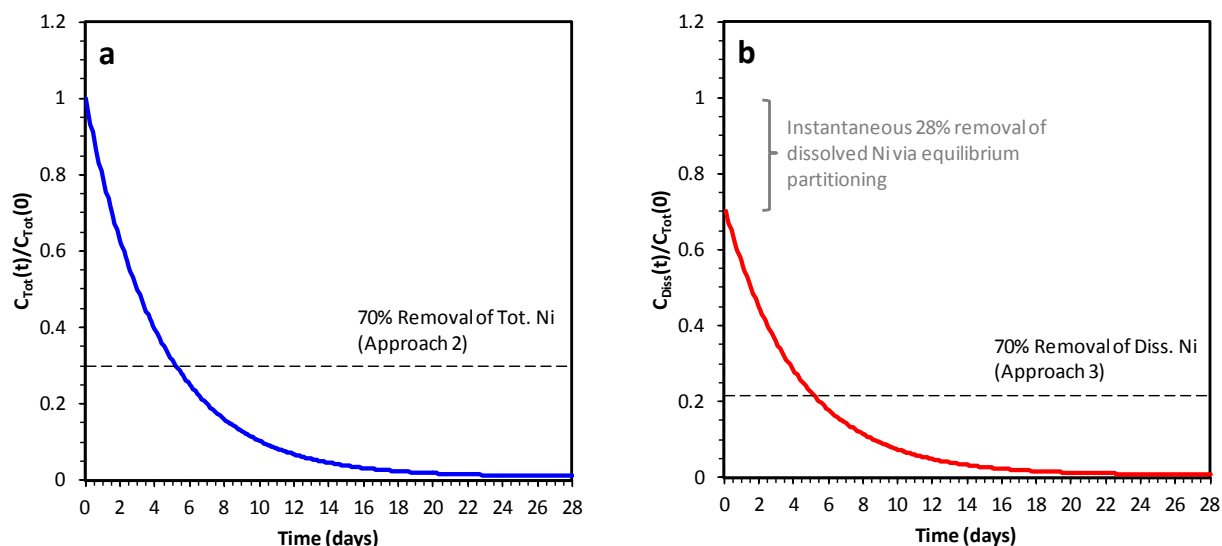


Figure 3-4. a) Total and b) dissolved nickel (Ni) removal from the water column using EUSES model parameters and the linear partitioning method. The initial total Ni concentration in the water column, $C_{Tot}(0)$, was specified at the pH 6 acute ecotoxicity reference value (ERV) of 120 $\mu\text{g/L}$. The horizontal dashed lines represents a) $C_{Tot}(t)/C_{Tot}(0) = 0.3$ (70% removal of total Ni) and b) $C_{Diss}(t)/C_{Diss}(0) = 0.3$ (70% removal of dissolved Ni).

3.4.2. Nickel Water Column Results – Speciation Model Method (WHAM V)

Table 3-14, Table E-1 and Table E-2 (Appendix E) summarize the results of the various model simulations made using the speciation model method. For the pH 6 and 7 simulations with the default model parameters and initial concentrations set at the acute and chronic ERVs, 70% removal was achieved within 28 days of addition for Approach 1. At pH 6, 70% removal occurs within 28 days for Approaches 2 and 3 as well. At pH 8, more than 70 days were required for 70% removal under all approaches.

Table 3-14. Water Column Removal Results for Nickel (WHAM V)

Scenario		Water Chemistry		
		pH 6	pH 7	pH 8
Empirical K_D Approach				
Acute/Chronic ERV and Upper Chronic Cutoff ¹			●	
Model Speciation Approach				
Acute and Chronic ERV	Default	●	◐	○
	No Ca/Mg Comp.	●	●	●
Upper Chronic Cutoff	Default	◐	○	○
	No Ca/Mg Comp.	●	●	●

Legend:

● Greater than 70% removal achieved in 28 days for Approaches 1, 2, and 3

- Greater than 70% removal achieved in 28 days for a subset of approaches
- Less than 70% removal achieved in 28 days for none of the three approaches

Footnotes:

¹ ERV Values:

Scenario	Initial Ni Concentration, µg/L	
	pH = 6	pH = 8
Acute	120	68
Chronic	2.4	2.4

Upper Chronic Cutoff = 1 mg/L; pH 7 calculation was made using 68 µg/L

Calculated values of log K_D and the proportion of Ni associated with the particulate phase generally decreased with increasing pH (Table E-1 in Appendix E). The reduction in log K_D that occurred as pH was increased is primarily a function of the increased alkalinity and hardness associated with the high pH water chemistries (Table 2-1). At higher alkalinities, Ni has a greater tendency to form complexes with carbonate thereby decreasing the amount bound to POC. Additionally, at higher hardness values, Ca/Mg competition for binding sites reduces the amount of Ni on POC.

The upper chronic cutoff value of 1,000 µg Ni/L is far greater than the chronic and acute ERVs, and simulations using this much higher Ni concentrations resulted in lower predicted log K_D values (non-linear partitioning) and lower removal rates (Table E-1 in Appendix E). As a result, greater than 28 days were required for 70% removal at pH 7 and 8 while the removal benchmark was only achieved at pH 6 when removal was calculated using Approach 1 (Table 3-14 and E-1).

Calculated log K_D values (range = 3.14 – 3.61) are notably lower than the guidance document value of 4.42. This deviation can be caused by one or more of the factors listed above for Zn. Among these factors is hardness cation (Ca and Mg) competition for binding sites on POC. Similar to their observations for Zn, Lofts and Tipping (2000) noted improvement in log K_D prediction when the effect of hardness cation (Ca and Mg) competition for binding sites on organic matter was excluded from their WHAM calculations. For the three water chemistries in Table 2-1 increases in log K_D were obtained when Ca/Mg binding to organic matter was eliminated from the calculation (Tables E-1 and E-2). Additional TICKET-UWM simulations were performed to demonstrate Ni removal in the absence of hardness cation competition for binding sites on organic matter. The results are shown in Table 3-14 and Table E-2. Without Ca/Mg competition, the log K_D values increased dramatically (range = 3.87 – 5.30). This range brackets the empirical value of 4.42. As a result of the increased log K_D values, the time required for 70% removal decreased from 24.6 – 75.3 days to instantaneously – 14.3 days (Tables E-1 and E-2). Without Ca/Mg competition, the 70% removal benchmark was achieved at all water chemistries (Table 3-14).

Calculations were also made to assess the effect of HFO and HMO on the model-calculated K_D value. Typical water column HFO and HMO concentration were used (see Section 3.2.2). At pH 7 with an initial Ni concentration of 68 µg/L, inclusion of HFO and HMO increased the predicted log K_D from 3.56 to 3.65 – 3.68. At pH 8 with an initial Ni concentration of 68 µg/L, inclusion of HFO and HMO increased the predicted log K_D from approximately 3.16 to 3.46 – 3.49.

3.4.3. Nickel Water Column Sensitivity Analysis Results (WHAM V)

A sensitivity analysis was conducted to evaluate the critical depth at which exactly 70% removal was achieved in 28 days using Approach 1 for a system with an initial Ni at the pH-specific acute value (Table 2-2). Results are shown in Table 3-15. For the linear partitioning method, rapid removal is possible at depths more than seven times the default generalized lake depth of 3 meters. For simulations using the default WHAM V speciation calculations, critical depths ranged from 3.35 to 1.26 meters. The low predicted log K_D values restrict rapid removal to shallow lakes and ponds.

Table 3-15. Maximum Depth to Achieve 70% Removal of Nickel in 28 Days (WHAM V) ^a

Simulation Description	Depth (m)
Linear Partitioning	21.8
pH 6.09	3.35
pH 7.07	3.04
pH 8.00	1.26

^a Initial Ni concentration was set at the pH-specific acute ERV (Table 2-2)

Another sensitivity analysis was conducted to assess removal with settling velocity decreased from the EUSES value of 2.5 m/d to 0.24 m/d. A settling rate of 0.24 m/d represents the lower end of the POC range from Burns and Rosa, (1980). The results are shown in Table 3-16. For the linear partitioning method, the time required to obtain 70% removal was 37.6 days. For the speciation model method simulations, removal times in excess of 200 days were required to reach 70% removal. At pH 8, over a year was required to achieve 70% removal. Therefore, for what could potentially be considered a minimum or “worst-case” settling velocity, Ni was not rapidly removed from the water column.

Table 3-16. Water Column Removal Results for Nickel with Decreased Settling Velocity (WHAM V) ^{a,b}

Simulation Description	Removal Result
Linear Partitioning	○
6.09	○
7.07	○
8.00	○

Legend:

- Greater than 70% removal achieved in 28 days for Approaches 1, 2, and 3
- ◐ Greater than 70% removal achieved in 28 days for a subset of approaches
- Less than 70% removal achieved in 28 days for none of the three approaches

Footnotes:

^a Settling velocity = 0.24 m/d

^b Initial Ni concentration was set at the pH-specific acute ERV (Table 2-2)

3.4.4. Model Update for Nickel

As mentioned in section 2.2.2, TICKET-UWM currently utilizes WHAM V to describe metal partitioning to natural organic matter. The decision to use WHAM V during TICKET-UWM development was based primarily on its use in the HydroQual BLM (upon which the EPA WQC for Cu is based). As noted above, there are shortcomings with respect to the ability of WHAM V to accurately predict solid/solution distribution coefficients (K_D) for Ni. The WHAM family of models has been developed over the past 25 years in an iterative fashion, with each newer version having been calibrated to an increasing number of datasets. Each model number has been reported to be more accurate with respect to modeling metal speciation and has incorporated new and emerging chemical insight into the interaction of metals with natural organic matter. For example, the newest version of WHAM, WHAM 7 (Tipping et al., 2011), incorporates recent research on linear free energy relationships for metals (Carbonaro and Di Toro, 2007).

Recently, WHAM6 and WHAM7 were integrated into the TICKET-UWM framework (Mutch Associates, 2013). Preliminary model simulations were made to assess the impact of model choice on predicted Ni logarithmic distribution coefficient values ($\log K_D$). The pH 8 water chemistry (Table 2-1) was selected for this analysis since it possesses the highest hardness of the three and, when used for WHAMV speciation calculations, yielded the biggest discrepancy between the model-predicted and empirical Ni $\log K_D$. The concentration of nickel used in the calculations was the pH 8 chronic ecotoxicity reference value (ERV) of 68 $\mu\text{g/L}$. Iron and aluminum activities in WHAM6 simulations were fixed according to Lofts et al. (2008). Iron and aluminum activities in WHAM7 simulations were fixed according to Tipping et al. (2011).

Simulation results (Figure 3-5) indicate that the $\log K_D$ value increased moving from WHAMV to newer versions of the model. WHAM7 yielded the largest $\log K_D$ value of 3.46 which is 0.35 log units greater than the WHAMV value. However, even with this increase associated with use of the newer model, there is still almost an order of magnitude difference between the model-predicted and empirical Ni K_D values (Figure 3-5).

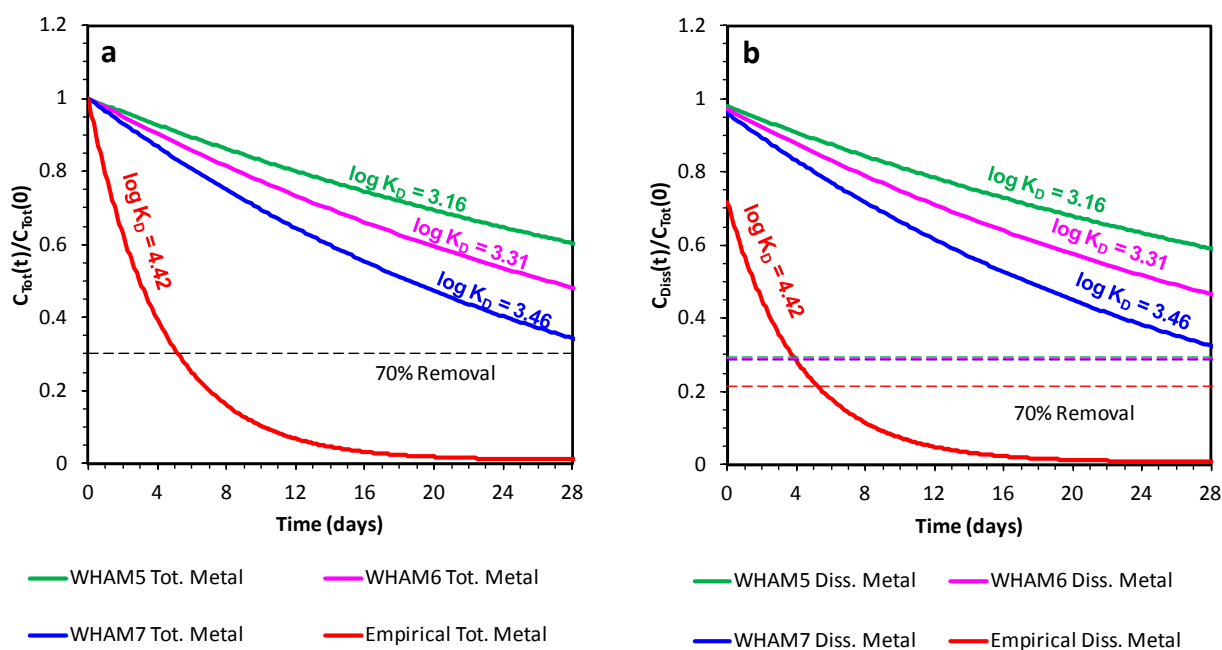


Figure 3-5. a) Total and b) dissolved nickel (Ni) removal from the water at pH 8 using different versions of the WHAM speciation model. The initial concentration of the Ni in each simulation is 68 µg/L. The horizontal dashed lines represents a) $C_{\text{Tot}}(t)/C_{\text{Tot}}(0) = 0.3$ (70% removal of total Ni) and b) $C_{\text{Diss}}(t)/C_{\text{Diss}}(0) = 0.3$ (70% removal of dissolved Ni). Note for b) the color of the dashed line corresponds model simulation to which it applies (Empirical, WHAM5, WHAM6, or WHAM7).

In addition to integration of WHAM6 and WHAM7 into the TICKET-UWM, an assessment of the WHAM inorganic stability constant database was performed. This assessment included 1) a comparison of the WHAM stability constants to values in other speciation software databases and 2) a targeted review of recent literature on Ni speciation. This assessment revealed some shortcoming in the WHAM inorganic stability constant database for Ni implemented in the default version of the TICKET-UWM. Based on this assessment, the default WHAM database in TICKET-UWM was modified to include recent stability constant values for Ni complexes with hydroxide (OH^-) (Plyasunova et al., 1998), carbonate and bicarbonate (CO_3^{2-} and HCO_3^-) (Hummel and Curti, 2003; Baeyens et al., 2003), sulfate (SO_4^{2-}) (Hummel et al., 2002), chloride (Cl^-) (Hummel et al., 2002), and bisulfide (HS^-) (Hummel et al., 2002; Wilkin and Rogers, 2010). Solubility products for $\text{Ni}(\text{OH})_2(\text{cr})$ (Plyasunova et al., 1998), $\text{NiCO}_3 \cdot 6\text{H}_2\text{O}(\text{cr})$ (Hummel and Curti, 2003; Wallner et al., 2002) and $\text{NiS}(\text{s})$ (Wilkin and Rogers, 2010) were updated as well. A detailed account of the inorganic stability constant database assessment and a table with the final selected stability constants are included in Appendix E (Table E-4). It should be noted that the use of alternate inorganic stability constant databases with WHAM is not unprecedented. Alternate inorganic stability constants databases were employed in the development of biotic ligand models for Ni (Deleebeeck et al., 2008) and Co (Lock et al., 2006).

3.4.5. Nickel Water Column Results (WHAM7 with Revised Inorganic Database)

TICKET-UWM Ni simulations at pH 8 with the WHAM7 speciation model (Section 3.4.5 and Figure 3-5) were re-run using the revised Ni inorganic database. Results for simulations with initial Ni at 68 µg/L are shown in Figure 3-6. There is a significant increase in K_D and removal rate associated with use of the revised database (compare green and magenta lines and K_D values). The detailed speciation model output data (not shown) indicate that this is primarily due to the diminished complexation with carbonate and bicarbonate. Complexation with carbonate and bicarbonate tends to draw Ni away from POC and into the aqueous phase. Using the revised inorganic database, 70% removal is achieved within 15.1 – 16.4 days of dosing at pH 8 (Figure 3-6 and Table E-5). Simulations were also made including HFO and HMO as additional sorbent phases using typical water column HFO and HMO concentrations based on data from surface water samples (see Section 3.2.2). The effect of these additional phases is to increase the log K_D value by approximately 0.2 (i.e., from 3.73 to 3.93). This is within just one-half logarithmic unit of the empirical log K_D value of 4.42. For this final scenario (revised inorganic database plus oxides), 70% removal is achieved within 9.7 – 11.1 days of dosing at pH 8 (Figure 3-6 and Table E-5).

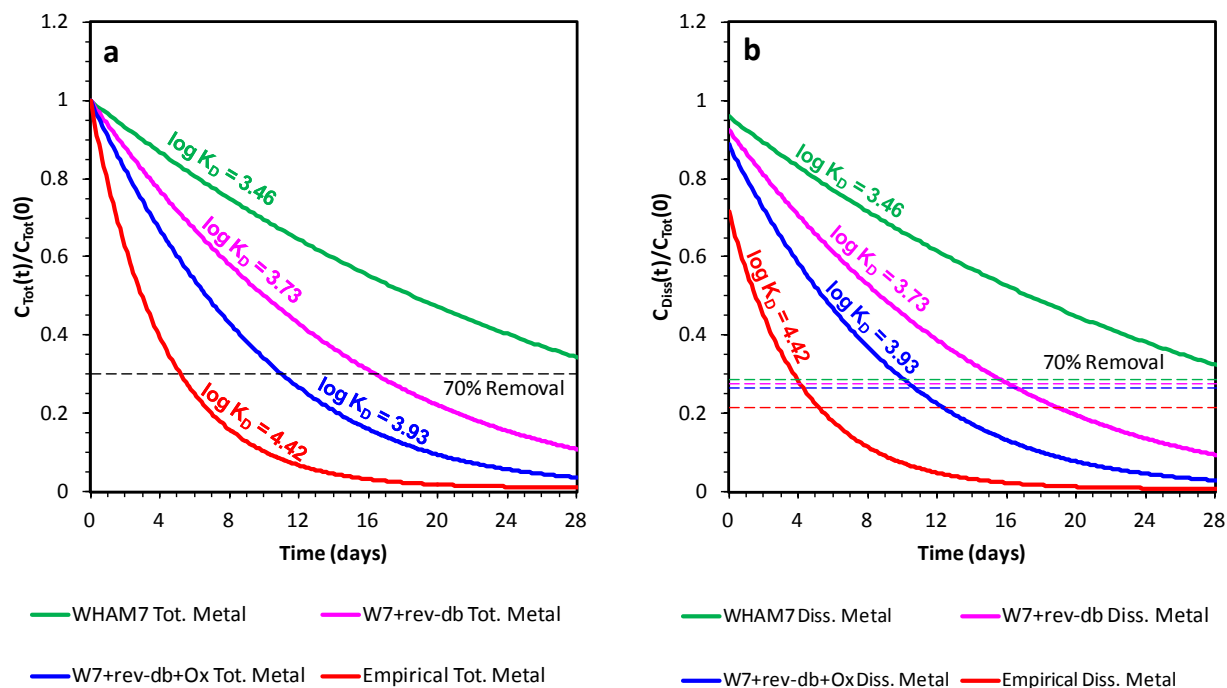


Figure 3-6. a) Total and b) dissolved nickel (Ni) removal from the water at pH 8 using WHAM7 (“WHAM7” series), WHAM7 with revised inorganic database (“W7+rev-db” series) and WHAM7 with revised inorganic database and iron and manganese oxides (“W7+rev-db+Ox” series). The initial concentration of the Ni in each simulation is 68 $\mu\text{g/L}$. The horizontal dashed lines represents a) $C_{Tot}(t)/C_{Tot}(0) = 0.3$ (70% removal of total Ni) and b) $C_{Diss}(t)/C_{Diss}(0) = 0.3$ (70% removal of dissolved Ni). Note for b) the color of the dashed line corresponds model simulation to which it applies (Empirical, WHAM5, WHAM6, or WHAM7).

Simulations with the revised database (both with and without HFO and HMO) were made for other starting concentrations and water chemistries (Table 3-17). Greater than 70% removal within 28 days was observed in the model results for all scenarios considered with initial Ni at the acute/chronic ERV values. At the upper chronic cutoff value of 1000 $\mu\text{g/L}$, 70% removal in 28 days is achieved in most cases. One exception is the simulation at pH 7 without HFO and HMO. In the simulations at pH 8 with Ni at the upper chronic cutoff, the solubility of $\text{Ni}(\text{OH})_2(\text{cr})$ is exceeded early in the simulations where water column Ni concentration were high. Precipitation of Ni as $\text{Ni}(\text{OH})_2(\text{cr})$ hastens removal (Approaches 1 and 2) by increasing the particulate Ni (i.e., the $\log K_D$) (see Tables E-5 and E-6 in Appendix E). The pH 8 simulation with WHAM7 and the revised inorganic data base is unique in that 70% removal was achieved using Approaches 1 and 2, but not Approach 3. Simulations results indicate that the $\text{Ni}(\text{OH})_2(\text{cr})$ remained saturated until day five of the simulation. During the first five days, the total Ni in the water column decreased as $\text{Ni}(\text{OH})_2(\text{cr})$ settled. However, the dissolved phases Ni concentration was held constant according to the solubility project. Once the total Ni concentration decreased to the point where $\text{Ni}(\text{OH})_2(\text{cr})$ became undersaturated, the dissolve Ni concentration started to decrease with time. In essence, the onset of dissolved phase Ni removal was “delayed” by 5 days. This was enough to prevent 70% dissolved phase removal in 28 days (Approach 3).

The pH 8 simulations at the upper chronic cutoff value were repeated with the formation constant for $\text{Ni}(\text{OH})_2(\text{cr})$ decreased from the value in Plyasunova et al. (1998) (-10.52) to the value determined by

Gamsjäger et al. (2002) of (-11.1). Under this scenario, Ni(OH)₂(cr) was not predicted to precipitate and the 70% removal benchmark was not met for the simulations with the revised database without oxides. However, for the simulation with the Gamsjäger et al. (2002) formulation constant for the solid, the revised database and oxides, the benchmark was met.

Table 3-17. Water Column Removal Results for Nickel (WHAM7 with Revised Inorganic Database)

Scenario		Water Chemistry		
		pH 6	pH 7	pH 8
Model Speciation Approach				
Acute and Chronic ERV ^a	With the revised inorganic database	●	●	●
	With the revised inorganic database plus HFO and HMO	●	●	●
Upper Chronic Cutoff ^a	With the revised inorganic database	●	○	◐ ^b
	With the revised inorganic database plus HFO and HMO	●	●	● ^b

Legend:

- Greater than 70% removal achieved in 28 days for Approaches 1, 2, and 3
- ◐ Greater than 70% removal achieved in 28 days for a subset of approaches
- Less than 70% removal achieved in 28 days for none of the three approaches

Footnotes:

^a ERV Values:

Scenario	Initial Ni Concentration, µg/L	
	pH = 6	pH = 8
Acute	120	68
Chronic	2.4	2.4

Upper Chronic Cutoff = 1 mg/L; pH 7 calculation was made using 68 µg/L

^b Precipitation of Ni solid occurred.

3.4.6. Nickel Water Column Sensitivity Analysis Results (WHAM7 with Revised Inorganic Database)

The sensitivity analyses documented in Section 3.4.3 above were rerun using the WHAM7 sub-model with the revised database (no oxides). The results are presented in Table 3-18. The maximum depths at which 70% removal can be achieved in 28 days increased relative to the initial analysis (compare Tables 3-15 and 3-18). Whereas the critical depth initially ranged from 1.26 – 3.35 meters, it now ranges between 5.46 and 6.45.

Table 3-18. Maximum Depth to Achieve 70% Removal of Nickel in 28 Days (WHAM7 with Revised Inorganic Database) ^a

Simulation Description	Depth (m)
------------------------	-----------

pH 6.09	5.89
pH 7.07	6.45
pH 8.00	5.46

^a Initial Ni concentration was set at the pH-specific acute ERV (Table 2-2)

The results from the revised removal analysis with the lowered settling velocity (0.24 m/d) (Table E-7) indicate that, although use of the new model with revised inorganic database results in shorter 70% removal times, these times are still considerably greater than 28 days.

3.4.7. Preliminary Assessment of Nickel Remobilization Potential from Sediments (WHAM V)

To model the formation and dissolution of nickel sulfide (NiS) in a quantitative manner, a solubility product, K_{sp} , is required. In a recent review, Thoenen (1998) indicates that published values vary considerably. For example, for the reaction



Experimentally-determined $\log K_{s0}$ values range from -17.8 to -27.7. Thiel and Gessner (1914) determined $\log K_{s0}$ values of -20.5, -26, -27.7 for NiS(s, α), NiS(s, β), and NiS(s, γ), respectively. The authors indicate that the values were estimates. Furthermore, they were not able to describe the structural details of the various forms due to limitations of the technology available at the time (Thoenen, 1998). Values for the reaction



were calculated by Dyrssen and Kremling (1990) using the Thiel and Gessner data. These $\log {}^*K_s$ values of -5.6, -11.1, and -12.8 have been incorporated into compilations of stability constants such as the MINTEQA2 database.

The Dyrssen and Kremling (1990) constants have been used to assess the degree of NiS(s) saturation in natural systems based on calculated ion activity products ($IAP = \{M^{2+}\}\{HS^-\}/\{H^+\}$). In an investigation by Huerta-Diaz et al. (1998), IAP values were found to be generally consistent with either NiS(s, α) or NiS(s,millerite). The $\log {}^*K_s$ value for NiS(s,millerite) (-9.23) was referenced from Smith and Martell (1977). This same value for NiS(s,millerite) was used in Di Toro et al. (1992). IAP data near the sediment surface from a study by Canavan et al. (2007) were generally consistent with NiS(s, α). Recent investigations (Huang et al., 2009; Huang et al., 2010) indicate that the initial nickel sulfide precipitated at low temperature from aqueous solutions can be modeled as “crystalline millerite-type, NiS cores with a hydrated shell phase exhibiting considerable structural disorder” but do not provided any new solubility data. Wilkin and Rogers (2010), have investigated the solubility of a NiAs-type hexagonal NiS solid formed at a range of temperatures including 25°C. They did not detect millerite in any of their synthesis experiments. However, their experimentally-determined $\log {}^*K_s$ for hexagonal NiS (-9.71) is very close to the value quoted above for millerite.

Given the variability in the solubility products, selection of a single appropriate value is difficult if not impossible. However, given that the first solid to form is typically the most soluble form, and that the remobilization potential analyses are meant to examine short term additions of nickel to a lake and its

sediment, the NiS(α) value was selected for general use. Use of the NiS(α) value will produce the highest porewater nickel concentrations and therefore represent a realistic worst-case scenario for nickel toxicity to benthic organisms and transport out of the sediment via diffusion. An additional calculation will be performed, however, using the NiS(s,millerite) \log^*K_s value to indicate the implications of a less soluble nickel sulfide form

With AVS at the 10th percentile value of 1 $\mu\text{mol/g}$, pseudo steady-state water column concentrations were greater than 4 times below those representing 70% removal (Table E-8). Although there was sufficient AVS available to bind all Ni in the sediment, NiS solubility, as dictated by the magnitude of the solubility product of NiS(α), was great enough to prevent sulfide precipitation from dominating Ni speciation in the sediment (Table 3-19). Partial NiS formation resulted in a relatively small sediment Ni $\log K_D$ values. The values ranged between 2.72 and 2.87 (Table E-8). These sediment $\log K_D$ values were smaller than the water column values (range: 3.53 – 3.54). As a result, the integrated dissolved Ni flux was directed out of the sediment. Only the first criterion was met in this case.

With AVS at the 50th percentile value of 9.1 $\mu\text{mol/g}$, pseudo steady-state water column concentrations were again greater than 5 times below those representing 70% removal satisfying the first sequestration criteria (Tables 3-19 and E-8). In the sediment, Ni was associated with both POC and AVS. At the acute ERV and 100 $\mu\text{g/L}$ loadings, the relatively high NiS(α) solubility again limits the amount of Ni bound by sulfide in the sediment. Similar to the 1 $\mu\text{mol/g}$ simulation, there was very little increase in the sediment Ni $\log K_D$ over the POC-only (i.e., no AVS) case (Table E-8). The sediment $\log K_D$ was still less than the water column $\log K_D$ and the integrated diffusive flux was directed out of the sediment layer. With the initial concentration at the upper chronic cutoff, Ni speciation in the sediment was dominated by precipitation with sulfide and all three sequestration criteria were met.

Table 3-19. Sediment Remobilization Results for Nickel (WHAM V)

Scenario			Sequestration Criteria			Sediment Binding Phases
			Sustained 70% removal	$K_{D, \text{sed}} > K_{D, \text{wc}}$	Diffusive Flux into Sediment	
Anoxic, AVS = 1 $\mu\text{mol/g}$	Default	Acute ERV				56.9% POC; 43.1% AVS
		Lower Chronic Cutoff	●	○	○	61.0% AVS; 39.0% POC
		Upper Chronic Cutoff				67.0% POC; 33.0% AVS
	No Ca/Mg Comp.	Acute ERV, Lower and Upper Chronic Cutoff	●	○	○	100% POC
Anoxic, AVS = 9.1 $\mu\text{mol/g}$	Default	Acute ERV	●	○	○	56.9% POC; 43.1% AVS
		Lower Chronic Cutoff	●	○	○	61.0% AVS; 39.0% POC
		Upper Chronic Cutoff	●	●	●	96.1% AVS; 3.9% POC
	No Ca/Mg Comp.	Acute ERV, Lower and Upper Chronic Cutoff	●	○	○	100% POC
Oxic	Default	Acute ERV				61.9% HFO; 36.9% POC; 1.2% HMO
		Lower Chronic Cutoff	●	○	○	61.3% HFO; 37.4% POC; 1.2% HMO
		Upper Chronic Cutoff				49.0% POC; 49.7% HFO; 1.3% HMO
	No Ca/Mg Comp.	Acute ERV				
		Lower Chronic Cutoff	●	○	○	99.0% POC; 1.0% HFO
		Upper Chronic Cutoff				98.8% POC; 1.2% HFO

Legend:

- Sequestration criterion is met
- Sequestration criterion is not met

Footnotes:

^a Lower Chronic Cutoff = 0.1 mg/L; Upper Chronic Cutoff = 1 mg/L

Results from no Ca/Mg competition simulations indicate that, following the initial dosing, water column Ni concentrations were maintained at levels more than 50 times lower than that representing 70% removal. The first sequestration criterion was satisfied (Tables 3-19 and E-9). However, in all scenarios considered, removal of Ca/Mg competition allowed Ni-POC interactions to dominate Ni speciation in sediment. As a result, the sediment $\log K_D$ was less than the water column value and the integrated

diffusive flux was directed out of the sediment layer (Table 3-19). For all scenarios considered, the second and third sequestration criteria were not met.

Results from anoxic simulations with NiS(s,millerite) (Table 3-20, E-10, and E-11) indicate a significant change in sediment speciation compared to those with NiS(α). The simulation results indicate that Ni speciation in sediment was dominated by NiS(s) precipitation for scenarios in which AVS was present in excess of Ni (Table 3-20). This was true whether or not Ca/Mg competition for binding sites on organic matter was eliminated. Only when the amount of Ni in sediment exceeded the AVS present was Ni bound to POC in appreciable amounts (Table 3-20). The three sequestration criteria were met in all scenarios except when the Ni loading was at the upper chronic cutoff value.

Table 3-20. Sediment Remobilization Results for Nickel with NiS(s,millerite) ($\log^*K_s = -9.23$) (WHAM V)

Scenario			Sequestration Criteria			Sediment Binding Phases
			Sustained 70% removal	$K_{D, \text{sed}} > K_{D, \text{wc}}$	Diffusive Flux into Sediment	
Anoxic, AVS = 1 $\mu\text{mol/g}$	Default	Acute ERV and Lower Chronic Cutoff ^a	●	●	●	100% AVS
		Upper Chronic Cutoff ^a	●	○	○	67.0% POC; 33% AVS
	No Ca/Mg Comp.	Acute ERV	●	●	●	97.7% AVS; 2.3% POC
		Lower Chronic Cutoff	●	●	●	98.4% AVS; 1.6% POC
		Upper Chronic Cutoff	●	○	○	68.9% POC; 31.1% AVS
	Anoxic, AVS = 9.1	Default	Acute ERV, Lower and Upper Chronic Cutoff ^a	●	●	●
Acute ERV			●	●	●	97.7% AVS; 2.3% POC
No Ca/Mg Comp.		Lower Chronic Cutoff	●	●	●	98.4% AVS; 1.6% POC
		Upper Chronic Cutoff	●	●	●	99.8% AVS; 0.2% POC

Legend:

- Sequestration criterion is met
- Sequestration criterion is not met

Footnotes:

^a Lower Chronic Cutoff = 0.1 mg/L; Upper Chronic Cutoff = 1 mg/L

TICKET-UWM results for simulations with an oxic layer and the default WHAM V parameters indicate that, following the initial dosing, water column Ni concentrations were maintained at levels more than a factor of four lower than those representing 70% removal (Table E-8) indicating that the first

sequestration criterion was met. Depending on the Ni loading, the majority of sediment Ni is either associated with HFO or POC. However, in none of the oxic scenarios considered was the sediment Ni log K_D greater than the water column log K_D (Table E-8). The second and third criteria were not met for any of the oxic scenarios with the default WHAM parameters (Table 3-19).

Results from no Ca/Mg competition simulations for oxic sediment indicate that, following the initial dosing, water column Ni concentrations were maintained at levels far below those representing 70% removal (Table E-9). However, with competition removed, most sediment Ni was associated with POC. Neither of the remaining two sequestration criteria was met.

3.4.8. Preliminary Assessment of Nickel Remobilization Potential from Sediments (WHAM7 with Revised Inorganic Database)

The results from the revised sediment analysis (Table 3-21 and E-12) are similar to those presented in Tables 3-19 (oxic simulations) and 3-20 (anoxic simulations). The similarity between the revised anoxic sediment results (made using hexagonal NiS) and those made with millerite is a consequence of the similarity in the two solubility products (Table E-4). The key point from the sediment analysis is when the metal accumulated in the sediment is less than the available AVS (anoxic sediment), all three sequestration criteria are met and sediment metal speciation is dominated by metal sulfide precipitation. For AVS at 1 $\mu\text{mol/g}$, this occurs for initial loadings at the acute ERV and the lower chronic cutoff of 100 $\mu\text{g/L}$. For AVS at 9.1 $\mu\text{mol/g}$, this occurs for all initial loadings assessed.

Table 3-21. Sediment Remobilization Results for Nickel (WHAM7 with Revised Inorganic Database) ^a

Scenario		Sequestration Criteria			Sediment Binding Phases
		Sustained 70% removal	$K_{D,\text{sed}} > K_{D,\text{wc}}$	Diffusive Flux into Sediment	
Anoxic, AVS = 1 $\mu\text{mol/g}$	Acute ERV and Lower Chronic Cutoff ^a	●	●	●	100% AVS
	Upper Chronic Cutoff ^a	● (after 29.0 days)	○	○	68.1% POC; 31.9% AVS
Anoxic, AVS = 9.1 $\mu\text{mol/g}$	Acute ERV and Lower Chronic Cutoff ^a	●	●	●	100% AVS
	Upper Chronic Cutoff ^a	● (after 28.9 days)	●	●	100% AVS
Oxic	Acute ERV	●	○	○	61.9% POC; 37.4% HFO; 0.7% HMO
	Lower Chronic Cutoff	●	○	○	61.5% POC; 37.8% HFO; 0.7% HMO
	Upper Chronic Cutoff	● (after 29.0 days)	○	○	58.1% POC; 40.8% HFO; 1.0% HMO

Legend:

- Sequestration criterion is met
- Sequestration criterion is not met

Footnotes:

^a Lower Chronic Cutoff = 0.1 mg/L; Upper Chronic Cutoff = 1 mg/L

A remobilization potential analysis was also made using the linear partitioning method and the empirical $\log K_D$ values listed in Table 2-3. The results indicated that there was sustained 70% removal. However the water column $\log K_D$ was greater than the sediment $\log K_D$ and the integrated diffusive flux was directed out of the sediment. Only the first sequestration criterion was met for Ni using the linear partitioning method.

3.5. Cobalt

3.5.1. Cobalt Water Column Results – Linear Partitioning Method

TICKET-UWM output for total and dissolved cobalt (Co) remaining versus time for the linear partitioning method is shown in Figure 3-7. Based on the suspended solids concentration of 15 mg/L and the empirical $\log K_D$ (Table 2-3), approximately 37% of the Co added to the water column was bound to suspended particles. According to Approach 1 for calculating removal, the rapid removal benchmark was met 2.5 days after addition (Figure 3-7b, red line). Under the more conservative approach where removal is based on total Co (Approach 2), the rapid removal benchmark was met 4.0 days after Co addition (Figure 3-7a, blue line). The time for rapid removal using Approach 3 was essentially equal to that for Approach 2.

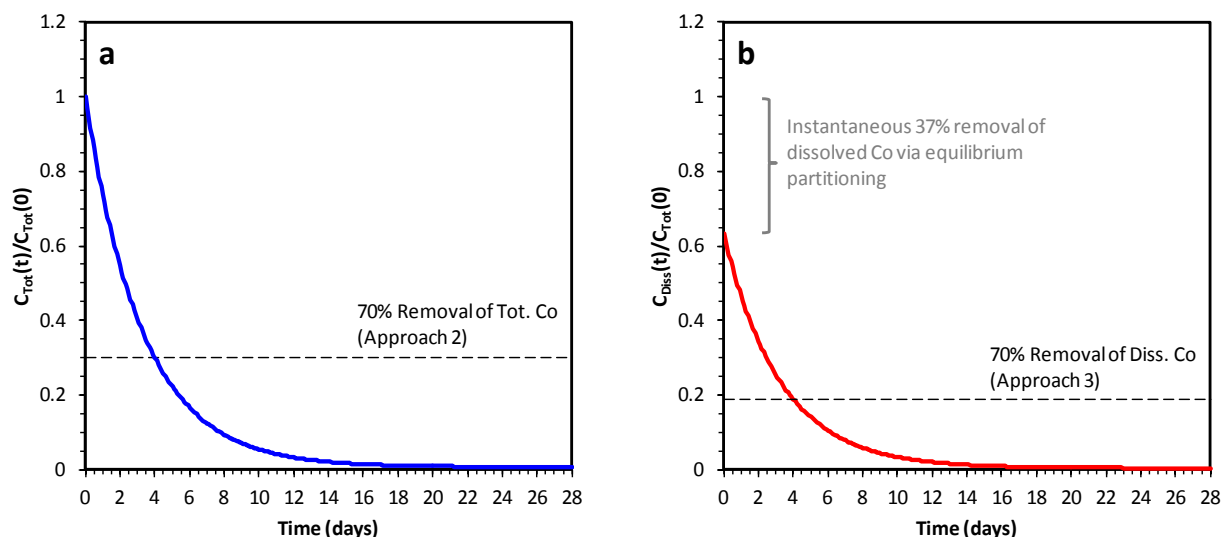


Figure 3-7. a) Total and b) dissolved cobalt (Co) removal from the water column using EUSES model parameters and the linear partitioning method. The initial total Co concentration in the water column, $C_{Tot}(0)$, is specified at the acute ecotoxicity reference value (ERV) of 90.1 $\mu\text{g/L}$. The horizontal dashed lines represents a) $C_{Tot}(t)/C_{Tot}(0) = 0.3$ (70% removal of total Co) and b) $C_{Diss}(t)/C_{Diss}(0) = 0.3$ (70% removal of dissolved Co).

3.5.2. Cobalt Water Column Results – Speciation Model Method

Tables 3-22, F-1 and F-2 (Appendix F) summarize the results of the various model simulations made using the speciation model method. For the pH 6 and 7 simulations with the default model parameters and initial concentrations set of the acute and chronic ERVs, 70% removal was achieved within 28 days of addition. At pH 8, more than 70 days were required for 70% removal.

The log K_D and fraction particulate values generally decreased with increasing pH (Table F-1 in Appendix F). The reduction in log K_D that occurred as pH was increased is primarily a function of the increased alkalinity and hardness associated with the high pH water chemistries (Table 2-1). At higher alkalinities, Co has a greater tendency to form complexes with carbonate thereby decreasing the amount bound to POC. Additionally, at higher hardness values, Ca/Mg competition for binding sites reduces the amount of Co on POC.

For simulations using the upper chronic cutoff value, the increased Co concentrations resulted in lower predicted log K_D values (non-linear partitioning) and lower removal rates (Table F-1 in Appendix F). As a result, greater than 28 days were required for 70% removal at pH 7 and 8 while the removal benchmark was only achieved at pH 6 when removal was calculated using dissolved Co (Approaches 1 and 3).

Table 3-22. Water Column Removal Results for Cobalt

Scenario		Water Chemistry		
		pH 6	pH 7	pH 8
Empirical K_D Approach				
Acute/Chronic ERV and Upper Chronic Cutoff ^a		●		
Model Speciation Approach				
Acute and Chronic ERV	Default	●	●	○
	No Ca/Mg Comp.	●	●	●
Upper Chronic Cutoff	Default	◐	○	○
	No Ca/Mg Comp.	●	●	●

Legend:

- Greater than 70% removal achieved in 28 days for Approaches 1, 2, and 3
- ◐ Greater than 70% removal achieved in 28 days for a subset of approaches
- Less than 70% removal achieved in 28 days for none of the three approaches

Footnotes:

^a Acute ERV = 90.1 µg/L; Chronic ERV = 4.9 µg/L; Upper Chronic Cutoff = 1 mg/L

The calculated log K_D values (range = 3.26 – 3.64) are all notably lower than the guidance document value of 4.59. This deviation can be caused by the factors discussed above for Zn.

Speciation calculations revealed that for the three water chemistries in Table 2-1 increases in $\log K_D$ were obtained when Ca/Mg binding to organic matter was eliminated from the calculation. Therefore, additional TICKET-UWM simulations were performed to demonstrate Co removal in the absence of hardness cation competition for binding sites on organic matter. The results are shown in Table 3-22 and Table F-2 (Appendix F). Without Ca/Mg competition, the $\log K_D$ values increased (range = 3.93 – 5.64). This range brackets the empirical value of 4.59. As a result of the increased $\log K_D$ values, the time required for 70% removal decreased from 23 – 54 days to instantaneously – 9.3 days (Tables F-1 and F-2). Without Ca/Mg competition, the 70% removal benchmark was met at all water chemistries (Table 3-22).

Calculations were also made to assess the effect of HFO and HMO on the model-calculated K_D value. Typical water column HFO and HMO concentration were used (Section 3.2.2). At pH 7 with an initial Co concentration of 90.1 $\mu\text{g/L}$, the inclusion of HFO and HMO increased the predicted $\log K_D$ from approximately 3.61 to 3.68 – 3.74. At pH 8 with the same initial Co concentration of 90.1 $\mu\text{g/L}$, the inclusion of HFO and HMO increased the predicted $\log K_D$ from approximately 3.33 to 3.50 – 3.59. It should be noted that even with this increase in $\log K_D$, the 28-day removal is still less than 70%.

3.5.3. Cobalt Water Column Sensitivity Analysis Results

A sensitivity analysis was conducted to evaluate the critical depth at which exactly 70% removal was achieved in 28 days using Approach 1 for a system with initial Co at the pH-specific acute value (Table 2-2). The results are shown in Table 3-23. For the linear partitioning method, rapid removal is possible at depths more than ten times the default generalized lake depth of 3 meters. For simulations using the default WHAM V speciation calculations, critical depths (for a settling velocity of 2.5 m/d) ranged from 3.58 to 1.82 meters. The low predicted $\log K_D$ values restrict rapid removal to shallow lakes and ponds.

Table 3-23. Critical Depth to Achieve 70% Removal of Cobalt in 28 Days ^a

Simulation Description	Depth (m)
Linear Partitioning	33.2
pH 6.09	3.58
pH 7.07	3.45
pH 8.00	1.82

^a Initial Co concentration was set at the pH-specific acute ERV (Table 2-2)

Another sensitivity analysis was conducted to assess removal with settling velocity decreased from the EUSES value of 2.5 m/d to 0.24 m/d. A settling rate of 0.24 m/d represents the lower end of the POC range from Burns and Rosa, (1980). The results are shown in Table 3-24. For the linear partitioning method, the time required to obtain 70% removal was 24.9 days (Approach 1) and 40.4 days (Approaches 2 and 3). For the speciation model method simulations, removal times in excess of 200 days were required to reach 70% removal. At pH 8, approximately a year is required to achieve 70% removal. Therefore, for what could potentially be considered a minimum or “worst-case” settling velocity, Co is not rapidly removed from the water column.

Table 3-24. Water Column Removal Results for Cobalt with Decreased Settling Velocity ^a

Simulation Description	Removal Result
Linear Partitioning	●
pH 6.09	○
pH 7.07	○
pH 8.00	○

Legend:

- Greater than 70% removal achieved in 28 days for Approaches 1, 2, and 3
- ◐ Greater than 70% removal achieved in 28 days for a subset of approaches
- Less than 70% removal achieved in 28 days for none of the three approaches

Footnotes:

- ^a Settling velocity = 0.24 m/d
- ^b Initial Co concentration was set at the pH-specific acute ERV (Table 2-2)

3.5.4. Preliminary Assessment of Cobalt Remobilization Potential from Sediments

With AVS at the 10th percentile value of 1 $\mu\text{mol/g}$ and the initial concentration set at the acute ERV, pseudo steady-state water column concentrations were greater than 5 times below those representing 70% removal (Table F-4). In addition, there was sufficient AVS available to bind all the Co in the sediment (Table 3-25). The additional Co binding afforded by the AVS resulted in a sediment $\log K_D$ of 4.98 (Table F-4) which is significantly greater than the value calculated for the water column of 3.61. As a result, the integrated dissolved Co flux was directed into the sediment. All three sequestration criteria were met in this case. However, with the Co loading increased to the upper chronic cutoff value, available AVS in the sediment was exhausted (Table 3-25). Sediment Co was divided between AVS and POC. Consequently, the sediment $\log K_D$ was less than the water column $\log K_D$ (Table F-4). As a result, the integrated diffusive flux was directed out of the sediment.

With AVS at the 50th percentile value of 9.1 $\mu\text{mol/g}$, pseudo steady-state water column concentrations were again greater than 5 times below those representing 70% removal satisfying the first sequestration criterion (Tables 3-25 and F-4). This time AVS dominated sediment Co speciation at both loading concentrations. The additional Co binding afforded by AVS resulted in larger $\log K_D$ values in the sediment compared to the water column K_D . The integrated diffusive flux was directed into the sediment.

As was the case for the simulations with default TICKET-UWM parameterization, results from no Ca/Mg competition simulations indicate that, following the initial dosing, water column Co concentrations were maintained at levels far below those representing 70% removal satisfying the first sequestration criterion (Tables 3-25 and F-5). Compared to the default simulation, distribution coefficients calculated in no Ca/Mg competition simulations increased in the water column for all cases (Tables F-4 and F-5). In the sediments, the lack of Ca/Mg competition shifted much of the particulate Co that was formerly associated with AVS to POC (Tables 3-25 and F-5). The end result was that the water column $\log K_D$ was larger than the sediment $\log K_D$ and the second and third sequestration criteria were not met for most of the no Ca/Mg competition scenarios (Table 3-25).

Table 3-25. Sediment Remobilization Results for Cobalt

Scenario			Sequestration Criteria			Sediment Binding Phases
			Sustained 70% removal	$K_{D, \text{sed}} > K_{D, \text{wc}}$	Diffusive Flux into Sediment	
Anoxic, AVS = 1 $\mu\text{mol/g}$	Default	Acute ERV	●	●	●	99.4% AVS; 0.6% POC;
		Upper Chronic Cutoff	●	○	○	67.2% POC; 32.8% AVS
	No Ca/Mg Comp.	Acute ERV	●	○	○	100% POC
		Upper Chronic Cutoff	●	○	○	68.8% POC; 31.2% AVS
Anoxic, AVS = 9.1 $\mu\text{mol/g}$	Default	Acute ERV	●	●	●	> 99% AVS; < 1% POC
		Upper Chronic Cutoff	●	●	●	> 99% AVS; < 1% POC
	No Ca/Mg Comp.	Acute ERV	●	○	○	100% POC
		Upper Chronic Cutoff	●	○	●	90.4% AVS; 9.6% POC
Oxic	Default	Acute ERV	●	○	○	60.1% POC; 21.0% HFO 18.9% HMO
		Upper Chronic Cutoff	●	○	○	72.0% POC; 22.6% HFO 5.4% HMO
	No Ca/Mg Comp.		●	○	○	> 99% POC , < 1% oxides

Legend:

- Sequestration criterion is met
- Sequestration criterion is not met

Footnotes:

^a Lower Chronic Cutoff = 0.1 mg/L; Upper Chronic Cutoff = 1 mg/L

TICKET-UWM results for simulations with an oxic layer and the default WHAM V parameters indicate that, following the initial dosing, water column Co concentrations were maintained at levels far below those representing 70% removal (Table F-5) indicating that the first sequestration criterion was met. At both loadings, a significant fraction of sediment Co was associated with oxides. Most sediment Co is associated with POC, however, and the sediment $\log K_D$ were lower than the surface water values. As a result, the integrated diffusive flux was directed out of the sediment. Both the second and third sequestration criteria were not met.

Results from no Ca/Mg competition simulations for oxic sediment indicate that, following the initial dosing, water column Co concentrations were maintained at levels far below those representing 70% removal (Table F-5). The first sequestration criterion was met. However, with competition removed, most sediment Co is associated with POC. Neither of the remaining two sequestration criteria were met.

A remobilization potential analysis was also made using the linear partitioning method and the empirical $\log K_D$ values listed in Table 2-3. The results indicated that there was sustained 70% removal. However

the water column $\log K_D$ was greater than the sediment $\log K_D$ and the integrated diffusive flux was directed out of the sediment. Only the first sequestration criterion was met for Co using the linear partitioning method.

3.6. Cadmium

3.6.1. Cadmium Water Column Results – Linear Partitioning Method

TICKET-UWM output for total and dissolved Cd remaining versus time for the linear partitioning method is shown in Figure 3-8. Based on the suspended solids concentration of 15 mg/L and the empirical $\log K_D$ (Table 2-3), approximately 66% of the Cd added to the water column was bound to suspended particles. Thus, according to Approach 1 for calculating removal, the rapid removal benchmark was met almost immediately by virtue of equilibrium partitioning. The benchmark was met 0.23 days after addition (Figure 3-8b, red line). Under the more conservative approach where removal is based on total Cd (Approach 2), the rapid removal benchmark was met 2.3 days after Cd addition (Figure 3-8a, blue line). The time for rapid removal using Approach 3 was essentially equal to that for Approach 2.

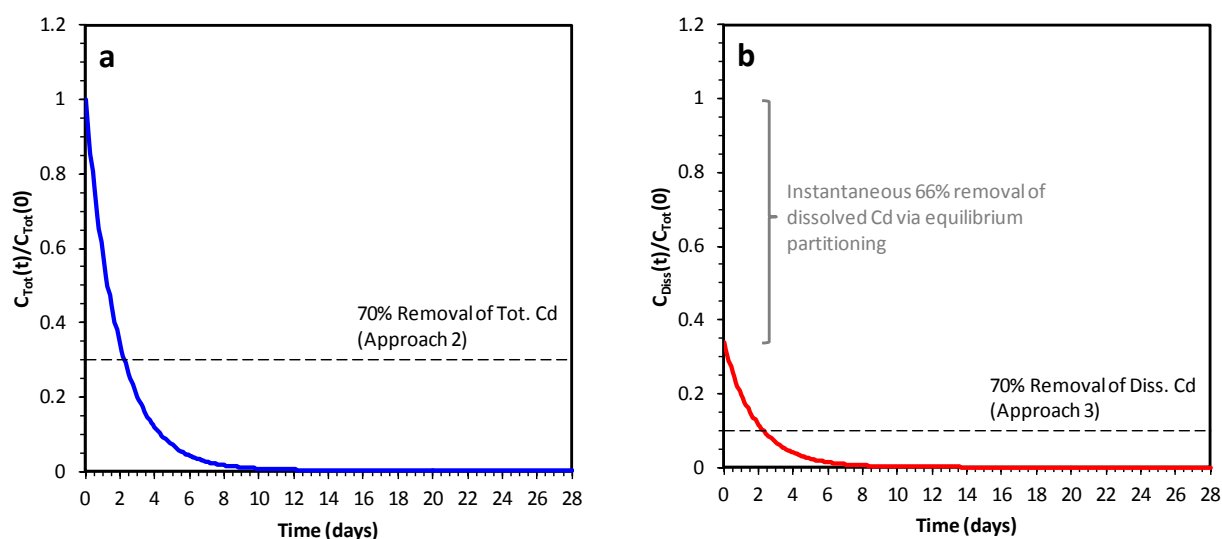


Figure 3-8. a) Total and b) dissolved cadmium (Cd) removal from the water column using EUSES model parameters and the linear partitioning method. The initial total Cd concentration in the water column, $C_{Tot}(0)$, is specified at the acute ecotoxicity reference value (ERV) of 18 $\mu\text{g/L}$. The horizontal dashed lines represents a) $C_{Tot}(t)/C_{Tot}(0) = 0.3$ (70% removal of total Cd) and b) $C_{Diss}(t)/C_{Diss}(0) = 0.3$ (70% removal of dissolved Cd).

3.6.2. Cadmium Water Column Results – Speciation Model Method

Tables 3-26 and G-1 (Appendix G) summarize the results of the various model simulations made using the speciation model method. The Cd results (Table 3-26) are similar qualitatively to those for Co: For the pH 6 and 7 simulations with the default model parameters and initial concentrations set of the acute and chronic ERVs, 70% removal was achieved within 28 days of addition. At pH 8, more than 70 days were required for 70% removal. Similar to Co, $\log K_D$ and fraction particulate values for Cd generally decreased with increasing pH (Table G-1).

For simulations using the upper chronic cutoff value, increased Cd concentrations generally resulted in lower predicted log K_D values (non-linear partitioning) and lower removal rates (Table G-1). Greater than 28 days were required for 70% removal at pH 7. The high alkalinity associated with the pH 8 water chemistry resulted in precipitation of $\text{CdCO}_3(\text{s})$. This resulted in immediate attainment of 70% removal according to Approach 1. Precipitation increased the log K_D and the removal rate of Cd based on Approach 2 relative to the log K_D and the removal rate from other pH 8 runs at different loadings. As a result, the removal at day 28 for the chronic cutoff loading was greater than 70% in contrast to the pH 8 results for the acute and chronic ERVs (Table 3-26). Similar to Ni simulations in which $\text{Ni}(\text{OH})_2(\text{cr})$ formed, the precipitation of $\text{CdCO}_3(\text{s})$ resulted in approximately constant dissolved Cd concentrations. As a result, 70% removal was not achieved according to Approach 3 (Tables 3-26 and G-1).

Table 3-26. Water Column Removal Results for Cadmium

Scenario		Water Chemistry		
		pH 6	pH 7	pH 8
Empirical K_D Approach				
Acute/Chronic ERV and Upper Chronic Cutoff ¹			●	
Model Speciation Approach				
Acute and Chronic ERV	Default	●	●	○
	No Ca/Mg Comp.	●	●	●
Upper Chronic Cutoff	Default	●	○	◐
	No Ca/Mg Comp.	●	●	●

Legend:

- Greater than 70% removal achieved in 28 days for Approaches 1, 2, and 3
- ◐ Greater than 70% removal achieved in 28 days for a subset of approaches
- Less than 70% removal achieved in 28 days for none of the three approaches

Footnotes:

¹ Acute ERV = 18 $\mu\text{g/L}$; Chronic ERV = 0.21 $\mu\text{g/L}$; Upper Chronic Cutoff = 1 mg/L

Excluding the pH 8 value at the chronic cut-off concentration, calculated log K_D values for Cd (range = 3.48 – 3.63) were all significantly lower than the guidance document value of 5.11. The possible reasons for the discrepancy are the same as those listed above for Zn. Additional TICKET-UWM simulations were performed to demonstrate Cd removal in the absence of hardness cation competition. The results from TICKET-UWM simulations with no Ca/Mg competition are shown in Table 3-26 and Table G-2 (Appendix G). Without Ca/Mg competition, the log K_D values generally increased (range = 3.84 – 5.60). This range brackets the empirical value of 5.11. As a result of the increased log K_D values, the time required for 70% removal according to Approach 1 decreased from 24 – 33 (excluding the pH 8 simulation at the chronic cut-off concentration) days to instantaneously – 15.7 days (Tables G-1 and G-2). Without Ca/Mg competition, the 70% removal benchmark was achieved at all water chemistries (Table 3-26).

Calculations were also made to assess the effect of HFO and HMO on the model-calculated K_D value. Typical water column HFO and HMO concentration were used (Section 3.2.2). At pH 7 with an initial Cd concentration of 18 $\mu\text{g/L}$, the inclusion of HFO and HMO increased the predicted log K_D from approximately 3.60 to 3.73 – 3.74. At pH 8 with the same initial Cd concentration of 18 $\mu\text{g/L}$, the inclusion of HFO and HMO increased the predicted log K_D from approximately 3.48 to 3.84 – 3.88. These ranges are still inconsistent with the empirical value. However, it should be noted that for the pH 8 simulation, the increase in log K_D associated the inclusion of HFO and HMO was sufficient to allow greater than 70% removal within 28-days unlike the default case at this pH and loading (Table 3-26).

3.6.3. Cadmium Water Column Sensitivity Analysis Results

A sensitivity analysis was conducted to evaluate the critical depth at which exactly 70% removal was achieved in 28 days using Approach 1 for a system with an initial Cd at the pH-specific acute value (Table 2-2). The results are shown in Table 3-27. For the linear partitioning method, rapid removal is possible at depths more than 100 times the default generalized lake depth of 3 meters. Such a large critical depth was possible in this case because, as discussed in Section 3.6.1, 70% removal (according to Approach 1) was achieved almost instantaneously due to the initial partitioning. For simulations using the default WHAM V speciation calculations, critical depths (for a settling velocity of 2.5 m/d) ranged from 3.51 to 2.56 meters.

Table 3-27. Critical Depth to Achieve 70% Removal of Cadmium in 28 Days ^a

Simulation Description	Depth (m)
Linear Partitioning	364
pH 6.09	3.51
pH 7.07	3.30
pH 8.00	2.56

^a Initial Cd concentration was set at the pH-specific acute ERV (Table 2-2)

Another sensitivity analysis was conducted to assess removal with settling velocity decreased from the EUSES value of 2.5 m/d to 0.24 m/d. A settling rate of 0.24 m/d represents the lower end of the POC range from Burns and Rosa, (1980). The results are shown in Table 3-28. The marked discrepancy between the empirical and speciation-mode-predicted log K_D values yielded very different. For the linear partitioning method, the time required to obtain 70% removal was 2.31 days (Approach 1) and 22.7 days (Approaches 2 and 3). For the speciation model method simulations, removal times in excess of 200 days were required to reach 70% removal.

Table 3-28. Water Column Removal Results for Cadmium with Decreased Settling Velocity ^{a,b}

Simulation Description	Removal Result
Linear Partitioning	●
pH 6.09	○
pH 7.07	○
pH 8.00	○

Legend:

- Greater than 70% removal achieved in 28 days for Approaches 1, 2, and 3
- ◐ Greater than 70% removal achieved in 28 days for a subset of approaches
- Less than 70% removal achieved in 28 days for none of the three approaches

Footnotes:

- ^a Settling velocity = 0.24 m/d
- ^b Initial Cd concentration was set at the pH-specific acute ERV (Table 2-2)

3.6.4. Preliminary Assessment of Cadmium Remobilization Potential from Sediments

In anoxic simulations, the first sequestration criterion is met in all scenarios (Table 3-29 and G-4) with pseudo steady-state water column concentrations more than 5 times lower than the 70% removal concentration. The model predicts strong interaction between Cd and sulfide in sediment. For the anoxic sediment simulations at the 10th and 90th percentile AVS concentrations (both with and without Ca/Mg competition), as long as AVS was in excess of the Cd transported to the sediment, CdS(s) formation dominated Cd sediment speciation (Table 3-29) and the second and third sequestration criteria were met. For simulations at the upper chronic cutoff (both with and without Ca/Mg competition) and AVS at the 10th percentile value, excess Cd was bound by POC. In this case, the extent to which Cd binding is enhanced in the sediment over the water column was limited and the second and third sequestration criteria were not met.

Table 3-29. Sediment Remobilization Results for Cadmium

Scenario			Sequestration Criteria			Solid-Phase Speciation
			Sustained 70% removal	$K_{D, sed} > K_{D, wc}$	Diffusive Flux into Sediment	
Anoxic, AVS = 1 $\mu\text{mol/g}$	Default	Acute ERV and Lower Chronic Cutoff	●	●	●	100% AVS
		Upper Chronic Cutoff	●	○	○	62.5% AVS; 37.5% POC
	No Ca/Mg Comp.	Acute ERV and Lower Chronic Cutoff	●	●	●	100% AVS
		Upper Chronic Cutoff	●	○	○	59.6% AVS; 40.4% POC
Anoxic, AVS = 9.1 $\mu\text{mol/g}$	Default	Acute ERV, Lower and Upper Chronic Cutoff	●	●	●	100% AVS
	No Ca/Mg Comp.	Acute ERV, Lower and Upper Chronic Cutoff				
Oxic	Default	Acute ERV	●	○	○	60.5% HFO; 35.2% POC; 4.3% HMO

		Lower Chronic Cutoff				59.3% HFO; 36.5% POC; 4.2% HMO
		Upper Chronic Cutoff				50.1% POC; 46.9% HFO; 3.0% HMO
	No Ca/Mg Comp.		●	○	○	~ 99% POC; ~ 1% HFO; ~0.1% HMO

Legend:

- Sequestration criterion is met
- Sequestration criterion is not met

Footnotes:

^a Lower Chronic Cutoff = 0.1 mg/L; Upper Chronic Cutoff = 1 mg/L

TICKET-UWM results for simulations with an oxic layer and the default WHAM V parameters indicate that, following the initial dosing, water column Cd concentrations were maintained at levels far below those representing 70% removal (Table G-4) indicating that the first sequestration criterion was met (Table 3-29). At all loadings, a significant fraction of sediment Cd was associated with oxides. The predicted sediment log K_D values were lower than the surface water values. As a result, the integrated diffusive flux was directed out of the sediment. Both the second and third sequestration criteria were not met.

Results from no Ca/Mg competition simulations for oxic sediment indicate that, following the initial dosing, water column Cd concentrations were maintained at levels far below those representing 70% removal (Table G-5). However, with competition removed, most sediment Cd was associated with POC. Neither of the remaining two sequestration criteria were met.

A remobilization potential analysis was also made using the linear partitioning method and the empirical log K_D values listed in Table 2-3. The results indicated that there was sustained 70% removal. However the water column log K_D was greater than the sediment log K_D and the integrated diffusive flux was directed out of the sediment. Only the first sequestration criterion was met for Cd using the linear partitioning method.

3.7. Silver

3.7.1. Silver Water Column Results – Linear Partitioning Method

TICKET-UWM output for total and dissolved silver (Ag) remaining versus time for the linear partitioning method is shown in Figure 3-9. Based on the suspended solids concentration of 15 mg/L and the empirical log K_D of 5.28 (Table 2-3), approximately 74% of the Ag added to the water column was bound to suspended particles. Thus, according to Approach 1 for calculating removal, the rapid removal benchmark was met immediately by virtue of equilibrium partitioning (Figure 3-9b, red line). Under the more conservative approach where removal is based on total Ag (Approach 2), the rapid removal benchmark was met 2.0 days after Ag addition (Figure 3-9a, blue line). The time for rapid removal using Approach 3 was essentially equal to that for Approach 2.

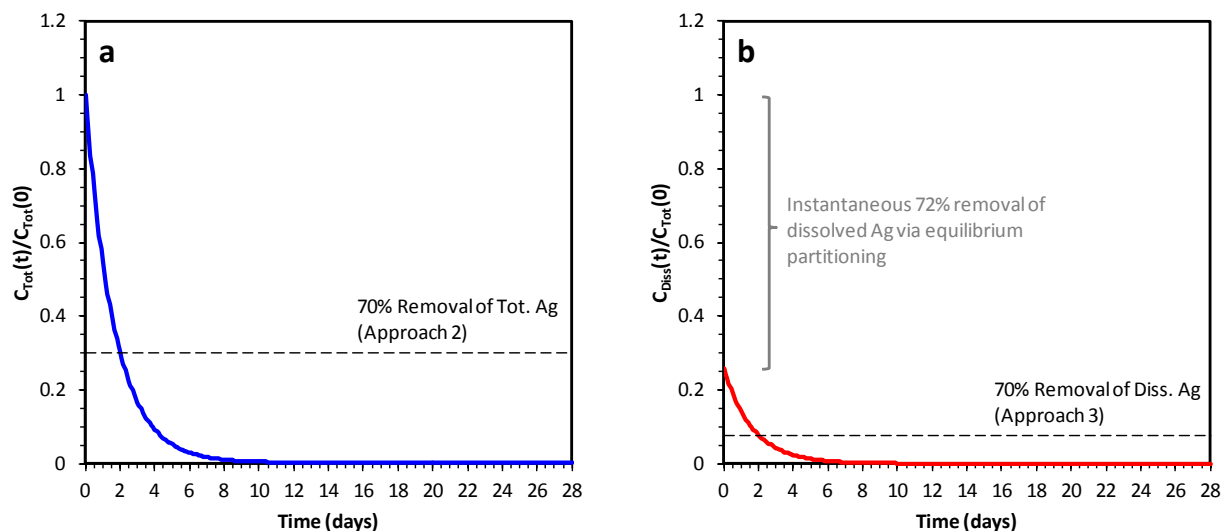


Figure 3-9. a) Total and b) dissolved silver (Ag) removal from the water column using EUSES model parameters and the linear partitioning method. The initial total Ag concentration in the water column, $C_{Tot}(0)$, is specified at the acute ecotoxicity reference value (ERV) of 220 ng/L. The horizontal dashed lines represents a) $C_{Tot}(t)/C_{Tot}(0) = 0.3$ (70% removal of total Ag) and b) $C_{Diss}(t)/C_{Diss}(0) = 0.3$ (70% removal of dissolved Ag).

3.7.2. Silver Water Column Results – Speciation Model Method

Tables 3-30, H-1 and H-2 (Appendix H) summarize results of the various model simulations made using the speciation model method. The key particulate Ag species in these simulations were precipitated Ag ($AgCl(s)$) and Ag sorbed to POC. Silver interaction with the carboxylic and phenolic functional groups comprising organic matter is generally weak (Carbonaro and Di Toro, 2007; Paquin and Di Toro, 2008). These functional groups are the dominant sites considered by WHAM V and, accordingly, Ag binding to DOC and POC in the TICKET-UWM simulations was limited. At the acute and chronic ERV values, where all Ag solids were undersaturated, model-predicted $\log K_D$ were low (2.93 – 3.22) (Table H-1) and the time required to achieve 70% removal exceeded 28 days for the three removal evaluation approaches and the three water column pH values (Tables 3-30 and H-1). For model runs with an initial Ag concentration of 100 $\mu g/L$, some Ag precipitation was predicted early in the simulation, and, as a result, maximum $\log K_D$ values increased and 70% removal times decreased (Table H-1). However, the increase in removal rate afforded by precipitation was not sufficient bring about 70% removal in 28 days (3-30 and H-1). For simulations with initial Ag concentrations at the chronic cutoff, however, the impact of precipitation was more substantial. Rapid removal was achieved for Approaches 1 and 2 and all three pH values. Similar to Ni and Cd simulations in which solids formed, the precipitation of $AgCl(s)$ resulted in approximately constant dissolved phase Ag concentrations. As a result 70% removal was not achieved according to Approach 3 (Tables 3-30 and H-1).

Table 3-30. Water Column Removal Results for Silver

Scenario	Water Chemistry			
	pH 6	pH 7	pH 8	
Empirical K_D Approach				
Acute/Chronic ERV, Upper and Lower Chronic Cutoff ^a		●		
Model Speciation Approach				
Acute ERV and Chronic ERV	Default	○	○	○
	No Ca/Mg Comp.	○	●	●
Lower Chronic Cutoff	Default	○ ^b	○ ^b	○ ^b
	No Ca/Mg Comp.	○	● ^b	● ^b
Upper Chronic Cutoff	Default	◐ ^b	◐ ^b	◐ ^b
	No Ca/Mg Comp.	◐ ^b	◐ ^b	● ^b

Legend:

- Greater than 70% removal achieved in 28 days for Approaches 1, 2, and 3
- ◐ Greater than 70% removal achieved in 28 days for a subset of approaches
- Less than 70% removal achieved in 28 days for none of the three approaches

Footnotes:

^a Acute ERV = 220 ng/L; Chronic ERV = 120 ng/L; Lower Chronic Cutoff = 0.1 mg/L; Upper Chronic Cutoff = 1 mg/L

^b Precipitation of Ag solid occurred.

With the exception of some of the simulations with starting concentrations at 100 and 1000 $\mu\text{g/L}$, the calculated surface water $\log K_D$ values (range = 2.93 – 3.22) were all markedly lower than the guidance document value of 5.28. To illustrate the potential impact of Ca/Mg competition for binding sites, simulations were made in which hardness cation competition for DOC/POC binding sites was excluded from the speciation calculation.

In general, with less competition for site on POC, $\log K_D$ and removal rate increased and removal times decreased (compare Tables H-1 and H-2). At the increased removal rate, the rapid removal benchmark was met for several cases for which it had not been met previously under the default WHAM V parameters. These cases include pH 7 and 8 simulations with starting Ag concentrations at the ERV values and 100 $\mu\text{g/L}$ (Table 3-30). However, at pH 6, greater than 28 days was still required to attain 70% removal. At the upper chronic cutoff value, greater than 70% removal in 28 days was achieved when considering Approaches 1 and 2. However, because of presence of AgCl(s) and its sustaining effect on dissolved Ag, rapid removal was not achieved at the upper chronic cutoff loading according to Approach 3.

At the acute and chronic ERV values, where all Ag solids were undersaturated, model-predicted $\log K_D$ values (without Ca/Mg competition) ranged between 3.40 and 4.18 (Table H-2). While this range represents an increase from the default case (Table H-1), it is still lower than the empirical water column $\log K_D$ of 5.28. It is likely that at lower Ag concentrations, where silver precipitates are undersaturated, Ag binding is the result of multiple binding mechanisms including, but not limited to, sorption to POC. A

series of sensitivity analyses were performed to test the impact of additional binding phases. In these simulations, additional binding phases were incorporated into the speciation submodel in addition to POC.

Model results indicate that the impact of HFO as an additional water column binding phase was negligible: the fraction of Ag bound to particles was essentially the same as with just POC. Another potential binding mechanism for Ag in the water column is complexation with inorganic and organic reduced sulfur, S(II⁻) which has been shown to be present in oxic waters (Bowles et al., 2003). The strong binding of Ag to dissolved phase sulfur ligands has been incorporated in the Ag biotic ligand model (BLM) (Paquin and Di Toro, 2008). The quantity chromium reducible sulfide (CRS) has been used as an estimate for the concentration of reduced sulfur ligands. Kramer et al. (2007) observed moderate correlation between CRS and TOC ($r^2 = 0.50$) and parameterized a linear relationship between the two quantities (Equation 3-3).

$$\text{CRS \{nM\}} = 14.5 \times \text{TOC \{mg/L\}} \quad (3-3)$$

They suggest that in the absence of direct CRS determination, the linear relationship can be used to estimate CRS from TOC. The approach was used to obtain an estimate of the CRS for the TICKET-UWM. Based on the default DOC and POC values of 2 and 1.5 mg/L, dissolved and particulate CRS value of 29 and 22 nmol/L, respectively were estimated. Thus according to this approach, 43% of the CRS is particulate. In an alternate approach, available total and filtered CRS data were collected (Table 3-31). Particulate CRS was taken as the difference between total and filtered CRS. These data indicate that, on average, approximately 28% of the CRS is particulate. For this approach, the TOC of the generalized lake system (3.5 mg/L) was used to estimate a total CRS of 51 nM based on Equation 3-3. According to the data from natural waters, 28% or 14 nM of the total CRS was specified as particulate with remainder of 37 nM as dissolved. Simulations were made using both approaches to estimate CRS. Binding of Ag to CRS was modeled using the same reaction stoichiometry and formation constant as the AgHS^0 aqueous complex in the TICKET-UWM database. The formation constant value used was 13.6. This value is slightly greater than the value used in the HydroQual, Inc. BLM software (13.38), but still consistent with values in the literature as summarized in Richard and Luther (2006).

It should be noted that nature of *particulate* CRS and its impact on Ag partitioning and transport to/from the water column have not yet been extensively studied. Therefore, the results of the model simulations described below should be viewed as preliminary.

Table 3-31. Data on Chromium Reducible Sulfide (CRS) in Natural Waters

Location	pH	TOC	DOC	POC ^a	Total CRS	Filtered CRS	Particulate CRS ^b		Source
		(mg/L)	(mg/L)	(mg/L)	(nM)	(nM)	(nM)	(%)	
Desjardins (January)	7.2	5.9	5.1	0.8	141	124	17	12.1	1
Desjardins (April)	7.5	5.8	5.3	0.5	188	147	41	21.8	1
Grand River	8.5	5.2	5.4	-0.2	78	36	42	53.8	1
Rochester	7.6	12	10.9	1.1	211	202	9	4.3	1
Black River	7.2	3	3.2	-0.2	50	48	2	4.0	1
Hamilton Harbour, ON	8.1	5	---	---	40	20	20	50.0	2

Sixteen Mile Ck., Oakville ON	7.7	6.1	---	---	68	39	29	42.6	2
Spencer Ck., Dundas ON	7.7	6.8	---	---	106	54	52	49.1	2
Beverley Swamp, Flamborough ON	7	7.3	---	---	54	45	9	16.7	2
Desjardin Canal, Dundas ON	7	21	---	---	89	66	23	25.8	2

^a Calculated as the difference between TOC and DOC

^b Calculated as the difference between total CRS and filtered CRS

Sources:

¹ Paquin and Di Toro, 2008

² Bowles et al., 2003

The results of model simulations at pH 7 with Ag binding to CRS are given in Table 3-32 and Table H-3. For these simulations, rapid removal is achieved using Approaches 1 and 2 at all initial Ag concentrations tested and for both methods of estimated CRS. With initial Ag at the chronic and acute ERVs, Ag binding to CRS increased the log K_D relative to the default TICKET-UWM simulations (compare Table H-3 to H-1) and decreased 70% removal time to below 28 days. Although consideration of Ag-CRS binding increased the log K_D values (from 3.22 to 4.41 – 4.70), there is still considerable discrepancy between calculated values and the empirical value of 5.28. In simulations with initial Ag at the upper chronic cutoff, precipitation as AgCl(s) remains the primary reason for rapid removal using Approach 1 and 2. In simulations with initial Ag at 100 µg/L, both precipitation and binding to CRS contributed to removal. As indicated in Table 3-32 and H-3, precipitation again prevented rapid removal according to Approach 3.

Table 3-32. Water Column Removal Results for Silver With Binding to Chromium Reducible Sulfide Considered

Scenario	Water Chemistry	
	Particulate CRS = 22 nM; Dissolved CRS = 29 nM	Particulate CRS = 14 nM; Dissolved CRS = 37 nM
Acute ERV and Chronic ERV ^a	●	●
100 µg/L	● ^b	◐ ^b
Chronic Cutoff	◐ ^b	◐ ^b

Legend:

● Greater than 70% removal achieved in 28 days for Approaches 1, 2, and 3

◐ Greater than 70% removal achieved in 28 days for a subset of approaches

○ Less than 70% removal achieved in 28 days for none of the three approaches

Footnotes:

^a Acute ERV = 220 ng/L; Chronic ERV = 120 ng/L; Chronic Cutoff = 1 mg/L

^b Precipitation of Ag solid occurred.

In summary, model simulations indicated disparate behavior depending on the method chosen to quantify Ag partitioning to particles. Linear partitioning calculations using empirical log K_D values indicate rapid

loss of Ag from the water column (i.e., greater than 70% in 28 days). However, in simulations where Ag speciation and partitioning to DOC/POC were calculated with WHAM V within TICKET-UWM, predicted log K_D values were significantly lower than the empirical value and, as a result, removal in many cases was not rapid. Precipitation of Ag as AgCl(s) did in some cases hasten removal based on Approaches 1 and 2. Omission of the competitive effects of Ca/Mg and inclusion of Ag binding to CRS did increase predicted log K_D values, but additional research is necessary to tell whether either of these two scenarios represent a better reflection of reality.

3.7.3. Silver Water Column Sensitivity Analysis Results

A sensitivity analysis was conducted to evaluate the critical depth at which exactly 70% removal was achieved in 28 days using Approach 1 for a system with an initial Ag at the acute ERV of 220 ng/L. The results are shown in Table 3-33. For the linear partitioning method, 70% removal occurs instantly via initial solid-solution equilibrium partitioning. Because of the relatively large empirical Ag surface water log K_D of 5.28, 70% removal can still be attained in 28 days (under the more conservative Approach 2) at a depth that is more than ten times greater than the default generalized lake depth of 3 meters. For the speciation model method simulations considering Ag interaction with water column DOC and POC only, relatively weak binding at the three water chemistries resulted in limited Ag removal such that depths less than 3 meters were required to produce 70% removal in 28 days. Preliminary assessments of silver binding to particulate CRS produced log K_D values larger enough to facilitate 70% removal in 28 days for lake depths more than seven times the default value.

Table 3-33. Maximum Depth to Achieve 70% Removal in 28 Days^a

Simulation Description	Depth (m)
Linear Partitioning	41.0 ^b
pH 6.09	0.75
pH 7.07	1.41
pH 8.00	1.15
Part. CRS = 14 nM	21.4
Part. CRS = 22 nM	44.8

^a Initial Ag concentration = 220 ng/L

^b Under Approach 1 70% removal occurs instantly via initial solid-solution equilibrium partitioning. The depth quoted refers to 70% removal of *total* Ag (Approach 2)

Another sensitivity analysis was conducted to assess removal with settling velocity decreased from the EUSES value of 2.5 m/d to 0.24 m/d. A settling rate of 0.24 m/d represents the lower end of the POC range from Burns and Rosa, (1980). The results are shown in Table 3-34 and Table H-4. The simulation with linear partition method and the calculation with the high particulate CRS are the only cases where the log K_D in the surface water was larger enough to counteract the slower settling velocity and allow for 70% removal within 28 days based on Approach 1.

Table 3-34. Water Column Removal Results for Silver with Decreased Settling Velocity^{a,b}

Simulation Description	Removal Result
------------------------	----------------

Linear Partitioning	●
pH 6.09	○
pH 7.07	○
pH 8.00	○
Part. CRS = 14 nM	○
Part. CRS = 22 nM	◐

Legend:

- Greater than 70% removal achieved in 28 days under Approach 1 and 2
- ◐ Greater than 70% removal achieved in 28 days under Approach 1 but not 2
- Less 70% removal achieved in 28 days under both approaches

Footnotes:

- ^a Settling velocity = 0.24 m/d
- ^b Initial Ag concentration = 220 ng/L

3.7.4. Preliminary Assessment of Silver Remobilization Potential from Sediments

For anoxic sediment simulations with AVS at 1 μmol/g (Tables 3-35, H-5 and H-6), the sediment Ag speciation was dominated by the formation of Ag₂S (s). All three sequestration criteria were met under both the default and the no Ca/Mg competition scenarios. It should be noted, however, that with the exception of the simulations at the chronic cutoff concentrations, the time required to first achieve 70% removal by Approach 1 exceeded 28 days. Pseudo steady-state water column concentrations were more than 1.7 times below the 70% removal concentrations (Table H-5). Very similar results were obtained in anoxic sediment simulations with AVS at 9.1 μmol/g.

The model predicted very weak binding of Ag to HFO. Consequently, the model results for the oxic sediment simulations are almost identical to those for an anoxic sediment with no AVS (Table 3-35, H-5 and H-6). The only simulation in which all sequestration criteria were met was the chronic cutoff scenario with the default WHAM V parameters.

Table 3-35. Sediment Remobilization Results for Silver

Scenario		Sequestration Criteria			Sediment Binding Phases
		Sustained 70% removal	$K_{D, sed} > K_{D, wc}$	Diffusive Flux into Sediment	
Anoxic, AVS = 1 μmol/g	Default and No Ca/Mg Comp.	Acute ERV	●	●	100% AVS
		Lower Chronic Cutoff			
		Upper Chronic Cutoff			
Anoxic, AVS = 9.1	Default and No Ca/Mg	Acute ERV	●	●	100% AVS
		Lower Chronic Cutoff			

μmol/g	Comp.	Upper Chronic Cutoff				
Oxic	Default	Acute ERV				
		Lower Chronic Cutoff	●	○	○	98.6% POC; 1.4% HFO
		Upper Chronic Cutoff	●	●	●	80.5% AgCl(s); 19.2% POC; 0.3% HFO
	No Ca/Mg Comp.	Acute ERV				
		Lower Chronic Cutoff	●	○	○	99.8% POC; 0.2% HFO
		Upper Chronic Cutoff				

Legend:

- Sequestration metric is met
- Sequestration metric is not met

Footnotes:

^a Lower Chronic Cutoff = 0.1 mg/L; Upper Chronic Cutoff = 1 mg/L

A remobilization potential analysis was also made using the linear partitioning method and the empirical $\log K_D$ values listed in Table 2-3. The results indicated that there was sustained 70% removal. However the water column $\log K_D$ was greater than the sediment $\log K_D$ and the integrated diffusive flux was directed out of the sediment. Only the first sequestration criterion was met for Ag using the linear partitioning method.

3.8. Barium

3.8.1. Barium Water Column Results – Speciation Model Method

Barium (Ba) is an example of a metal that binds weakly to organic carbon and is moderately toxic. Based on the AQUIRE database, EC50s, LC50, NOECs and MATCs (mean acceptable toxicant concentrations) for freshwater species in short term toxicity tests range between 12,000 μg/L and 76,000,000 μg/L. From the same database, chronic toxicity values range between 4000 μg/L and 500,000 μg/L. To assess the removal of Ba from the water column, a series of TICKET-UWM simulations were made at the three water chemistries (Table 2-1) and with Ba ranging from 0.01 mg/L to 20 mg/L. The results of these simulations are shown in Figure 3-10. Near the low end of the Ba concentration range tested, removal was not rapid at any of the water chemistries tested. The removal at 28-days was no greater than about 23%. The amount of removal at day 28 decreased with increasing pH due to the competitive effect of Ca and Mg. In all cases, as the Ba concentration was increased, BaSO₄(s) started to precipitate and the amount of removal in 28 days increased. For all water chemistries 70% removal was predicted to occur at concentrations less than the lowest chronic toxicity value of 4,000 μg/L (Figure 3-8). Therefore, Ba provides a somewhat unique example of a metal that, based upon predicted binding to POC, would not be predicted to be rapidly removed. However, at concentrations approaching toxicity values, precipitation enhances the removal rate.

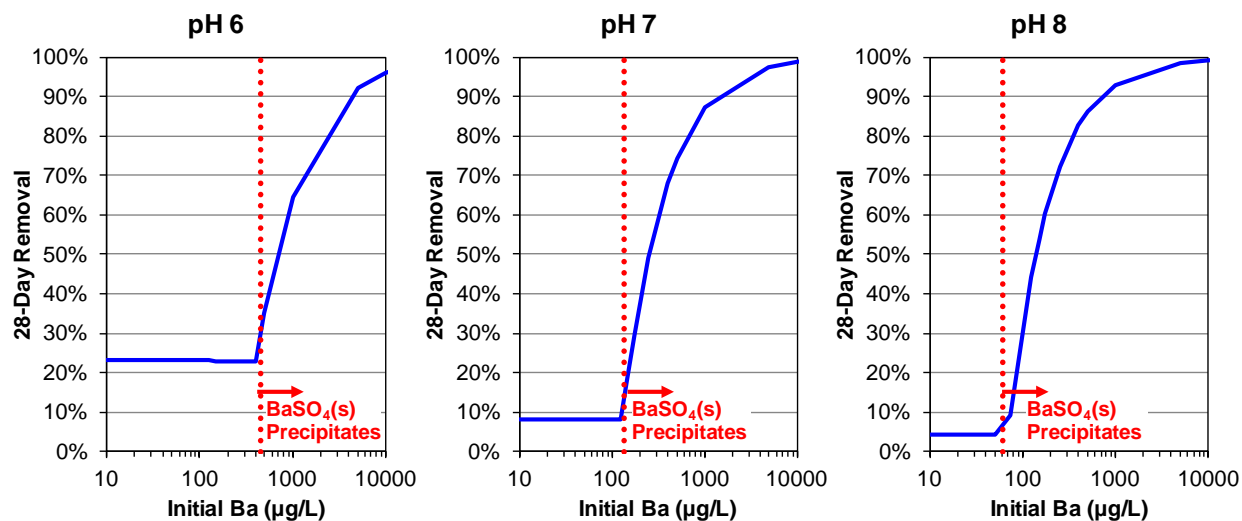


Figure 3-10. Dissolved barium (Ba) removal from the water column using EUSES model parameters and the speciation model method. The initial total barium concentration in the water column, $C_{Tot}(0)$, was varied. The horizontal dashed line represents $C(t)/C_{Tot}(0) = 0.3$ or 70% removal of Ba.

3.9. Arsenic

Aqueous phase speciation and partitioning of As were calculated using the speciation sub-models within the TICKET-UWM framework. To simplify As speciation for the present work, inter-conversion between the two As redox states typically found in surface water and sediment—As(III) and As(V)—was excluded. Methylation of As was also not considered. Water column removal and sediment remobilization were performed separately with As(III) and As(V). Speciation submodels were augmented (as necessary) to consider the following key speciation processes/reactions:

- Protonation/deprotonation of anionic As species (e.g. arsenate, AsO_4^{3-}) (Table I-1 and I-2);
- Complexation of As anions by di- and trivalent metal cations (e.g., Ca^{2+} , Mg^{2+} , Cu^{2+} , Fe^{2+}/Fe^{3+} , etc.) (Table I-3);
- Complexation of As anions by sulfur (S) ligands (thioarsenic species) (Table I-1 and I-2);
- Formation of As solids with S, O, Fe, Ca, and Mg (Table I-4); and
- Surface complexation of As to hydrous ferric oxides using the diffuse double layer model (DDL) of Dzombak and Morel (1990).

Speciation submodels were used to calculate speciation at each time steps in the simulation. Tables detailing speciation reactions added to the WHAMV database with their references are provide in Appendix I.

Important chemical processes for arsenic in sediment include:

- complexation to inorganic ligands in the sediment porewater;
- sorption to metal-binding phases on sediment particles such as HFO; and
- precipitation as As solids of S, O, Fe, Ca and Mg

Research has shown that the reaction of trace metals with sulfide, in the form of acid volatile sulfide (AVS), to form insoluble sulfides is a key process that mitigates the bioavailability and toxicity of this trace metal in sediments and influences its fate natural systems (Di Toro et al., 1992; Berry et al., 1996; Di Toro et al., 2001b). The reduction in trace metal bioavailability afforded by AVS has not been documented for As even though it forms sulfide solids (Nordstrom and Archer, 2003). There is evidence to suggest that the complexation of As by sulfide can reduce its bioavailability (Rader et al., 2004 and Planer-Friedrich et al., 2008); although analytical speciation of As-reduced sulfur species is problematic (Planer-Friedrich et al., 2010).

3.9.1. Arsenic(III) Water Column Removal Results

TICKET-UWM output for total and dissolved As(III) remaining versus time at the pH 7 water chemistry is shown in Figure 3-11. In Figure 3-11a, model results are presented as $C_{\text{Tot}}(t)/C_{\text{Tot}}(0)$ (Approach 2). Water column results for simulations with both an anoxic (solid lines) and oxic (dashed lines) sediment layer are shown. $C_{\text{Tot}}(t)/C_{\text{Tot}}(0)$ decreased as a function of time for both the anoxic and oxic cases, however 70% removal was achieved only for the oxic sediment case. In Figure 3-11b, model results are presented as $C_{\text{Diss}}(t)/C_{\text{Tot}}(0)$ (Approach 1). $C_{\text{Diss}}(t)/C_{\text{Tot}}(0)$ decreased as a function of time for both the anoxic and oxic cases. 70% removal was achieved for the oxic sediment case. For the anoxic case, removal approaches 70% removal in 28 days. The dashed line in Figure 3-11a represents 70% removal according to Approach 3. Rapid removal under Approach 3 occurs only for the oxic sediment cases.

As(III) speciation in the water column is dominated by dissolved inorganic complexes and surface complexes with HFO. As(III) bound to HFO is transported to the sediment via settling. No As(III) solids precipitated in the water column over the entire duration of the simulations.

As mentioned in Section 2.3, the key potential binding mechanism in the anoxic sediment case is precipitation. At the default pH of the sediment layer (7.56), all As(III) solids considered by the model were undersaturated and did not precipitate. Without any sorption/precipitation, As(III) delivered to the sediment with settling HFO particles was immediately solubilized and available for transport out of the sediment via diffusion. As a result, As(III) removal from the water column was quickly offset by back-diffusion from the sediment which sustained dissolved As concentrations. This prevented 70% As(III) removal from being achieved in simulations with anoxic sediment under data analysis Approaches 1, 2 and 3.

For the oxic case, As binding to HFO is operable in the sediment. Therefore, a trapping mechanism exists for As(III) in oxic sediments that did not exist in the anoxic sediment case. As(III) binding to HFO is strong enough that the mass flux resulting from diffusion to the overlying water is minimal. As a result, 70% removal is met under both Approach 1 and 2 for oxic sediments.

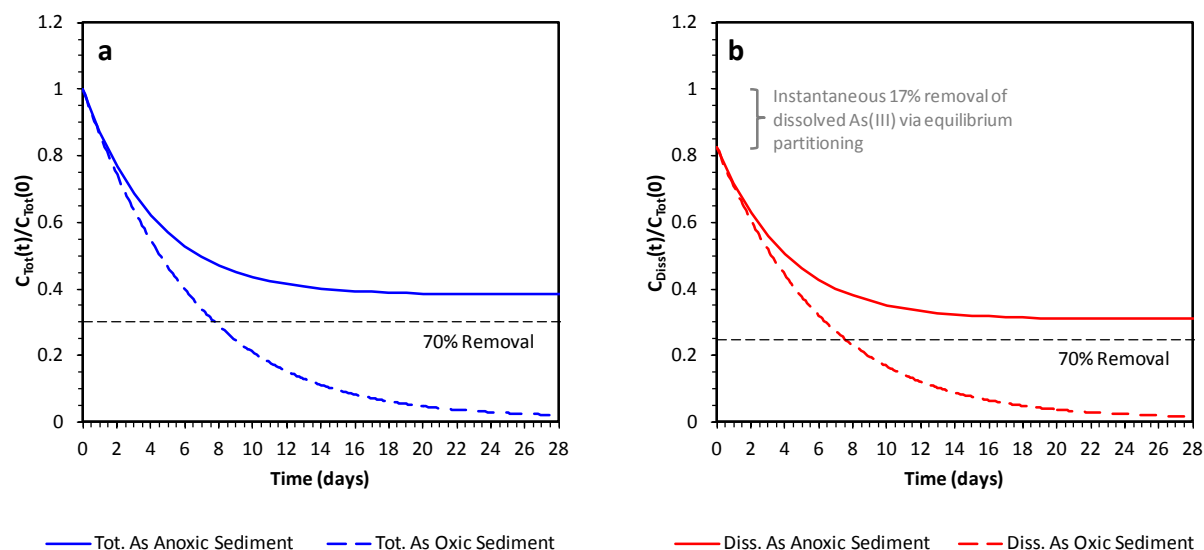


Figure 3-11. a) Total and b) dissolved arsenic(III), As(III), removal from the water column using EUSES model parameters with an anoxic sediment (solid lines) and an oxic sediment (dashed lines). The initial total As(III) concentration in the water column, $C_{Tot}(0)$, was specified at the chronic ecotoxicity reference value (ERV) of 40 $\mu\text{g/L}$. The horizontal dashed lines represents a) $C_{Tot}(t)/C_{Tot}(0) = 0.3$ [70% removal of total As(III)] and b) $C_{Diss}(t)/C_{Diss}(0) = 0.3$ [70% removal of dissolved As(III)].

The results of additional As(III) water column simulations are summarized in Table 3-36 and Table I-5 and I-6 (Appendix I). Table 3-36 presents a visual summary of results from the various permutations of water chemistries (pH 6, 7 and 8), sediment redox state (anoxic or oxic), and starting dose of As(III) (chronic ERV, acute ERV, and upper chronic cutoff).

In general, 70% removal was achieved for cases where oxic sediment was considered (Table 3-36 and Table I-6). Only at the highest loading (upper chronic cutoff) at pH 6 did 70% removal take longer than 28 days. This is likely due to saturation of available As(III) binding sites on HFO.

For the anoxic sediment cases, lack of sequestration of As(III) in the sediment precludes its rapid removal from the water column under most of the pH and initial concentration scenarios considered (Table 3-36). The exception is the simulation at pH 8 with a starting As(III) concentration of 40 $\mu\text{g/L}$. At the lowest concentration, the extent of As(III) binding to HFO in the water column is large enough to allow rapid removal of greater than 70% of the As(III) before back-diffusion halts As(III) loss from the water column. However, $\log K_D$ values (and fraction particulate values) increase as As(III) concentration decreases due to non-linear partitioning (this is evident in the detailed simulation results, Table I-5)

Since orpiment (As_2S_3) is most likely to form at low pH, the pH 6 water column simulations with anoxic sediment were rerun with the sediment pH set to 6.09 rather than the default value of 7.56. Orpiment precipitates in the sediment in all loadings with the water column and sediment at pH 6. However, the decrease in back-diffusion is limited, particularly at the higher starting concentrations where As(III) exceeds the available sulfide in the sediment. Only at the chronic ERV loading does removal approach 70% in 28 days (Table I-5).

These results suggest that the extent of As(III) removal from the water column may be dependent on the redox state of the sediment. The results confirm that the sequestration afforded by the formation of orpiment is possible only at low pH.

Table 3-36. Water Column Removal Results for Arsenic(III)

Scenario		Water Chemistry			
		pH 6	pH 6 (alt)	pH 7	pH 8
Chronic ERV ^a	Anoxic Sediment	○	○	○	●
	Oxic Sediment	●	--	●	●
Acute ERV	Anoxic Sediment	○	○	○	○
	Oxic Sediment	●	--	●	●
Upper Chronic Cutoff	Anoxic Sediment	○	○	○	○
	Oxic Sediment	○	--	●	●

Legend:

- Greater than 70% removal achieved in 28 days for Approaches 1, 2, and 3
- ◐ Greater than 70% removal achieved in 28 days for a subset of approaches
- Less than 70% removal achieved in 28 days for none of the three approaches

Footnotes:

^a Chronic ERV = 40 µg/L; Acute ERV = 480 µg/L; Upper Chronic Cutoff = 1 mg/L

3.9.2. Arsenic(III) Water Column Sensitivity Analysis Results

Maximum Depth for Rapid Removal of Arsenic(III)

A sensitivity analysis was conducted to evaluate the maximum depth at which exactly 70% removal was achieved in 28 days (under Approach 1) for a system with an anoxic sediment and an initial As(III) of 480 µg/L. The results are shown in Table 3-37. Moderate sorption and negligible binding in the sediment limit arsenic removal such that relatively shallow depths are necessary to ensure 70% removal.

Table 3-37. Maximum Depth to Achieve 70% Removal in 28 Days^a

pH	Depth (m)
6.09	0.74
6.09 (alt)	2.55
7.07	1.40
8.00	1.80

^a Anoxic sediment; initial As(III) concentration = 480 µg/L

Removal of Arsenic(III) with Lowered Settling Velocity

Another sensitivity analysis was conducted to assess removal with settling velocity decreased from the EUSES value of 2.5 m/d to 0.24 m/d. A settling rate of 0.24 m/d represents the lower end of the POC range from Burns and Rosa, (1980). As(III) removal was very limited in model runs with an anoxic

sediment and an initial As(III) of 480 $\mu\text{g/L}$ with the reduced settling velocity of 0.24 m/d. At the default sediment pH of 7.56, water column behavior was generally similar across the three water column pH values assessed. The pH 7 output is provided below in Figure 3-12. Water column total and dissolved As(III) concentrations leveled off after approximately 30 days at concentrations representing removal of 8.5 to 12.1% (under Approach 1).

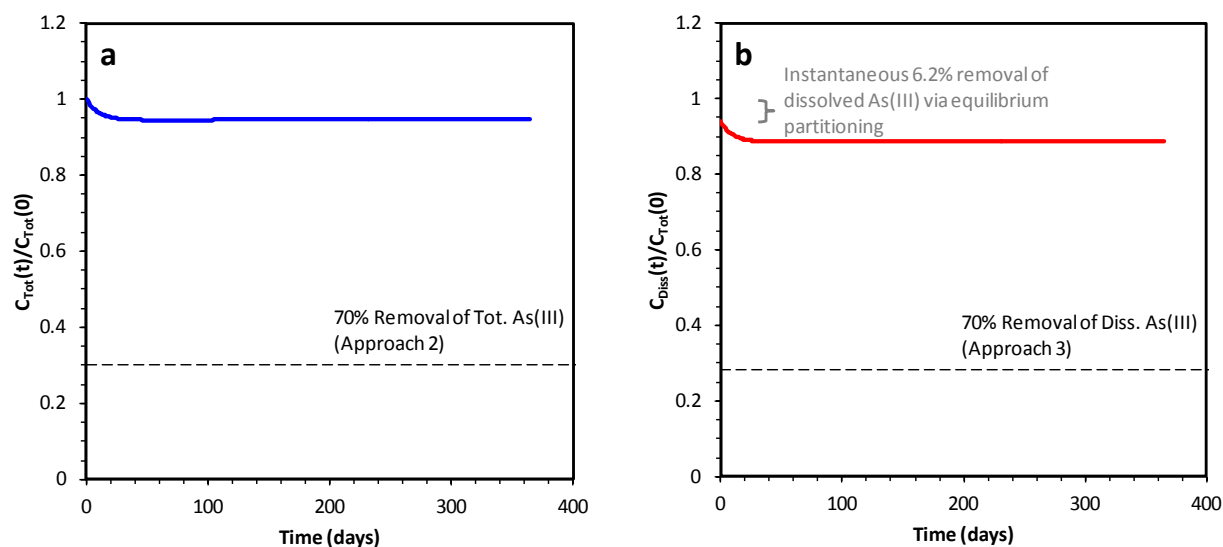


Figure 3-12. a) Total and b) dissolved arsenic(III), As(III), removal from the water column at pH 7 using the lowered settling velocity of 0.24 m/d. The initial total As(III) concentration in the water column, $C_{\text{Tot}}(0)$, is 480 $\mu\text{g/L}$. The horizontal dashed lines represent a) $C_{\text{Tot}}(t)/C_{\text{Tot}}(0) = 0.3$ [70% removal of total As(III)] and b) $C_{\text{Diss}}(t)/C_{\text{Diss}}(0) = 0.3$ [70% removal of dissolved As(III)].

3.9.3. Arsenic(III) Sediment Remobilization Results

TICKET-UWM results for sediment remobilization simulations are shown in Table 3-38. Three criteria were considered to assess As sequestration in the sediment: i) sustained 70% removal; ii) a larger value of the partition coefficient in the sediment than in the water column ($K_{D,\text{sed}} > K_{D,\text{wc}}$), and iii) a diffusive flux of As into the sediment.

For the anoxic sediment cases, none of the sequestration criteria were met (Table 3-38). As discussed above, at the default pH of the sediment (7.56), orpiment did not precipitate. Since this is the key retention mechanism for As(III) in anoxic sediment considered in the model, it is not surprising that these criteria were not met. Table I-7 (Appendix I) indicates that the pseudo steady state dissolved and total concentrations were greater than that representing 70% removal for the three loadings (sequestration criteria 1).

For the oxic sediment simulations, the three sequestration criteria were met for all scenarios considered (Table 3-38). Table I-7 indicates pseudo steady-state water column concentrations at least 20 times lower than those representing 70% removal for all initial water column As(III) concentrations. Furthermore, the sediment log K_D is greater than the water column value and the integrated diffusive flux was positive (directed into the sediment) for all three initial concentrations. Although the binding of As(III) was

strong enough to allow rapid removal and limited remobilization for oxic sediments, As(III) binding to HFO, as a surface complexation reaction, generally cannot be considered permanent/irreversible.

Table 3-38. Sediment Remobilization Results for Arsenic(III)

Scenario		Sequestration Metric			Sediment Binding Phases
		Sustained 70% removal	$K_{D, \text{sed}} > K_{D, \text{wc}}$	Diffusive Flux into Sediment	
Anoxic, AVS = 1 $\mu\text{mol/g}$	Chronic ERV ^a	○	○	○	None
	Acute ERV	○	○	○	None
	Upper Chronic Cutoff	○	○	○	None
Oxic	Chronic ERV	●	●	●	HFO
	Acute ERV	●	●	●	HFO
	Upper Chronic Cutoff	●	●	●	HFO

Legend:

- Sequestration metric is met
- Sequestration metric is not met

Footnotes:

^a Chronic ERV = 40 $\mu\text{g/L}$; Acute ERV = 480 $\mu\text{g/L}$; Upper Chronic Cutoff = 1 mg/L

3.9.4. Arsenic(V) Water Column Removal Results

The results of As(V) water column removal simulations are presented in Table 3-39, and Tables I-8 and I-9 (Appendix I). For As(V), a high percentage of the simulations (12 out of 18) showed greater than 70% removal in 28 days. This is a larger percentage than observed for As(III). In general, whether a scenario resulted in rapid removal was not dependent upon the method used to assess removal (i.e. Approach 1, 2, or 3). For As(V), rapid removal was a function of the magnitude of the initial concentration in the water column. At the chronic ERV initial concentration (40 $\mu\text{g/L}$), rapid removal was achieved for all three water chemistries for both anoxic and oxic sediments. At the acute ERV (480 $\mu\text{g/L}$), rapid removal was achieved for all three water chemistries for only the oxic sediments. For anoxic sediments, rapid removal was not achieved. For the chronic cutoff initial concentration (1 mg/L), rapid removal was achieved in 3 out of 6 cases, but the pattern is complicated. Specifically, rapid removal was achieved for the oxic pH 6 case, the oxic pH 8 case, and the anoxic pH 8 case (Approaches 1 and 2).

At the low initial As(V) concentrations of chronic ERV (40 $\mu\text{g/L}$), there is a significant fraction of As(V) bound to HFO which results in a relatively large K_D and effective settling of As(V) down into the sediment. Binding of As(V) to HFO in the water column is strong enough to meet the removal criteria despite the mass flux of As(V) back into the water column. As(V) binding onto HFO is known to be better at low pH, and this can be seen in the increasing times required to achieve 70% removal as pH increases (Table I-8 and I-9).

At the larger initial concentration of the acute ERV (480 µg/L), binding sites on HFO were depleted and the values of K_D for As(V) decreased (Table I-8 and I-9). The situation for As(V) at the increased starting concentration is much like that already discussed for As(III). Rapid removal is dependent upon whether the sediment in the simulations was oxic or anoxic. In the oxic cases, As(V) binding to HFO in the sediment provided a trapping mechanism which limited diffusion back into the water column and rapid removal was achieved. For the anoxic cases, an As(V)-containing solid precipitated in the sediment ($Mg_3(AsO_4)_2(s)$), but its high solubility did not lower dissolved As(V) concentrations in the sediment enough to prevent a significant diffusive flux to the overlying water to allow for the rapid removal criteria to be met.

For the chronic cutoff initial concentration (1 mg/L), rapid removal was met at pH 8 for both the anoxic and oxic sediment cases using Approaches 1 and 2. Precipitation $Mg_3(AsO_4)_2(s)$ in the water column at this higher total As(V) concentration allowed for a larger fraction of the total As(V) mass to be associated with settling particulates. For the anoxic sediment case, precipitation occurred in the water column and sediment, thus limiting diffusion of As(V) back to the water column. Similar to Ni, Cd, and Ag simulations in which solids formed, the precipitation of $Mg_3(AsO_4)_2(s)$ in the water column resulted in approximately constant dissolved phase As(V) concentrations. As a result, 70% removal was not achieved according to Approach 3 for anoxic sediment (Tables 3-39 and I-8).

Table 3-39. Water Column Removal Results for Arsenic(V)

Scenario		Water Chemistry		
		pH 6	pH 7	pH 8
Chronic ERV ^a	Anoxic Sediment	●	●	●
	Oxic Sediment	●	●	●
Acute ERV	Anoxic Sediment	○ ^s	○ ^s	○ ^{w,s}
	Oxic Sediment	●	●	● ^w
Upper Chronic Cutoff	Anoxic Sediment	○ ^s	○ ^s	◐ ^{w,s}
	Oxic Sediment	●	○	● ^w

Legend:

- Greater than 70% removal achieved in 28 days for Approaches 1, 2, and 3
- ◐ Greater than 70% removal achieved in 28 days for a subset of approaches
- Less than 70% removal achieved in 28 days for none of the three approaches

Footnotes:

- ^a Chronic ERV = 40 µg/L; Acute ERV = 480 µg/L ; Upper Chronic Cutoff = 1 mg/L
- ^w Arsenic(V) precipitates in water column
- ^s Arsenic(V) precipitates in sediment

3.9.5. Arsenic(V) Water Column Sensitivity Analysis Results

Maximum Depth for Rapid Removal of Arsenic(V)

A sensitivity analysis was conducted to evaluate the maximum depth at which exactly 70% removal was achieved in 28 days (under Approach 1) for a system with an anoxic sediment and an initial As(V) of 480 µg/L. The results are shown in Table 3-40. Though generally deeper than the corresponding depths for As(III), relatively shallow maximum depths were calculated for As(V) to insure 70% removal.

Table 3-40. Maximum Depth to Achieve 70% Removal in 28 Days ^a

pH	Depth (m)
6.09	2.91
7.07	1.84
8.00	1.39

^a Anoxic sediment; initial As(V) concentration = 480 µg/L

Removal of Arsenic(V) with Lowered Settling Velocity

Another sensitivity analysis was conducted to assess removal with settling velocity decreased from the EUSES value of 2.5 m/d to 0.24 m/d. A settling rate of 0.24 m/d represents the lower end of the POC range from Burns and Rosa, (1980). As(V) removal was very limited in model runs with an anoxic sediment and an initial As(V) of 480 µg/L with the reduced settling velocity of 0.24 m/d. At the default sediment pH of 7.56, water column behavior was generally similar at pH 6 and 7. Water column total and dissolved As(III) concentrations leveled off within the first 40 days of the simulation at concentrations representing removal of 10 to 13% (under Approach 1). At pH 8, Mg₃(AsO₄)₂(s) forms in the water column and increases the dissolved phase Approach 1 removal to approximately 61% (Figure 3-13).

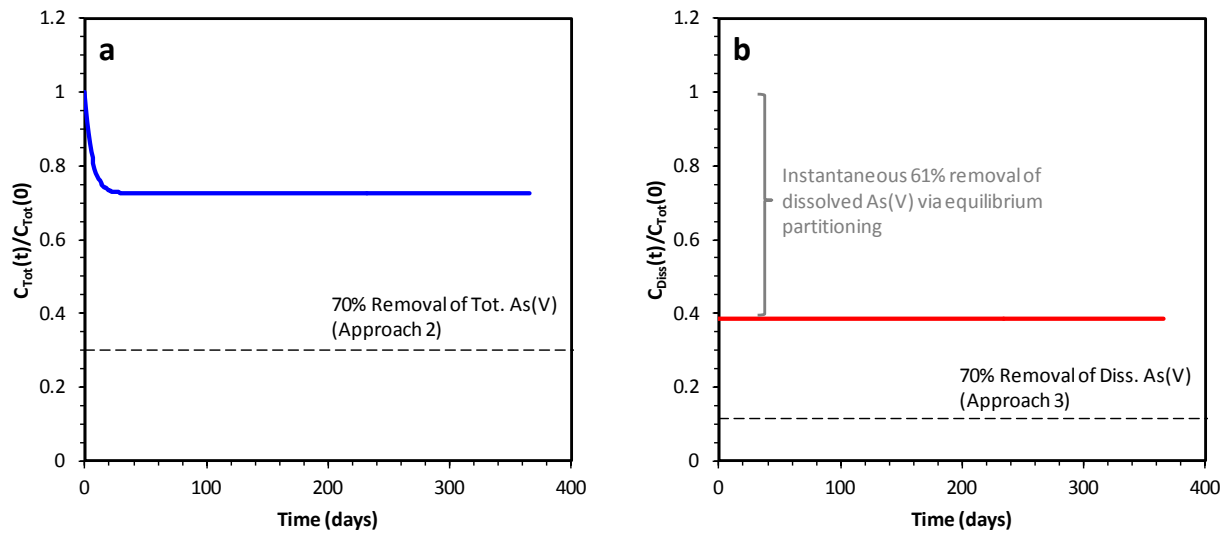


Figure 3-13. a) Total and b) dissolved arsenic(V), As(V), removal from the water column at pH 8 using the lowered settling velocity of 0.24 m/d. The initial total As(V) concentration in the water column, $C_{Tot}(0)$, is 480 µg/L. The horizontal dashed lines represents a) $C_{Tot}(t)/C_{Tot}(0) = 0.3$ [70% removal of total As(V)] and b) $C_{Diss}(t)/C_{Diss}(0) = 0.3$ [70% removal of dissolved As(V)].

3.9.6. Arsenic(V) Sediment Remobilization Results

TICKET-UWM results for sediment simulations are shown in Table 3-41 and Table I-10 (Appendix I). In the anoxic sediment simulations, long term maintenance of 70% removal occurs at the three loadings. However, only for the lowest loading (40 µg/L), where As(V) partitioning to HFO was greatest, did 70% removal occur within 28 days. Precipitation of $Mg_3(AsO_4)_2(s)$ at the higher loadings was not sufficient to produce a larger log K_D in the sediment than in the water column and the integrated diffusive flux was directed out of the sediment.

As(V) remobilization potential was more limited in the oxic sediment simulations (Table 3-41). Here, 70% removal was maintained over the 365-day simulation. Only for the chronic cutoff did 70% removal take longer than 28 days. At the three loadings, the integrated flux was directed into the sediment even though the log K_D values for the sediment are smaller than in the overlying water (Table I-10 in Appendix I). As with As(III), although the binding of As(V) to HFO was strong enough to allow rapid removal and limited remobilization for oxic sediments, As(V) binding to HFO, as a surface complexation reaction, generally cannot be considered permanent/irreversible.

Table 3-41. Sediment Remobilization Results for Arsenic(V)

Scenario		Sequestration Metric			Sediment Binding Phases
		Sustained 70% removal	$K_{D, sed} > K_{D, wc}$	Diffusive Flux into Sediment	
Anoxic, AVS = 1 µmol/g	Chronic ERV	●	○	○	None
	Acute ERV	● (69-81) ^b	○	○	$Mg_3(AsO_4)_2(s)$
	Upper Chronic Cutoff	● (140-150)	○	○	$Mg_3(AsO_4)_2(s)$
Oxic	Chronic ERV	●	○	●	HFO
	Acute ERV	●	○	●	HFO
	Upper Chronic Cutoff	● (33-34)	○	●	HFO

Legend:

- Sequestration metric is met
- Sequestration metric is not met

Footnotes:

^a Chronic ERV = 40 µg/L; Acute ERV = 480 µg/L ; Upper Chronic Cutoff = 1 mg/L

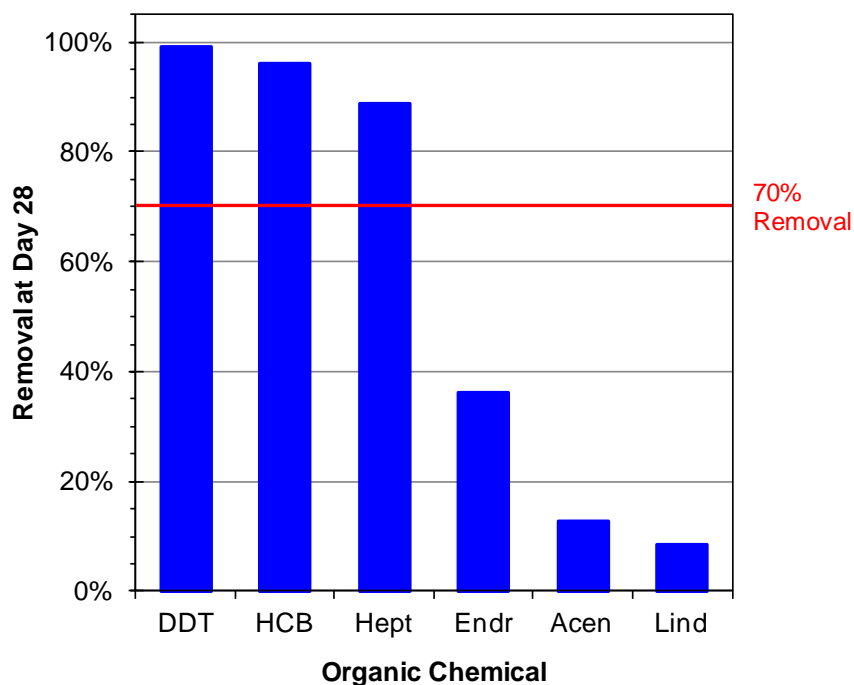
^b Number in parentheses is the range time (in days) required to achieve 70% removal according to the three removal approaches. When no range is quoted, the time required for 70% removal is less than 28 days for all removal approaches.

3.10. Organic Chemicals

3.10.1. Water Column Results for Organics

The results of the TICKET-UWM simulations with organic chemical are shown in Figure 3-14 and Table J-1. Of the six organics selected for analysis, three leave the water column rapidly through absorption and settling. The remaining three exhibited removals that were less than 70% in 28 days. Two of these

three, acenaphthene and lindane, required more than 4 years to leave the water column via absorption and settling. It is worthwhile to note that the partitioning of non-ionizable organics is not affected as much by pH as is the sorption of metals. Therefore, the removal behavior is not expected to change significantly with changes in water chemistry.



Legend:
 DDT: 4,4'-DDT
 HCB: Hexachlorobenzene
 Hept: Heptachlor
 Endr: Endrin
 Acen: Acenaphthene
 Lind: Lindane

Figure 3-14. Removal of select organic chemicals from the water column using EUSES model parameters. The initial total concentration in the water column, $C_{Tot}(0)$, of each organic chemical was 1 $\mu\text{g/L}$. Day 28 removal is expressed using Approach 3 [$C_{Diss}(28)/C_{Diss}(0)$]

3.10.2. Water Column Sensitivity Analysis Results for Organic Chemicals

A sensitivity analysis was conducted for three of the six selected organic chemicals to evaluate the critical depth at which exactly 70% removal was achieved using Approach 1 in 28 days. The results are shown in Table 3-42. The three selected organic chemicals demonstrate a range in critical depths going from more than three times deeper than the default depth to more than a factor of 2.5 times shallower. For low log K_{OW} species like endrin, the low predicted log K_D values restrict rapid removal to shallow lakes and ponds.

Table 3-42. Critical Depth to Achieve 70% Removal of Organic Chemicals in 28 Days^a

Simulation Description	Depth (m)
Hexachlorobenzene	10.4
Heptachlor	6.22
Endrin	1.12

^a Initial concentration was set at 1 µg/L

Another sensitivity analysis was conducted to assess removal with settling velocity decreased from the EUSES value of 2.5 m/d to 0.24 m/d. A settling rate of 0.24 m/d represents the lower end of the POC range from Burns and Rosa, (1980). As in the previous analysis, hexachlorobenzene, heptachlor, and endrin were selected for the analysis. The results are shown in Table J-2. None of the three chemicals were removed rapidly from the water column in the simulations. The time required for 70% removal ranged from more than two months (hexachlorobenzene) to up to more than a year and a half (endrin).

3.10.3. Preliminary Assessment of the Remobilization Potential of Organic Chemicals from Sediments

TICKET-UWM results for sediment simulations with the selected organic chemicals are shown in Tables 3-43 and J-3. Since linear absorption to POC is the only binding mechanisms for organics in TICKET-UWM, there is no need to specify redox conditions in the sediment for the definition of relevant binding phases. Naturally, the solid-phase speciation of all organics was dominated by POC. By virtue of the decrease in f_{OC} between the water column solids and the sediment solids (Tables 2-1 and 2-4), the sediment $\log K_D$ was less than the water column $\log K_D$ for all organic chemicals tested (second and third sequestration criteria were not met). In fact, this will be the case for any organic chemicals whose distribution coefficient is estimated by Equation 2-5. For four of the organic chemicals assessed, 70% removal was achieved and maintained during the 365-day simulation Table 3-43. However, for acenaphthene, and lindane, 70% removal did not occur within 365 days. Therefore, the first sequestration criterion was the only one met in the organic sediment runs and it was not met for every chemical.

Table 3-43. Sediment Remobilization Results for Organic Chemicals^a

Scenario	Sequestration Criteria			Solid-Phase Speciation
	Sustained 70% removal	$K_{D, sed} > K_{D, wc}$	Diffusive Flux into Sediment	
4,4'-DDT	●	○	○	100% POC
Hexachlorobenzene	●	○	○	100% POC
Heptachlor	●	○	○	100% POC
Endrin	●	○	○	100% POC
Acenaphthene	○	○	○	100% POC
Lindane	○	○	○	100% POC

● Sequestration criterion is met

○ Sequestration criterion is not met

^a Initial concentration was set at 1 µg/L

4. SUMMARY AND CONCLUSIONS

TICKET-UWM was used to assess the “degradation” of soluble metal salts in a generalized lake environment resulting from metal removal from the water column and sequestration in sediment. The two primary processes modeled to understand the “degradability” of metals include 1) removal of soluble metal salts from the water column through speciation transformations and sedimentation of particulate metal, and 2) metal speciation transformations and remobilization potential in sediments. The key findings and lesson learned related to metal removal from the water column include the following:

1. The “degradation capacity” of metals depends on the extent to which they bind to particles (i.e. particle-reactivity). Elimination from the water column is fast/extensive for highly particle-reactive metals, while less particle-reactive metals tend to remain in the water column for longer periods. Between those two ends there is a scaling of affinities and removal capacities.
2. TICKET-UWM simulations with the EUSES lake parameters with the water column distribution coefficient ($\log K_D$) specified at empirical values indicated greater than 70% removal in 28 days for copper, zinc, lead, nickel, cobalt, cadmium, and silver. Simulations with empirical $\log K_D$ values were not performed for barium.
3. Model results from simulations where WHAM V was used to calculate the $\log K_D$ at each time step in the simulation were less consistent. For metals like copper, lead, and zinc, predicted $\log K_D$ values supported rapid removal (i.e., >70% in 28 days) at the three water chemistries and all initial metal concentrations investigated. For metals like nickel, cobalt, cadmium, and silver, predicted $\log K_D$ values supported rapid removal for a subset of the scenarios considered.
4. Removal at the high pH/high hardness scenario and chronic cutoff scenarios was generally not rapid for nickel, cobalt, cadmium, and silver. WHAM V predicted $\log K_D$ values for these metals were significantly lower than the empirical values. Removing competition from the hardness cations, calcium and magnesium, for binding sites on organic carbon markedly increased the WHAM V predicted $\log K_D$ values and brought them more in line with the empirical values. Without calcium and magnesium competition, rapid removal was achieved for these metals in almost all scenarios.
5. For nickel, revised removal analyses were conducted using WHAM7 and a revised inorganic thermodynamic database. The water column $\log K_D$ values predicted in these simulations were closer to the empirical value than in the initial simulations with WHAM V—particularly when nickel binding to iron and manganese oxides was included in the model calculations. As a result of the increase in predicted $\log K_D$, greater than 70% nickel removal was achieved under the three pH scenarios with metal loadings at the acute and chronic ERVs. At the upper chronic cutoff value of 1 mg/L, rapid removal was achieved for pH 6 and 8 without binding to iron and manganese oxides and for all three pH values with binding to iron and manganese oxides.

6. Precipitation of silver as silver chloride, AgCl(s) , did in some cases hasten removal and bring predicted $\log K_D$ values more in line with empirical values. However, precipitation occurred mainly at the higher concentrations assessed. Omission of the competitive effects of calcium/magnesium and inclusion of silver binding to chromium reducible sulfide (CRS) did increase predicted $\log K_D$ values, but not enough to bring them completely in line with the empirical values.
7. Rapid removal of both As(III) and As(V) are sensitive to initial concentrations in the water column, the water column chemistry, and assumed sediment redox conditions. Oxidic sediment conditions favored rapid removal of both As(III) and As(V) and limited remobilization potential. Although the binding of As(III) and As(V) to HFO is strong enough to allow rapid removal and limited remobilization for oxidic sediments, this binding, as a surface complexation reaction, generally cannot be considered permanent/irreversible. As(III) precipitation as orpiment is predicted to be significant only at low pH values (below the default pH used for sediment simulations). As(V) sorbs more strongly to HFO than As(III) and, as a result, generally is removed more rapidly from the water column than As(III).
8. Clearly, $\log K_D$ is a critical factor affecting the water column removal rate of metals. Since model-predicted K_D values may deviate from empirical values, it is important to consider model results with both empirical and WHAM V-predicted solid-solution distribution in hazard classification.
9. Sensitivity analyses indicated that 70% removal in 28 days could be achieved at depths much greater than 3 m for very particle-reactive metals such as lead. However, at the low $\log K_D$ values predicted by WHAM V for metals like cadmium (see point number 4 above), rapid removal from the water column would be restricted to very shallow systems.
10. Sensitivity analyses also indicated the impact settling velocity had on removal rates. Using the lowered settling velocity, removal was not uniformly rapid across all metals when the empirical $\log K_D$ values were used. With the lowered settling velocity and empirical $\log K_D$ values, copper and nickel required more than 28 days for 70% removal. The lowered settling velocity also limited removal when the speciation model method was used. For example, whereas zinc removal was rapid for all scenarios using the default settling velocity, zinc removal was only rapid at the higher pH values using Approach 1 when the lower settling velocity was used.

The key findings and lesson learned related to metal remobilization potential from sediment include the following:

1. For copper, zinc, lead, nickel, cobalt, cadmium, and silver, feedback from sediment did not interfere with attainment of low concentrations in the water column. Though resuspension and diffusion did sustain some dissolved metal in the water column, the concentrations were typically well below levels representing 70% removal (based on the total metal added).

2. For copper, zinc, lead, cobalt, cadmium, and silver, model-predicted metal precipitation as metal sulfides maintains diffusive flux directed into the sediment when sufficient AVS was present to bind all sediment metal. For nickel, the extent of precipitation of the sulfide solid was limited when the most soluble solid form was used. Use of the next less soluble solids, such as millerite or hexagonal NiS, yielded nickel behavior in sediment that was consistent with copper, zinc, lead, cobalt, cadmium, and silver.
3. Sediment remobilization potential simulations were performed using the linear partitioning method and empirical water column and sediment $\log K_D$ values for copper, zinc, lead, nickel, cobalt, cadmium, and silver. For all metals, feedback from sediment did not interfere with attainment of low concentrations in the water column. Though resuspension and diffusion did sustain some dissolved metal in the water column, the concentrations were typically well below levels representing 70% removal (based on the total metal added). For all metals, the empirical $\log K_D$ value in the water column exceeded the value in the sediment which is supportive of metal release from the sediment via diffusion. For a subset of metals (copper, zinc, and lead) the integrated diffusive flux was directed *into* the sediment. The remainder had integrated diffusive fluxes directed out of the sediment.
4. As observed in the water column analysis, discrepancies exist between the model-predicted and empirical sediment K_D values. There are benefits and shortcomings associated with use of both empirical and model-predicted K_D values. It is important, therefore, to consider both in hazard classification. Emphasis was placed in this study on the use of model-predicted sediment K_D values since changes in speciation are central to the metal classification scheme outlined in the GHS.

The key findings and lesson learned related to the organic chemical analysis are as follows:

1. Some of the more hydrophobic organic chemicals can exhibit greater than 70% removal from the water column in 28 days.
2. However, for organics, there is no change in speciation upon entering the sediment. POC remains the primary binding phase.
3. Unlike metals, there is no speciation transformation to a less (or non) toxic form.
4. Consequently, the model-predicted integrated diffusive flux is directed out of the sediment.
5. Based on these findings it is unlikely that the degradability assessment framework proposed for metals would indicate that persistent organic pollutant (POPs) are rapidly degraded.

The above analyses demonstrate the utility of the TICKET-UWM in assessing the fate of metals and organics in lacustrine systems and indicate that model represents a useful tool for evaluating metal “degradation” in the aquatic environment.

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APPENDIX A – DISTRIBUTION COEFFICIENT DISCUSSION

Use of Empirical K_D values versus the Chemical Speciation Approach

Modeling approaches for metals and inorganic chemicals in aquatic systems require a mathematical description of partitioning between the water and solids compartments. Historically, Unit World Models for metals used a simple linear partitioning approach which was originally developed for organic chemicals (Harvey et al., 2007; Mackay et al., 1996). The value of K_D is prescribed based on either previous field studies or database compilations (Diamond et al., 1990). However, this approach does not consider the complexities of metal speciation. Metal ions are fundamentally different than organic chemicals. They transform from one form into another and existing in different forms simultaneously. Each chemical form or species has unique physical, chemical, and toxicological properties, which greatly complicates modeling. A K_D approach is therefore not always robust enough to accomplish the intended modeling task. Modern approaches to describing partitioning of metals involve the use of chemical speciation calculations (Diamond et al., 1992; Farley et al., 2011; Mackay and Diamond, 1989).

Empirical K_D Values

The use of a linear partitioning description between the water column and sediment requires selection of a K_D value. Compilations of K_D values exist for many metals but information about the specific site (i.e. water chemistry, physical characteristics) is not provided. This makes selection of an appropriate K_D values for the water column and sediment a difficult task. Site-specific K_D values are preferable but not usually available for the system of interest.

Site specificity is of great importance in the sediment compartment. For example, measured values of K_D in sediments are known to depend on the redox state and AVS concentration. Lee et al. (2000) showed that the measured K_D values for several metal ions (Ni^{2+} , Cd^{2+} , Zn^{2+}) was inversely proportional to the excess SEM (i.e. SEM – AVS). The total variation in sediment K_D was nearly 6 orders of magnitude. Compilations typically do not provide information about sediment redox state nor is it used to qualify the reported K_D values.

Measured K_D values are also influenced by the type of solids extraction employed in the laboratory. Solids not dissolved by typical digestions (often referred to as the residual solid) contain mainly aluminum and iron containing primary and secondary minerals, which hold trace metals within their crystal structure (Tessier et al., 1979). To liberate all metals in a sediment sample, the use of hydrofluoric acid (HF) is required (Chen and Ma, 1998). Digestion methods utilizing HF are commonly used throughout the geochemical literature whenever metals are used as geochemical tracers for source identification (Loring, 1991; Schopp and Windom, 1988). For mass balance purposes, a digestion utilizing HF (hydrofluoric acid) is also required so that all of the metal is liberated. HF extractions are not commonplace because of the difficulties of the hazards associated with handling and storage of HF. Thus, the experimentally-determined K_D reported for a particular water body may not be representative of the true solid-solution distribution of metal ions.

Finally, to quantify the particulate metal concentration, the sediment must be removed from its natural state. This disturbance can potentially alter metal speciation. For example, if anaerobic sediment is

exposed to air during sampling, oxidation of sulfide and iron could occur. This can also affect porewater analysis if the porewater is extracted after the sediment is removed from its natural state.

	Empirical K_D Approach	Chemical Speciation Model Approach
<u>Implementation</u>	Easy to incorporate into mass balance models.	Requires specialized software to perform calculations; databases are continually evolving.
<u>Accuracy</u>	K_D values are not linked to water chemistry of interest. Empirical K_D values are not considered to be accurate unless site-specific data is available. Site-specific values (when available) may be more accurate than model calculated values.	Accuracy can depend upon the model used for the calculation. Investigation of the accuracy of these models is an active area of study. Different speciation models and thermodynamic databases often yield different results. (Bhavsar et al., 2008)
<u>Bioavailability</u>	Does not provide a means of assessing bioavailable fraction	Compatible with modern methods of assessing ecotoxicological effects
<u>Applicability</u>	Available for nearly all metal ions of interest. Site specific values are not available for many systems.	Calibration data sets for metals are not complete enough to provide a complete calibration. LFERs have been used to extrapolate to a wider set of metal ions.
<u>Information on Binding Phases</u>	Does not provide information on important metal binding phases	Calculates distribution of metal bound to various binding phases.
<u>Acceptance</u>	Empirical approach was the first approach used for metals risk and hazards assessment. This approach is not considered modern or state of the art.	Developed as an improvement upon the empirical approach. Generally accepted by the scientific community.

Chemical Speciation Models

The use of chemical speciation models to describe solid solution partitioning is an active area of research. Descriptions of metal binding to humic and fulvic acids are continually being evaluated (Lofts and Tipping, 2000) and refined (Tipping et al., 2011). The most recent version of the Windermere Humic Aqueous Model (WHAM) is reported to be more accurate than its predecessors. Considerable attention has been given to the identification of the strong binding sites present in natural organic matter that are responsible for metal binding at low free metal ion activities (Cabaniss, 2009, 2010).

Metal sulfide soluble complex equilibria is an active area of research (and controversy) (Helz et al., 2011; Rickard and Luther, 2006). There is increasing evidence that the distribution of soft to borderline metal ions is controlled by sulfide equilibria. It is well-known that presence of sulfide (H_2S and HS^-) in reducing sediments leads to formation of metal sulfide solids. However, excess sulfide in the pore water results in the formation of soluble complexes which increase dissolved metal concentrations and lower sediment K_D values. The presence of zero-valent sulfur leads to formation of polysulfides which also complex with metal ions (Shea and Helz, 1988; Thompson and Helz, 1994). Complexes with sulfide and polysulfides are believed to be more important than complexes with DOC for many divalent transition metals (Wang and Tessier, 2009).

Discrepancies Between Empirical and Model-Calculated K_D Values

In the water column, TICKET-UWM calculated log K_D values are often *less* than empirical K_D values. Possible reasons for this include:

- The set of reactions and sorptive processes considered in the TICKET-UWM speciation model may not include all metal-particle interactions. Specifically, oxide binding phases such as HFO and HMO are known to be important for some metal ions.
- Inaccuracies or deficiencies in inorganic thermodynamic databases. For example, positive bias in carbonate complexation constants can draw more metal into the aqueous phase thereby lowering model-calculated K_D values.
- Difficulties in handling metal-metal competition. For example, Ca^{2+} and Mg^{2+} competition with trace metals for occupation of humic and fulvic acid binding sites.

In the sediment, TICKET-UWM calculated log K_D values are often *greater* than empirical K_D values. Possible reasons for this include:

- Lack of reliable thermodynamic data for metal sulfide aqueous complexes. Soluble aqueous complexes with bisulfide, sulfide and polysulfides increase dissolved metal concentrations and lower K_D values. These constants are difficult to measure experimentally, and consistent thermodynamic compilations do not exist.

Both the Empirical *and* Model Calculated K_D approach have shortcomings. However, the metal speciation approach to fate and transport is the more robust approach. This approach is compatible with methods for assessing bioavailability, is site-specific, and is continually being refined and improved. The current recommended approach in TICKET-UWM rapid removal and remobilization calculations is to use *both* approaches.

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APPENDIX B – COPPER TABLES

Table B-1. Summary of Water Column Runs for Copper with the Speciation Model Method

Removal Approach and Output Quantity	pH = 6.09			pH = 7.07			pH = 8.00		
	20 µg/L	25 µg/L	1,000 µg/L	7 µg/L	35 µg/L	1,000 µg/L	11 µg/L	30 µg/L	1,000 µg/L
1: $C_D(t)/C_T(0)$									
Time for 70% removal, days	--- ^a	--- ^a	1.80	--- ^a	--- ^a	1.64	--- ^a	--- ^a	--- ^a
Log K_D range ^b	6.19	6.17	4.48 - 4.77	6.16	6.01	4.51 - 4.79	5.59	5.57	5.60
Fraction particulate range ^b	0.959	0.957	0.311 - 0.469	0.956	0.939	0.328 - 0.480	0.854	0.847	0.855
2: $C_T(t)/C_T(0)$									
Time for 70% removal, days	1.56	1.57	3.17	1.57	1.59	3.04	1.75	1.76	2.09
Log K_D range ^b	6.19 - 6.27	6.17 - 6.26	4.48 - 5.12	6.16 - 6.18	6.01 - 6.14	4.51 - 5.12	5.59 - 5.60	5.57 - 5.59	5.00 - 5.60
Fraction particulate range ^b	0.959 - 0.965	0.957 - 0.965	0.311 - 0.662	0.956 - 0.958	0.939 - 0.954	0.328 - 0.664	0.854 - 0.856	0.847 - 0.854	0.600 - 0.855
3: $C_D(t)/C_D(0)$									
Time for 70% removal, days	1.37	1.32	2.35	1.50	1.26	2.21	1.73	1.69	3.02
Log K_D range ^b	6.19 - 6.26	6.17 - 6.25	4.48 - 4.89	6.16 - 6.18	6.01 - 6.12	4.51 - 4.92	5.59 - 5.60	5.57 - 5.59	5.00 - 5.60
Fraction particulate range ^b	0.959 - 0.965	0.957 - 0.964	0.311 - 0.535	0.956 - 0.958	0.939 - 0.952	0.328 - 0.557	0.854 - 0.856	0.847 - 0.854	0.600 - 0.855

^a 70% removal occurs instantly via initial solid-solution equilibrium partitioning. Instead of log K_D and fraction particulate value ranges, the values at $t = 0$ are indicated.

^b These ranges were calculated using data prior to the time at which 70% removal was achieved.

Table B-2. Summary of Water Column Runs for Copper with Lowered Settling Velocity ^a

Removal Approach and Output Quantity	Linear Partitioning	pH = 6.09	pH = 7.07	pH = 8.00
1: $C_D(t)/C_T(0)$				
Time for 70% removal, days	32.6	--- ^b	--- ^b	--- ^b
Log K_D range ^c	4.48	6.17	6.01	5.57
Fraction particulate range ^c	0.312	0.957	0.939	0.847
2: $C_T(t)/C_T(0)$				
Time for 70% removal, days	47.3	15.7	15.9	17.7
Log K_D range ^c	4.48	6.17 - 6.26	6.01 - 6.14	5.57 - 5.59
Fraction particulate range ^c	0.312	0.957 - 0.965	0.939 - 0.954	0.847 - 0.854

^a Initial total Cu concentration at acute ERVs: 20 (pH 6), 35 (pH 7) and 30 (pH 8)

^b 70% removal occurs instantly via initial solid-solution equilibrium partitioning. Instead of log K_D and fraction particulate value ranges, the values at $t = 0$ are indicated.

^c These ranges were calculated using data prior to the time at which 70% removal was achieved

Table B-3. Summary of Copper Sediment Runs ^a

Removal Approach and Output Quantity	AVS = 0 $\mu\text{mol/g}$			Anoxic, AVS = 1 $\mu\text{mol/g}$		
	35 $\mu\text{g/L}$	100 $\mu\text{g/L}$	1,000 $\mu\text{g/L}$	35 $\mu\text{g/L}$	100 $\mu\text{g/L}$	1,000 $\mu\text{g/L}$
Time to Quasi Steady State, days	18	18	20	18	18	20
Tot. Cu Range, $\mu\text{g/L}$ ^b	0.0885 - 0.0981	0.253 - 0.280	2.53 - 2.80	0.0882 - 0.0978	0.252 - 0.280	2.53 - 2.80
Diss. Cu Range, $\mu\text{g/L}$ ^b	0.00366 - 0.00405	0.0105 - 0.0116	0.107 - 0.119	0.00365 - 0.00404	0.0104 - 0.0116	0.107 - 0.119
Total Settling IN, tonnes	223	637	6360	223	636	6360
Total Resusp. OUT, tonnes	96.9	277	2760	96.9	277	2760
Total Diffusion NET, tonnes ^c	-0.309	-0.879	-6.78	0.0100	0.0351	-3.48
Total Burial OUT, tonnes	11.9	34.0	340	11.9	34.0	340
Water column log K_D , L/kg ^b	6.19	6.19	6.18	6.19	6.19	6.18
Sediment log K_D , L/kg ^b	4.34	4.34	4.32	16.2	16.7	4.50
Time for 70% Removal, days (Approach 1)	--- ^d	--- ^d	1.76	--- ^d	--- ^d	1.76
$[0.3 \times C_T(0)] / \text{Max QSS } C_T$ ^e	107	107	107	107	107	107

^a Select simulation parameters: water column pH 7.07; sediment pH 7.56; settling velocity 2.5 m/d. For additional parameters, see Table 2.4.

^b Ranges and average are based on data from the quasi-steady state period of the simulation.

^c This number is the diffusive flux integrated over the *entire* 365-day simulation. Negative diffusive flux values are directed out of the sediment and positive diffusive flux values are directed into the sediment.

^d 70% removal occurs instantly via initial solid-solution equilibrium partitioning.

^e This quantity is the ratio of the total Cu concentration representing 70% removal ($0.3 \times C_T(0)$) to the maximum total concentration during the quasi-steady-state period (Max QSS C_T). This is meant to give an indication of where sustained water column concentrations lie relative to the 70% removal benchmark.

Table B-3. Continued ^a

Removal Approach and Output Quantity	Anoxic, AVS = 9.1 µmol/g			Oxic		
	35 µg/L	100 µg/L	1,000 µg/L	35 µg/L	100 µg/L	1,000 µg/L
Time to Quasi Steady State, days	18	18	20	18	18	19
Tot. Cu Range, µg/L ^b	0.0882 - 0.0978	0.252 - 0.280	2.52 - 2.79	0.0884 - 0.0981	0.253 - 0.280	2.53 - 2.82
Diss. Cu Range, µg/L ^b	0.00365 - 0.00404	0.0104 - 0.0116	0.107 - 0.119	0.00365 - 0.00403	0.0104 - 0.0116	0.107 - 0.119
Total Settling IN, tonnes	223	636	6350	223	637	6360
Total Resusp. OUT, tonnes	96.9	277	2760	96.9	277	2760
Total Diffusion NET, tonnes ^c	0.0100	0.0351	2.74	-0.303	-0.861	-6.60
Total Burial OUT, tonnes	11.9	34.0	340	11.9	34.0	340
Water column log K_D , L/kg ^b	6.19	6.19	6.18	6.19	6.19	6.18
Sediment log K_D , L/kg ^b	16.2	16.7	17.7	4.35	4.35	4.33
Time for 70% Removal, days (Approach 1)	--- ^d	--- ^d	1.76	--- ^d	--- ^d	1.75
$[0.3 \times C_T(0)] / \text{Max QSS } C_T$ ^e	107	107	107	107	107	107

^a Select simulation parameters: water column pH 7.07; sediment pH 7.56; settling velocity 2.5 m/d. For additional parameters, see Table 2.4.

^b Ranges and average are based on data from the quasi-steady state period of the simulation.

^c This number is the diffusive flux integrated over the *entire* 365-day simulation. Negative diffusive flux values are directed out of the sediment and positive diffusive flux values are directed into the sediment.

^d 70% removal occurs instantly via initial solid-solution equilibrium partitioning.

^e This quantity is the ratio of the total Cu concentration representing 70% removal ($0.3 \times C_T(0)$) to the maximum total concentration during the quasi-steady-state period (Max QSS C_T). This is meant to give an indication of where sustained water column concentrations lie relative to the 70% removal benchmark.

APPENDIX C – ZINC TABLES

Table C-1. Summary of Water Column Runs for Zinc with the Speciation Model Method

Removal Approach and Output Quantity	pH = 6.09			pH = 7.07		pH = 8.00		
	82 µg/L	413 µg/L	1,000 µg/L	136 µg/L	1,000 µg/L	19 µg/L	136 µg/L	1,000 µg/L
1: $C_D(t)/C_T(0)$								
Time for 70% removal, days	2.99	4.15	6.08	1.57	5.29	2.05	2.13	5.04
Log K_D range ^b	4.49 - 4.52	4.29 - 4.42	4.08 - 4.29	4.67 - 4.77	4.10 - 4.37	4.66 - 4.66	4.61 - 4.65	4.12 - 4.39
Fraction particulate range ^b	0.315 – 0.333	0.224 – 0.283	0.152 – 0.228	0.412 – 0.467	0.160 – 0.262	0.406 – 0.408	0.380 – 0.403	0.166 – 0.271
2: $C_T(t)/C_T(0)$								
Time for 70% removal, days	4.47	5.56	7.42	3.16	6.61	3.63	3.69	6.38
Log K_D range ^b	4.49 - 4.53	4.29 - 4.45	4.08 - 4.34	4.67 - 4.84	4.10 - 4.47	4.66 - 4.66	4.61 - 4.66	4.12 - 4.47
Fraction particulate range ^b	0.315 – 0.339	0.224 – 0.299	0.152 – 0.248	0.412 – 0.510	0.160 – 0.307	0.405 – 0.408	0.380 – 0.408	0.166 – 0.308
3: $C_D(t)/C_D(0)$								
Time for 70% removal, days	4.34	5.16	6.86	2.75	5.94	3.65	3.56	5.71
Log K_D range ^b	4.49 - 4.53	4.29 - 4.44	4.08 - 4.32	4.67 - 4.83	4.10 - 4.42	4.66 - 4.66	4.61 - 4.66	4.12 - 4.44
Fraction particulate range ^b	0.315 - 0.339	0.224 - 0.295	0.152 - 0.240	0.412 - 0.501	0.160 - 0.283	0.405 - 0.408	0.380 - 0.408	0.166 - 0.291

^a 70% removal occurs instantly via initial solid-solution equilibrium partitioning. Instead of log K_D and fraction particulate value ranges, the values at $t = 0$ are indicated.

^b These ranges were calculated using data prior to the time at which 70% removal was achieved

Table C-2. Summary of Water Column Runs for Zinc with Lowered Settling Velocity ^a

Removal Approach and Output Quantity	Linear Partitioning	pH = 6.09	pH = 7.07	pH = 8.00
1: $C_D(t)/C_T(0)$				
Time for 70% removal, days	4.64	41.6	16.0	21.5
Log K_D range ^b	5.04	4.29 - 4.42	4.67 - 4.77	4.61 - 4.65
Fraction particulate range ^b	0.622	0.224 - 0.283	0.412 - 0.469	0.380 - 0.403
2: $C_T(t)/C_T(0)$				
Time for 70% removal, days	24.1	55.5	31.9	37.2
Log K_D range ^b	5.04	4.29 - 4.45	4.67 - 4.84	4.61 - 4.66
Fraction particulate range ^b	0.622	0.224 - 0.299	0.412 - 0.511	0.380 - 0.408

^a Initial total Zn concentration at acute ERVs: 413 (pH 6), 136 (pH 7) and 136 (pH 8)

^b These ranges were calculated using data prior to the time at which 70% removal was achieved

Table C-3. Summary of Zinc Sediment Runs ^a

Removal Approach and Output Quantity	AVS = 0 $\mu\text{mol/g}$			Anoxic, AVS = 1 $\mu\text{mol/g}$		
	100 $\mu\text{g/L}$	136 $\mu\text{g/L}$	1,000 $\mu\text{g/L}$	100 $\mu\text{g/L}$	136 $\mu\text{g/L}$	1,000 $\mu\text{g/L}$
Time to Quasi Steady State, days	25	25	30	25	25	30
Tot. Zn Range, $\mu\text{g/L}$ ^b	0.441 - 0.491	0.599 - 0.669	4.45 - 4.96	0.431 - 0.481	0.587 - 0.655	4.42 - 4.93
Diss. Zn Range, $\mu\text{g/L}$ ^b	0.194 - 0.217	0.265 - 0.295	1.99 - 2.22	0.190 - 0.212	0.259 - 0.289	1.97 - 2.20
Total Settling IN, tonnes	639	869	6370	634	861	6350
Total Resusp. OUT, tonnes	275	375	2740	276	375	2740
Total Diffusion NET, tonnes ^c	-5.49	-7.42	-46.3	0.540	0.771	-26.0
Total Burial OUT, tonnes	33.9	46.1	337	33.9	46.1	337
Water column log K_D , L/kg ^b	4.93	4.93	4.92	4.93	4.93	4.92
Sediment log K_D , L/kg ^b	3.52	3.52	3.53	7.12	7.26	3.71
Time for 70% Removal, days (Approach 1)	1.63	1.80	5.51	1.63	1.80	5.51
$[0.3 \times C_T(0)] / \text{Max QSS } C_T$ ^d	61.1	61.0	60.4	62.4	62.3	60.9

^a Select simulation parameters: water column pH 7.07; sediment pH 7.56; settling velocity 2.5 m/d. For additional parameters, see Table 2.4.

^b Ranges and average are based on data from the quasi-steady state period of the simulation.

^c This number is the diffusive flux integrated over the *entire* 365-day simulation. Negative diffusive flux values are directed out of the sediment and positive diffusive flux values are directed into the sediment.

^d This quantity is the ratio of the total Zn concentration representing 70% removal ($0.3 \times C_T(0)$) to the maximum total concentration during the quasi-steady-state period (Max QSS C_T). This is meant to give an indication of where sustained water column concentrations lie relative to the 70% removal benchmark.

Table C-3. Continued ^a

Removal Approach and Output Quantity	Anoxic, AVS = 9.1 $\mu\text{mol/g}$			Oxic		
	100 $\mu\text{g/L}$	136 $\mu\text{g/L}$	1,000 $\mu\text{g/L}$	100 $\mu\text{g/L}$	136 $\mu\text{g/L}$	1,000 $\mu\text{g/L}$
Time to Quasi Steady State, days	25	25	30	25	25	30
Tot. Zn Range, $\mu\text{g/L}$ ^b	0.431 - 0.481	0.587 - 0.655	4.36 - 4.86	0.438 - 0.486	0.595 - 0.663	4.42 - 4.92
Diss. Zn Range, $\mu\text{g/L}$ ^b	0.190 - 0.212	0.259 - 0.289	1.95 - 2.17	0.192 - 0.213	0.262 - 0.290	1.97 - 2.18
Total Settling IN, tonnes	634	861	6310	638	868	6360
Total Resusp. OUT, tonnes	276	375	2740	276	375	2740
Total Diffusion NET, tonnes ^c	0.540	0.771	12.4	-4.36	-5.90	-36.9
Total Burial OUT, tonnes	33.9	46.1	337	33.9	46.1	337
Water column log K_D , L/kg ^b	4.93	4.93	4.92	4.93	4.93	4.92
Sediment log K_D , L/kg ^b	7.12	7.26	8.12	3.61	3.61	3.60
Time for 70% Removal, days (Approach 1)	1.63	1.80	5.51	1.62	1.80	5.49
$[0.3 \times C_T(0)] / \text{Max QSS } C_T$ ^d	62.4	62.3	61.7	61.7	61.6	61.0

^a Select simulation parameters: water column pH 7.07; sediment pH 7.56; settling velocity 2.5 m/d. For additional parameters, see Table 2.4.

^b Ranges and average are based on data from the quasi-steady state period of the simulation.

^c This number is the diffusive flux integrated over the *entire* 365-day simulation. Negative diffusive flux values are directed out of the sediment and positive diffusive flux values are directed into the sediment.

^d This quantity is the ratio of the total Zn concentration representing 70% removal ($0.3 \times C_T(0)$) to the maximum total concentration during the quasi-steady-state period (Max QSS C_T). This is meant to give an indication of where sustained water column concentrations lie relative to the 70% removal benchmark.

APPENDIX D – LEAD TABLES

Table D-1. Summary of Water Column Runs for Lead with the Speciation Model Method

Removal Approach and Output Quantity	pH = 6.09			pH = 7.07			pH = 8.00		
	17.8 µg/L	73.6 µg/L	1,000 µg/L	9 µg/L	52 µg/L	1,000 µg/L	23.4 µg/L	107 µg/L	1,000 µg/L
1: $C_D(t)/C_T(0)$									
Time for 70% removal, days	--- ^a	--- ^a	0.230	--- ^a	--- ^a	0.283	--- ^a	--- ^a	0.667
Log K_D range ^b	5.94	5.86	5.05 - 5.11	5.88	5.82	5.02 - 5.08	5.28	5.28	4.86 - 4.97
Fraction particulate range ^b	0.929	0.916	0.628 - 0.657	0.919	0.908	0.613 – 0.641	0.742	0.739	0.522 - 0.586
2: $C_T(t)/C_T(0)$									
Time for 70% removal, days	1.62	1.63	1.98	1.64	1.65	2.01	2.02	2.02	2.32
Log K_D range ^b	5.94 - 5.95	5.86 - 5.93	5.05 - 5.54	5.88 - 5.89	5.82 - 5.87	5.02 - 5.51	5.28 - 5.28	5.28 - 5.28	4.86 - 5.23
Fraction particulate range ^b	0.929 – 0.931	0.916 – 0.927	0.628 – 0.840	0.919 – 0.921	0.908 – 0.917	0.613 – 0.830	0.741 - 0.742	0.739 - 0.742	0.522 - 0.718
3: $C_D(t)/C_D(0)$									
Time for 70% removal, days	1.57	1.44	1.20	1.61	1.51	1.22	2.02	2.00	1.64
Log K_D range ^b	5.94 - 5.95	5.86 - 5.93	5.05 - 5.34	5.88 - 5.89	5.82 - 5.87	5.02 - 5.34	5.28 - 5.28	5.28 - 5.28	4.86 - 5.16
Fraction particulate range ^b	0.929 - 0.931	0.916 - 0.927	0.628 - 0.768	0.919 - 0.921	0.908 - 0.917	0.613 - 0.766	0.741 - 0.742	0.739 - 0.742	0.522 - 0.686

^a 70% removal occurs instantly via initial solid-solution equilibrium partitioning. Instead of log K_D and fraction particulate value ranges, the values at $t = 0$ are indicated.

^b These ranges were calculated using data prior to the time at which 70% removal was achieved

Table D-2. Summary of Water Column Runs for Lead with Lowered Settling Velocity ^a

Removal Approach and Output Quantity	Linear Partitioning	pH = 6.09	pH = 7.07	pH = 8.00
1: $C_D(t)/C_T(0)$				
Time for 70% removal, days	--- ^b	--- ^b	--- ^b	--- ^b
Log K_D range ^c	5.47	5.86	5.82	5.28
Fraction particulate range ^c	0.816	0.916	0.908	0.739
2: $C_T(t)/C_T(0)$				
Time for 70% removal, days	18.5	16.3	16.5	20.3
Log K_D range ^c	5.47 - 5.47	5.86 - 5.93	5.82 - 5.87	5.28 - 5.28
Fraction particulate range ^c	0.816 - 0.816	0.916 - 0.928	0.908 - 0.917	0.739 - 0.741

^a Initial total Pb concentration at acute ERVs: 73.6 (pH 6), 52 (pH 7) and 107 (pH 8)

^b 70% removal occurs instantly via initial solid-solution equilibrium partitioning. Instead of log K_D and fraction particulate value ranges, the values at $t = 0$ are indicated.

^c These ranges were calculated using data prior to the time at which 70% removal was achieved

Table D-3. Summary of Lead Sediment Runs

Removal Approach and Output Quantity	AVS = 0 $\mu\text{mol/g}$			Anoxic, AVS = 1 $\mu\text{mol/g}$		
	52 $\mu\text{g/L}$	100 $\mu\text{g/L}$	1,000 $\mu\text{g/L}$	52 $\mu\text{g/L}$	100 $\mu\text{g/L}$	1,000 $\mu\text{g/L}$
Time to Quasi Steady State, days	18	18	19	18	18	19
Tot. Pb Range, $\mu\text{g/L}$ ^a	0.137 - 0.153	0.264 – 0.294	2.64 – 2.93	0.137 - 0.152	0.263 – 0.292	2.63 – 2.91
Diss. Cu Range, $\mu\text{g/L}$ ^a	0.0110 - 0.0122	0.0212 – 0.0236	0.214 - 0.237	0.0110 - 0.0122	0.0211 – 0.0234	0.212 – 0.235
Total Settling IN, tonnes	332	638	6370	331	636	6360
Total Resusp. OUT, tonnes	144	277	2770	144	277	2770
Total Diffusion NET, tonnes ^c	-0.883	-1.70	-16.5	0.0279	0.0563	1.10
Total Burial OUT, tonnes	17.7	34.0	340	17.7	34.0	340
Water column log K_D , L/kg ^a	5.88	5.88	5.88	5.88	5.88	5.88
Sediment log K_D , L/kg ^a	4.06	4.06	4.05	7.25	7.85	8.85
Time for 70% Removal, days (Approach 1)	--- ^c	--- ^c	0.398	--- ^c	--- ^c	0.398
$[0.3 \times C_T(0)]/\text{Max QSS } C_T$ ^d	102	102	102	103	103	103

^a Ranges and average are based on data from the quasi-steady state period of the simulation

^b This number is the diffusive flux integrated over the *entire* simulation time. Negative diffusive flux values are directed out of the sediment and positive diffusive flux values are directed into the sediment

^c 70% removal occurs instantly via initial solid-solution equilibrium partitioning.

^d This quantity is the ratio of the total Pb concentration representing 70% removal ($0.3 \times C_T(0)$) to the maximum total concentration during the quasi-steady-state period (Max QSS C_T). This is meant to give an indication of where sustained water column concentrations lie relative to the 70% removal benchmark.

Table D-3. Continued

Removal Approach and Output Quantity	Anoxic, AVS = 9.1 $\mu\text{mol/g}$			Oxic		
	52 $\mu\text{g/L}$	100 $\mu\text{g/L}$	1,000 $\mu\text{g/L}$	52 $\mu\text{g/L}$	100 $\mu\text{g/L}$	1,000 $\mu\text{g/L}$
Time to Quasi Steady State, days	18	18	19	18	18	19
Tot. Pb Range, $\mu\text{g/L}$ ^a	0.137 - 0.152	0.263 – 0.292	2.63 – 2.91	0.137 - 0.152	0.263 - 0.292	2.63 - 2.92
Diss. Pb Range, $\mu\text{g/L}$ ^a	0.0110 - 0.0122	0.0211 – 0.0234	0.212 – 0.235	0.0109 - 0.0121	0.0210 - 0.0233	0.212 - 0.234
Total Settling IN, tonnes	331	636	6360	331	636	6360
Total Resusp. OUT, tonnes	144	277	2770	144	277	2770
Total Diffusion NET, tonnes ^c	0.0279	0.0563	1.10	0.0123	-0.0103	-5.31
Total Burial OUT, tonnes	17.7	34.0	340	17.7	34.0	340
Water column log K_D , L/kg ^a	5.88	5.88	5.88	5.88	5.88	5.88
Sediment log K_D , L/kg ^a	7.25	7.85	8.85	5.81	5.48	4.50
Time for 70% Removal, days (Approach 1)	--- ^c	--- ^c	0.398	--- ^c	--- ^c	0.397
$[0.3 \times C_T(0)]/\text{Max QSS } C_T$ ^d	103	103	103	103	103	103

^a Ranges and average are based on data from the quasi-steady state period of the simulation

^b This number is the diffusive flux integrated over the *entire* simulation time. Negative diffusive flux values are directed out of the sediment and positive diffusive flux values are directed into the sediment

^c 70% removal occurs instantly via initial solid-solution equilibrium partitioning.

^d This quantity is the ratio of the total Pb concentration representing 70% removal ($0.3 \times C_T(0)$) to the maximum total concentration during the quasi-steady-state period (Max QSS C_T). This is meant to give an indication of where sustained water column concentrations lie relative to the 70% removal benchmark.

APPENDIX E – NICKEL TABLES

Table E-1. Summary of Water Column Runs for Nickel with the Speciation Model Method (WHAM V)

Removal Approach and Output Quantity	pH = 6.09			pH = 7.07		pH = 8.00		
	2.4 µg/L	120 µg/L	1,000 µg/L	68 µg/L	1,000 µg/L	2.4 µg/L	68 µg/L	1,000 µg/L
1: $C_D(t)/C_T(0)$								
Time for 70% removal, days	24.6	25.0	27.9	27.6	32.2	73.4	72.4	73.7
Log K_D range ^b	3.61 - 3.61	3.60 - 3.61	3.52 - 3.58	3.56 - 3.56	3.45 - 3.53	3.16	3.16 - 3.17	3.14 - 3.17
Fraction particulate range ^b	0.0574 – 0.0575	0.0561 – 0.0570	0.0472 – 0.0539	0.0514 – 0.0519	0.0402 – 0.0481	0.0212	0.0214 – 0.0216	0.0202 – 0.0215
2: $C_T(t)/C_T(0)$								
Time for 70% removal, days	26.0	26.3	29.2	29.0	33.6	75.0	74.0	75.3
Log K_D range ^b	3.61 - 3.61	3.60 - 3.61	3.52 - 3.58	3.56 - 3.56	3.45 - 3.53	3.16	3.16 - 3.17	3.14 - 3.17
Fraction particulate range ^b	0.0574 – 0.0575	0.0561 – 0.0571	0.0472 – 0.0541	0.0514 – 0.0519	0.0402 – 0.0483	0.0212	0.0214 – 0.0216	0.0202 – 0.0215
3: $C_D(t)/C_D(0)$								
Time for 70% removal, days	26.0	26.3	29.0	29.0	33.3	75.0	74.0	75.2
Log K_D range ^b	3.61 - 3.61	3.60 - 3.61	3.52 - 3.58	3.56 - 3.56	3.45 - 3.53	3.16 - 3.16	3.16 - 3.17	3.14 - 3.17
Fraction particulate range ^b	0.0574 - 0.0575	0.0561 - 0.0571	0.0472 - 0.0541	0.0514 - 0.0519	0.0402 - 0.0483	0.0212 - 0.0212	0.0214 - 0.0216	0.0202 - 0.0215

^a 70% removal occurs instantly via initial solid-solution equilibrium partitioning. Instead of log K_D and fraction particulate value ranges, the values at $t = 0$ are indicated.

^b These ranges were calculated using data prior to the time at which 70% removal was achieved

Table E-2. Summary of Water Column Runs for Nickel with the Speciation Model Method With No Ca/Mg Competition for Sites on Organic Matter (WHAM V)

Removal Approach and Output Quantity	pH = 6.09			pH = 7.07		pH = 8.00		
	2.4 µg/L	120 µg/L	1,000 µg/L	68 µg/L	1,000 µg/L	2.4 µg/L	68 µg/L	1,000 µg/L
1: $C_D(t)/C_T(0)$								
Time for 70% removal, days	12.8	3.16	7.99	0.517	4.98	--- ^a	0.400	5.14
Log K_D range ^b	3.87 - 3.92	4.45 - 4.50	3.93 - 4.21	5.00 - 5.02	4.09 - 4.42	5.28	5.02 - 5.06	4.08 - 4.41
Fraction particulate range ^b	0.101 – 0.112	0.295 – 0.323	0.114 – 0.194	0.597 – 0.612	0.156 – 0.283	0.742	0.612 – 0.632	0.152 – 0.280
2: $C_T(t)/C_T(0)$								
Time for 70% removal, days	14.1	4.67	9.30	2.43	6.28	2.00	2.25	6.43
Log K_D range ^b	3.87 - 3.92	4.45 - 4.50	3.93 - 4.26	5.00 - 5.03	4.09 - 4.55	5.28 - 5.30	5.02 - 5.18	4.08 - 4.54
Fraction particulate range ^b	0.100 – 0.112	0.295 – 0.323	0.114 – 0.215	0.597 – 0.618	0.156 – 0.346	0.742 – 0.748	0.612 – 0.693	0.152 – 0.344
3: $C_D(t)/C_D(0)$								
Time for 70% removal, days	14.3	4.59	8.66	2.43	5.53	1.97	1.88	5.68
Log K_D range ^b	3.87 - 3.92	4.45 - 4.50	3.93 - 4.24	5.00 - 5.03	4.09 - 4.48	5.28 - 5.30	5.02 - 5.16	4.08 - 4.46
Fraction particulate range ^b	0.100 - 0.112	0.295 - 0.323	0.114 - 0.205	0.597 - 0.618	0.156 - 0.310	0.742 - 0.748	0.612 - 0.682	0.152 - 0.303

^a 70% removal occurs instantly via initial solid-solution equilibrium partitioning. Instead of log K_D and fraction particulate value ranges, the values at $t = 0$ are indicated.

^b These ranges were calculated using data prior to the time at which 70% removal was achieved

Table E-3. Summary of Water Column Runs for Nickel with Lowered Settling Velocity (WHAM V) ^a

Removal Approach and Output Quantity	Linear Partitioning	pH = 6.09	pH = 7.07	pH = 8.00
1: $C_D(t)/C_T(0)$				
Time for 70% removal, days	37.4	219	238	508
Log K_D range ^b	4.42	3.60 - 3.61	3.56 - 3.56	3.16 - 3.17
Fraction particulate range ^b	0.283	0.0561 - 0.0570	0.0514 - 0.0519	0.0214 - 0.0216
2: $C_T(t)/C_T(0)$				
Time for 70% removal, days	51.7	230	249	518
Log K_D range ^b	4.42 - 4.42	3.60 - 3.61	3.56 - 3.56	3.16 - 3.17
Fraction particulate range ^b	0.283 - 0.283	0.0561 - 0.0571	0.0514 - 0.0519	0.0214 - 0.0216

^a Initial total Ni concentration at acute ERVs: 120 (pH 6), 68 (pH 7) and 68 (pH 8)

^b These ranges were calculated using data prior to the time at which 70% removal was achieved

Inorganic Stability Constant Database Review

After WHAM6 and WHAM7 were integrated into the TICKET-UWM, an assessment of the WHAM inorganic stability constant database was made. This assessment included a comparison of the WHAM stability constants to values in other speciation programs and a targeted review of recent literature on Ni speciation. For Ni, WHAM5, WHAM6, and WHAM7 consider the same set of Ni complexes with hydroxide (OH^-), carbonate and bicarbonate (CO_3^{2-} and HCO_3^-), sulfate (SO_4^{2-}), and chloride (Cl^-) and use the same stability constant values (Table E-8). By default, the TICKET-UWM uses the same set of complexes and stability constants for OH^- , CO_3^{2-} and HCO_3^- , SO_4^{2-} , and Cl^- as WHAM7. Bisulfide (HS^-) complexes were added in TICKET-UWM along with hydroxide, carbonate, and sulfide solids. For comparison, thermodynamic data from several speciation programs are included in the table. Notable points from the table include the following:

1. WHAM7 and the TICKET-UWM consider fewer OH^- complexes than the other models
2. The first and second OH^- complex stability constants from WHAM7, TICKET-UWM, MINEQL, Visual MINTEQ and MINTEQA2 are essentially the same. Most of the OH^- stability constant data come from the Smith and Martell / NIST family of compilations.
3. WHAM7 and TICKET-UWM stability constants for the CO_3^{2-} and HCO_3^- complexes—taken from Mattigod and Sposito (1979)—are significantly higher than those for the other programs (which come from the Smith and Martell / NIST family of compilations).
4. Ni-Cl and Ni- SO_4 constants are generally consistent between the programs and are sourced from either the Smith and Martell / NIST family of compilations or the IUPAC database. The Visual MINTEQ constant for NiCl^+ is the only outlier.
5. Initially Ni-HS formation constants from Luther et al. (1996), Al-Farawati and van den Berg (1999) and Wilkin and Rogers (2010) were selected to include in the TICKET-UWM. Wilkin and Rogers (2010) determined a solubility product for hexagonal NiS. Most models employ the Thiel and Gessner (1914) data (Table E-8). However, as reported by Thoenen (1998), the Thiel and Gessner data were “crude estimates that were meant only to give some idea of the order of magnitude” (Thoenen, 1998). For this reason, as well as to remain consistent with their Ni-HS soluble complex formation constants, the Wilkin and Rogers (2010) solubility product for hexagonal NiS were initially added to the TICKET-UWM database.

Table E-4. Summary of Selected Ni Aqueous Complexes and Solids from Various Modeling Programs

Species	WHAM7	TICKET-UWM	MINEQL (v 4.6)	Visual MINTEQ (v3.0)	MINETQA2 (v. 4.0)	Revised TICKET-UWM
NiOH ⁺	-9.87 ^a	-9.87 ^a	-9.897 ⁱ	-9.897 ^m	-9.897 ⁱ	-9.50 ⁿ
Ni(OH) ₂ ⁰	-19.0 ^a	-19.0 ^a	-18.994 ⁱ	-18.994 ^m	-18.994 ⁱ	-18.0 ⁿ
Ni(OH) ₃ ⁻	---	---	-29.991 ⁱ	-29.991 ^m	-29.991 ⁱ	-29.7 ⁿ
Ni(OH) ₄ ²⁻	---	---	---	---	---	-44.96 ⁿ
Ni ₂ OH ³⁺	---	---	---	---	---	-9.8 ⁿ
Ni ₄ (OH) ₄ ⁴⁺	---	---	---	---	---	-27.9 ⁿ
Ni(OH) ₂ (s)	---	-10.8 ^d	-12.794 ^j	-10.79 (c) / -12.89 (am) ^m	-12.7940 ^j	-10.52 ⁿ
NiCO ₃ ⁰	5.78 ^b	5.78 ^b	4.572 ⁱ	4.57 ^m	4.5718 ⁱ	4.2 ^{o,p}
Ni(CO ₃) ₂ ²⁻	---	---	---	---	---	< 6 ^{o,p}
NiHCO ₃ ⁰	13.41 ^b	13.41 ^b	12.420 ⁱ	12.42 ^m	12.4199 ⁱ	< 11.7 ^{o,p}
NiCO ₃ ·6H ₂ O (cr)	---	6.9 ^d	6.870 ^j	11.2 ^m	6.87 ^j	7.51 ^{o,q}
NiSO ₄ ⁰	2.32 ^c	2.32 ^c	2.300 ⁱ	2.3 ^m	2.30 ⁱ	2.31 ^r
Ni(SO ₄) ₂ ²⁻	---	---	0.820 ^k	0.82 ^k	0.820 ^k	3.2 ^r
NiCl ⁺	0.4 ^c	0.4 ^c	0.408 ⁱ	-0.43 ^m	0.408 ⁱ	0.4 ^r
NiCl ₂ ⁰	---	---	-1.890 ^k	-1.89 ^k	-1.89 ^k	0.96 ^r
NiHS ⁺	---	5.49 ^e	---	5.49 ^e	---	5.8 ^r
Ni(HS) ₂ ⁰	---	11.5 ^f	---	---	---	11.6 ^r
Ni(HS) ₃ ⁻	---	18.7 ^g	---	---	---	18.7 ^g
NiS (hexagonal)	---	9.68 ^g	---	---	---	9.68 ^g
NiS (millerite)	---	9.23 ^h	---	---	---	---
NiS (α)	---	---	5.600 ⁱ	5.52 ⁱ	5.600 ⁱ	---
NiS (β)	---	---	11.100 ⁱ	11.02 ⁱ	11.100 ⁱ	---
NiS (γ)	---	---	12.800 ⁱ	12.72 ⁱ	12.800 ⁱ	---

Sources:

- | | |
|--|---|
| ^a Baes and Mesmer (1976) | ^j NIST (1997) |
| ^b Mattigod and Sposito (1979) | ^k International Union of Pure and Applied Chemistry (1998) |
| ^c Martell and Smith (1976) | ^l Dyrssen and Kremling (1990) |
| ^d HydroGeoLogic Inc., 1999 | ^m NIST (2003) |
| ^e Luther et al. (1996) | ⁿ Plyasunova et al. (1998) |
| ^f Al-Farawati and van den Berg (1999) | ^o Hummel and Curti (2003) |
| ^g Wilkin and Rogers (2010) | ^p Baeyens et al. (2003) |
| ^h Smith and Martell (1977) | ^q Wallner et al. (2002) |
| ⁱ NIST (1996) | ^r Hummel et al. (2002) |

Hummel and Curti (2003) expressed serious concern over the quality of available Ni thermodynamic data, specifically the formation constants and solubility products related to the Ni-OH and Ni-CO₃ systems.

In their review Hummel and Curti indicate that early compilations (Baes and Mesmer, 1976; Smith and Martell, 1976; Smith and Martell, 1989) of Ni-OH thermodynamic data present a generally consistent set of stability constants. A more recent review by Plyasunova et al. (1998), indicates that the Ni-OH system is poorly understood in comparison to that of other trace metals. They also indicate that 1) polynuclear species (Ni₂OH³⁺ and Ni₄(OH)₄⁴⁺) have been shown to form, 2) many of the early experiments used to determine stability constants for mononuclear Ni-OH species were at sufficiently high Ni to be impacted

by the polynuclear species, and 3) as a result, much of the early data needs to be refit considering *both* the mononuclear and polynuclear species. They refit the data and produced the set of stability constants shown in Table E-8.

Plyasunova et al. (1998) also indicate that Ni(OH)₂(cr) is thermodynamically more stable than NiO(cr) at ambient conditions and recommend solubility product values for the two solids based upon their review of available experimental data. When determining the mean solubility product for Ni(OH)₂(cr), the authors only used solubility products smaller than that of NiO(cr) to remain consistent with their above-mentioned statement regarding relative stabilities. Additional weight was placed on experiments with phase preparations favoring thermodynamically stable or ‘aged’ Ni(OH)₂(cr). Recently Gamsjäger et al. (2002) determined the solubility product of “well crystallized” β-Ni(OH)₂ (theophrastite) (Hummel and Curti, 2003). While Hummel and Curti seems to favor the results of this experimental solubility product determination, they indicate that its use with the stability constants and NiO(cr) solubility product of Plyasunova et al. (1998) produces an inconsistency: The increased solubility of Ni(OH)₂ solid determined by Gamsjäger et al. (2002) would imply that it is less stable than NiO(cr). Hummel and Curti (2003) conclude that more work needs to be done to produce a consistent set of thermodynamic data for the Ni-OH system.

Through a detailed review, Hummel and Curti (2003) highlight the uncertainties and deficiencies of the experiments and estimation procedures used to determine the Ni-CO₃ stability constants. They determined that what are referenced in Smith and Martell (1989) as measured stability constants for NiCO₃ and NiHCO₃⁺ are actually estimated values determined by Zhorov et al. (1976) from linear correlations of electronegativity versus carbonate complexation pK. However, the CO₃²⁻ correlation is defined by only three points (CuCO₃, CaCO₃, and MgCO₃) and the HCO₃⁻ correlation is defined by a mere two points (CaHCO₃⁺ and Mg HCO₃⁺)! Zhorov et al. (1976) corrected the estimates from an ionic strength of zero to seawater ionic strength using the Davies equation. This in itself introduces additional uncertainty since seawater ionic strength is generally beyond the valid range of the Davies equation. These stability constants were incorporated into the compilation of Smith and Martell (1989) as well as the other associated NIST databases and apparently into MINTEQ, Visual MINTEQ, and MINTEQA2 after correction back to zero ionic strength.

Hummel and Curti (2003) also express concerns over the method used by Mattigod and Sposito (1979) to estimate the carbonate and bicarbonate stability constants. These constants are the ones used in the WHAM7 and TICKET-UWM default database. Based upon their review of the estimation procedures of Mattigod and Sposito (1977) and Mattigod and Sposito (1979) and their attempts to recreate them, Hummel and Curti (2003) conclude that the generated values do not possess a high degree of certainty. They dismiss the initial analysis (Mattigod and Sposito, 1977) stating that the Ni-CO₃ stability constants “were estimated by calibrating the respective estimation formula to a single experimental data point.” Regarding the second study, Hummel and Curti (2003) were unable to recreate the estimated values and did not feel they were set on a firmer empirical basis as claimed. At the conclusion of their appraisal of Ni-CO₃ stability constant data, Hummel and Curti (2003) state:

“At the end of this adventure in the labyrinth of thermodynamic data collections we are left with the sobering fact that almost all nickel carbonate complexation constants published in literature are derived by dubious estimation procedures, and the only one

actually measured [33] is useless. This results in variations of more than four orders of magnitude. This is no longer a surprise, as a close inspection of the individual estimation procedures revealed that the estimated values are based on shaky grounds, to say the least.”

Fortunately, Hummel and Curti (2003) and Baeyens et al., (2003) have assembled a set of Ni-CO₃ stability constants that places an upper bound on the extent of Ni complexation by CO₃²⁻ and HCO₃⁻. This information, coupled with thermodynamic compilations by Plyasunova et al. (1998) and Hummel (2002) provide a relatively complete means of modeling the inorganic speciation of Ni in surface water and sediment. The inorganic database used by TICKET-UWM was modified to reflect this new compilation of thermodynamic data (Table E-8). It is worthwhile to note the following about the revisions in the thermodynamic database:

1. Based on the constants in the revised database, there will be a greater propensity for Ni complexation by hydroxide than with the default TICKET-UWM database.
2. The solubility of Ni(OH)₂ (cr) is slightly reduced in the revised database
3. The driving force for Ni complexation by CO₃²⁻ and HCO₃⁻ is reduced significantly in the revised database; and
4. The potential for Ni complexation by sulfate, chloride, and sulfide is either approximately equal or greater in the revised database

The revised database does not necessarily represent a final, definitive set of thermodynamic data (see, for example, comments on Ni hydroxide in Hummel and Curti (2003) and comments on Ni-HS complexes in Wilkin and Rogers (2011)). However, the database now reflects recent efforts to rectify shortcomings in previously-published Ni-CO₃ stability constants. It presents a consistent set of additional Ni inorganic complex stability constants that, if anything, tend to overestimate Ni complexation by OH⁻, SO₄²⁻, and HS⁻. Overestimation of Ni complexation by OH⁻, SO₄²⁻, and HS⁻ will tend to produce results that are more conservative with respect to Ni removal from the water and sequestration in sediment.

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Table E-5. Summary of Water Column Runs for Nickel (WHAM7 with Revised Inorganic Database)

Removal Approach and Output Quantity	pH = 6.09			pH = 7.07		pH = 8.00		
	2.4 µg/L	120 µg/L	1,000 µg/L	68 µg/L	1,000 µg/L	2.4 µg/L	68 µg/L	1,000 µg/L
1: $C_D(t)/C_T(0)$								
Time for 70% removal, days	9.17	14.0	24.2	12.7	28.5	8.77	15.1	7.26
Log K_D range ^a	4.03 - 4.04	3.80 - 3.89	3.53 - 3.68	3.83 - 3.94	3.45 - 3.63	4.04 - 4.06	3.73 - 3.88	3.48 - 5.14
Fraction particulate range ^a	0.138 - 0.142	0.0859 - 0.105	0.0489 - 0.0675	0.0920 - 0.115	0.0406 - 0.0600	0.142 - 0.147	0.0750 - 0.103	0.0430 - 0.676
2: $C_T(t)/C_T(0)$								
Time for 70% removal, days	10.5	15.3	25.6	14.1	29.9	10.1	16.4	8.64
Log K_D range ^a	4.03 - 4.04	3.80 - 3.90	3.53 - 3.69	3.83 - 3.95	3.45 - 3.64	4.04 - 4.06	3.73 - 3.90	3.48 - 5.14
Fraction particulate range ^a	0.138 - 0.142	0.0859 - 0.107	0.0489 - 0.0687	0.0920 - 0.118	0.0406 - 0.0611	0.142 - 0.148	0.0750 - 0.106	0.0430 - 0.676
3: $C_D(t)/C_D(0)$								
Time for 70% removal, days	10.5	15.0	25.2	13.8	29.4	10.1	16.0	39.2
Log K_D range ^a	4.03 - 4.04	3.80 - 3.90	3.53 - 3.69	3.83 - 3.95	3.45 - 3.63	4.04 - 4.06	3.73 - 3.89	3.48 - 5.14
Fraction particulate range ^a	0.138 - 0.142	0.0859 - 0.107	0.0489 - 0.0684	0.0920 - 0.117	0.0406 - 0.0608	0.142 - 0.148	0.0750 - 0.105	0.0430 - 0.676

^a These ranges were calculated using data prior to the time at which 70% removal was achieved

Table E-6. Summary of Water Column Runs for Nickel (WHAM7 with Revised Inorganic Database and Including Hydrous Ferric Oxide (HFO) and Hydrous Manganese Oxides (HMO) as Sorbents)

Removal Approach and Output Quantity	pH = 6.09			pH = 7.07		pH = 8.00		
	2.4 µg/L	120 µg/L	1,000 µg/L	68 µg/L	1,000 µg/L	2.4 µg/L	68 µg/L	1,000 µg/L
1: $C_D(t)/C_T(0)$								
Time for 70% removal, days	9.07	13.7	23.8	11.1	25.8	6.06	9.73	5.76
Log K_D range ^a	4.03 - 4.05	3.80 - 3.90	3.54 - 3.69	3.89 - 4.00	3.49 - 3.67	4.20 - 4.22	3.93 - 4.06	3.67 - 5.14
Fraction particulate range ^a	0.140 - 0.143	0.0873 - 0.106	0.0498 - 0.0687	0.104 - 0.130	0.0443 - 0.0661	0.194 - 0.199	0.113 - 0.148	0.0658 - 0.676
2: $C_T(t)/C_T(0)$								
Time for 70% removal, days	10.4	15.1	25.1	12.4	27.2	7.44	11.1	7.09
Log K_D range ^a	4.03 - 4.05	3.80 - 3.91	3.54 - 3.70	3.89 - 4.01	3.49 - 3.68	4.20 - 4.22	3.93 - 4.08	3.67 - 5.14
Fraction particulate range ^a	0.140 - 0.144	0.0873 - 0.108	0.0498 - 0.0700	0.104 - 0.133	0.0443 - 0.0676	0.194 - 0.200	0.113 - 0.153	0.0658 - 0.676
3: $C_D(t)/C_D(0)$								
Time for 70% removal, days	10.4	14.8	24.7	12.1	26.7	7.39	10.7	24.5
Log K_D range ^a	4.03 - 4.05	3.80 - 3.91	3.54 - 3.70	3.89 - 4.01	3.49 - 3.68	4.20 - 4.22	3.93 - 4.08	3.67 - 5.14
Fraction particulate range ^a	0.140 - 0.144	0.0873 - 0.108	0.0498 - 0.0696	0.104 - 0.133	0.0443 - 0.0670	0.194 - 0.200	0.113 - 0.152	0.0658 - 0.676

^a These ranges were calculated using data prior to the time at which 70% removal was achieved

Table E-7. Summary of Water Column Runs for Nickel with Lowered Settling Velocity using (WHAM7 with Revised Inorganic Database) ^a

Removal Approach and Output Quantity	pH = 6.09	pH = 7.07	pH = 8.00
1: $C_D(t)/C_T(0)$			
Time for 70% removal, days	131	121	141
Log K_D range ^b	3.80 - 3.89	3.83 - 3.94	3.73 - 3.88
Fraction particulate range ^b	0.0859 - 0.105	0.0920 - 0.115	0.0750 - 0.103
2: $C_T(t)/C_T(0)$			
Time for 70% removal, days	143	133	153
Log K_D range ^b	3.80 - 3.90	3.83 - 3.95	3.73 - 3.90
Fraction particulate range ^b	0.0859 - 0.107	0.0920 - 0.118	0.0750 - 0.106

^a Initial total Ni concentration at acute ERVs: 120 (pH 6), 68 (pH 7) and 68 (pH 8)

^b These ranges were calculated using data prior to the time at which 70% removal was achieved

Table E-8. Summary of Nickel Sediment Runs (WHAM V) ^a

Removal Approach and Output Quantity	AVS = 0 µmol/g			Anoxic, AVS = 1 µmol/g		
	68 µg/L	100 µg/L	1,000 µg/L	68 µg/L	100 µg/L	1,000 µg/L
Time to Quasi Steady State, days	92	92	99	95	95	101
Tot. Ni Range, µg/L ^b	3.88 – 5.35	5.71 - 7.87	55.8 – 77.4	3.60 – 4.92	5.11 - 7.05	53.1 – 73.1
Diss. Ni Range, µg/L ^b	3.69 – 5.08	5.43 - 7.48	53.1 – 73.7	3.42 – 4.68	4.86 - 6.71	50.6 – 69.6
Total Settling IN, tonnes	432	635	6,220	418	605	6070
Total Resusp. OUT, tonnes	167	245	2,440	168	248	2450
Total Diffusion NET, tonnes ^c	-34.0	-49.8	-383	-18.1	-15.8	-217
Total Burial OUT, tonnes	20.5	30.2	300	20.6	30.4	301
Water column log K_D , L/kg ^b	3.54	3.54	3.53	3.54	3.54	3.53
Sediment log K_D , L/kg ^b	2.48	2.48	2.56	2.72	2.87	2.72
Time for 70% Removal, days (Approach 1)	30.1	30.2	34.8	30.0	30.0	34.3
$[0.3 \times C_T(0)] / \text{Max QSS } C_T$ ^d	3.82	3.81	3.88	4.15	4.25	4.11

^a Select simulation parameters: water column pH 7.07; sediment pH 7.56; settling velocity 2.5 m/d. For additional parameters, see Table 2.4.

^b Ranges and average are based on data from the quasi-steady state period of the simulation.

^c This number is the diffusive flux integrated over the *entire* 365-day simulation. Negative diffusive flux values are directed out of the sediment and positive diffusive flux values are directed into the sediment.

^d This quantity is the ratio of the total Ni concentration representing 70% removal ($0.3 \times C_T(0)$) to the maximum total concentration during the quasi-steady-state period (Max QSS C_T). This is meant to give an indication of where sustained water column concentrations lie relative to the 70% removal benchmark.

Table E-8. Continued ^a

Removal Approach and Output Quantity	Anoxic, AVS = 9.1 µmol/g			Oxic		
	68 µg/L	100 µg/L	1,000 µg/L	68 µg/L	100 µg/L	1,000 µg/L
Time to Quasi Steady State, days	95	95	102	93	94	100
Tot. Ni Range, µg/L ^b	3.60 – 4.92	5.11 - 7.05	47.6 – 66.8	3.38 - 4.64	4.97 - 6.77	50.6 - 69.1
Diss. Ni Range, µg/L ^b	3.42 – 4.68	4.86 - 6.71	45.3 – 63.5	3.21 - 4.41	4.72 - 6.43	48.1 - 65.6
Total Settling IN, tonnes	418	605	5810	410	603	6020
Total Resusp. OUT, tonnes	168	248	2470	169	248	2460
Total Diffusion NET, tonnes ^c	-18.1	-15.8	88.7	-8.53	-12.7	-141
Total Burial OUT, tonnes	20.6	30.4	303	20.8	30.6	303
Water column log K_D , L/kg ^b	3.54	3.54	3.53	3.55	3.55	3.54
Sediment log K_D , L/kg ^b	2.72	2.87	3.88	2.90	2.90	2.85
Time for 70% Removal, days (Approach 1)	30.0	30.0	34.1	28.6	28.7	33.2
$[0.3 \times C_T(0)] / \text{Max QSS } C_T$ ^d	4.15	4.25	4.49	4.40	4.43	4.34

^a Select simulation parameters: water column pH 7.07; sediment pH 7.56; settling velocity 2.5 m/d. For additional parameters, see Table 2.4.

^b Ranges and average are based on data from the quasi-steady state period of the simulation.

^c This number is the diffusive flux integrated over the *entire* 365-day simulation. Negative diffusive flux values are directed out of the sediment and positive diffusive flux values are directed into the sediment.

^d This quantity is the ratio of the total Ni concentration representing 70% removal ($0.3 \times C_T(0)$) to the maximum total concentration during the quasi-steady-state period (Max QSS C_T). This is meant to give an indication of where sustained water column concentrations lie relative to the 70% removal benchmark.

Table E-9. Summary of Nickel Sediment Runs Without Ca/Mg Competition for Sites on Organic Matter (WHAM V) ^a

Removal Approach and Output Quantity	AVS = 0 µmol/g			Anoxic, AVS = 1 µmol/g		
	68 µg/L	100 µg/L	1,000 µg/L	68 µg/L	100 µg/L	1,000 µg/L
Time to Quasi Steady State, days	24	24	27	24	24	27
Tot. Ni Range, µg/L ^b	0.315 - 0.354	0.463 - 0.519	4.48 - 5.00	0.315 - 0.354	0.463 - 0.519	4.48 - 5.00
Diss. Ni Range, µg/L ^b	0.148 - 0.166	0.217 - 0.243	2.02 - 2.24	0.148 - 0.166	0.217 - 0.243	2.02 - 2.24
Total Settling IN, tonnes	435	639	6370	435	639	6370
Total Resusp. OUT, tonnes	187	276	2740	187	276	2740
Total Diffusion NET, tonnes ^c	-3.61	-5.28	-41.2	-3.61	-5.28	-41.2
Total Burial OUT, tonnes	23.0	33.9	337	23.0	33.9	337
Water column log K_D , L/kg ^b	4.88	4.88	4.91	4.88	4.88	4.91
Sediment log K_D , L/kg ^b	3.54	3.54	3.58	3.54	3.54	3.58
Time for 70% Removal, days (Approach 1)	0.688	0.816	5.14	0.688	0.816	5.14
$[0.3 \times C_T(0)] / \text{Max QSS } C_T$ ^d	57.7	57.8	60.0	57.7	57.8	60.0

^a Select simulation parameters: water column pH 7.07; sediment pH 7.56; settling velocity 2.5 m/d. For additional parameters, see Table 2.4.

^b Ranges and average are based on data from the quasi-steady state period of the simulation.

^c This number is the diffusive flux integrated over the *entire* 365-day simulation. Negative diffusive flux values are directed out of the sediment and positive diffusive flux values are directed into the sediment.

^d This quantity is the ratio of the total Ni concentration representing 70% removal ($0.3 \times C_T(0)$) to the maximum total concentration during the quasi-steady-state period (Max QSS C_T). This is meant to give an indication of where sustained water column concentrations lie relative to the 70% removal benchmark.

Table E-9. Continued ^a

Removal Approach and Output Quantity	Anoxic, AVS = 9.1 µmol/g			Oxic		
	68 µg/L	100 µg/L	1,000 µg/L	68 µg/L	100 µg/L	1,000 µg/L
Time to Quasi Steady State, days	24	24	27	24	24	27
Tot. Ni Range, µg/L ^b	0.315 - 0.354	0.463 - 0.519	4.48 - 5.00	0.315 - 0.353	0.462 - 0.517	4.47 - 4.98
Diss. Ni Range, µg/L ^b	0.148 - 0.166	0.217 - 0.243	2.02 - 2.24	0.148 - 0.165	0.217 - 0.242	2.02 - 2.23
Total Settling IN, tonnes	435	639	6370	435	639	6360
Total Resusp. OUT, tonnes	187	276	2740	187	276	2740
Total Diffusion NET, tonnes ^c	-3.61	-5.28	-41.2	-3.54	-5.20	-40.3
Total Burial OUT, tonnes	23.0	33.9	337	23.0	33.9	337
Water column log K_D , L/kg ^b	4.88	4.88	4.91	4.88	4.88	4.91
Sediment log K_D , L/kg ^b	3.54	3.54	3.58	3.54	3.54	3.58
Time for 70% Removal, days (Approach 1)	0.688	0.816	5.14	0.682	0.814	5.12
$[0.3 \times C_T(0)] / \text{Max QSS } C_T$ ^d	57.7	57.8	60.0	57.8	58.0	60.2

^a Select simulation parameters: water column pH 7.07; sediment pH 7.56; settling velocity 2.5 m/d. For additional parameters, see Table 2.4.

^b Ranges and average are based on data from the quasi-steady state period of the simulation.

^c This number is the diffusive flux integrated over the *entire* 365-day simulation. Negative diffusive flux values are directed out of the sediment and positive diffusive flux values are directed into the sediment.

^d This quantity is the ratio of the total Ni concentration representing 70% removal ($0.3 \times C_T(0)$) to the maximum total concentration during the quasi-steady-state period (Max QSS C_T). This is meant to give an indication of where sustained water column concentrations lie relative to the 70% removal benchmark.

Table E-10. Summary of Nickel Sediment Runs With NiS(s,millerite) ($\log^*K_s = -9.23$) (WHAM V) ^a

Removal Approach and Output Quantity	Anoxic, AVS = 1 $\mu\text{mol/g}$			Anoxic, AVS = 9.1 $\mu\text{mol/g}$		
	68 $\mu\text{g/L}$	100 $\mu\text{g/L}$	1,000 $\mu\text{g/L}$	68 $\mu\text{g/L}$	100 $\mu\text{g/L}$	1,000 $\mu\text{g/L}$
Time to Quasi Steady State, days	98	97	100	98	97	102
Tot. Ni Range, $\mu\text{g/L}$ ^b	3.18 - 4.36	4.68 - 6.48	53.1 - 73.8	3.18 - 4.36	4.68 - 6.48	47.1 - 66.3
Diss. Ni Range, $\mu\text{g/L}$ ^b	3.02 - 4.14	4.45 - 6.16	50.6 - 70.2	3.02 - 4.14	4.45 - 6.16	44.9 - 63.1
Total Settling IN, tonnes	396	582	6070	396	582	5780
Total Resusp. OUT, tonnes	170	249	2450	170	249	2470
Total Diffusion NET, tonnes ^c	7.30	10.8	-214	7.30	10.8	117
Total Burial OUT, tonnes	20.8	30.7	301	20.8	30.7	304
Water column $\log K_D$, L/kg ^b	3.54	3.54	3.53	3.54	3.54	3.53
Sediment $\log K_D$, L/kg ^b	6.33	6.50	2.72	6.33	6.50	7.50
Time for 70% Removal, days (Approach 1)	29.4	29.5	34.3	29.4	29.5	34.0
$[0.3 \times C_T(0)]/\text{Max QSS } C_T$ ^d	4.68	4.63	4.07	4.68	4.63	4.52

^a Select simulation parameters: water column pH 7.07; sediment pH 7.56; settling velocity 2.5 m/d. For additional parameters, see Table 2.4.

^b Ranges and average are based on data from the quasi-steady state period of the simulation.

^c This number is the diffusive flux integrated over the *entire* 365-day simulation. Negative diffusive flux values are directed out of the sediment and positive diffusive flux values are directed into the sediment.

^d This quantity is the ratio of the total Ni concentration representing 70% removal ($0.3 \times C_T(0)$) to the maximum total concentration during the quasi-steady-state period (Max QSS C_T). This is meant to give an indication of where sustained water column concentrations lie relative to the 70% removal benchmark.

Table E-11. Summary of Nickel Sediment Runs With NiS(s,millerite) ($\log^*K_s = -9.23$) and Without Ca/Mg Competition for Sites on Organic Matter (WHAM V) ^a

Removal Approach and Output Quantity	Anoxic, AVS = 1 $\mu\text{mol/g}$			Anoxic, AVS = 9.1 $\mu\text{mol/g}$		
	68 $\mu\text{g/L}$	100 $\mu\text{g/L}$	1,000 $\mu\text{g/L}$	68 $\mu\text{g/L}$	100 $\mu\text{g/L}$	1,000 $\mu\text{g/L}$
Time to Quasi Steady State, days	25	24	27	25	24	27
Tot. Ni Range, $\mu\text{g/L}$ ^b	0.309 - 0.344	0.454 - 0.508	4.45 - 4.97	0.309 - 0.344	0.454 - 0.508	4.40 - 4.91
Diss. Ni Range, $\mu\text{g/L}$ ^b	0.145 - 0.162	0.213 - 0.238	2.01 - 2.23	0.145 - 0.162	0.213 - 0.238	1.99 - 2.21
Total Settling IN, tonnes	431	634	6350	431	634	6310
Total Resusp. OUT, tonnes	188	276	2740	188	276	2740
Total Diffusion NET, tonnes ^c	0.224	0.372	-25.7	0.224	0.372	11.3
Total Burial OUT, tonnes	23.1	33.9	337	23.1	33.9	337
Water column $\log K_D$, L/kg ^b	4.88	4.88	4.91	4.88	4.88	4.91
Sediment $\log K_D$, L/kg ^b	5.17	5.33	3.73	5.17	5.33	6.33
Time for 70% Removal, days (Approach 1)	0.684	0.816	5.14	0.684	0.816	5.14
$[0.3 \times C_T(0)]/\text{Max QSS } C_T$ ^d	59.3	59.0	60.4	59.3	59.0	61.1

^a Select simulation parameters: water column pH 7.07; sediment pH 7.56; settling velocity 2.5 m/d. For additional parameters, see Table 2.4.

^b Ranges and average are based on data from the quasi-steady state period of the simulation.

^c This number is the diffusive flux integrated over the *entire* 365-day simulation. Negative diffusive flux values are directed out of the sediment and positive diffusive flux values are directed into the sediment.

^d This quantity is the ratio of the total Ni concentration representing 70% removal ($0.3 \times C_T(0)$) to the maximum total concentration during the quasi-steady-state period (Max QSS C_T). This is meant to give an indication of where sustained water column concentrations lie relative to the 70% removal benchmark.

Table E-12. Summary of Nickel Sediment Runs (WHAM7 with Revised Inorganic Database) ^a

Removal Approach and Output Quantity	AVS = 0 µmol/g			Anoxic, AVS = 1 µmol/g		
	68 µg/L	100 µg/L	1,000 µg/L	68 µg/L	100 µg/L	1,000 µg/L
Time to Quasi Steady State, days	61	64	97	62	65	97
Tot. Ni Range, µg/L ^b	1.16 - 1.37	1.73 - 2.04	23.2 - 28.7	1.07 - 1.26	1.60 - 1.87	22.0 - 27.3
Diss. Ni Range, µg/L ^b	0.988 - 1.16	1.47 - 1.74	20.5 - 25.6	0.912 - 1.07	1.36 - 1.59	19.4 - 24.3
Total Settling IN, tonnes	434	637	6320	419	615	6200
Total Resusp. OUT, tonnes	180	265	2550	181	266	2560
Total Diffusion NET, tonnes ^c	-12.4	-18.4	-247	2.85	4.46	-117
Total Burial OUT, tonnes	22.2	32.5	314	22.3	32.7	315
Water column log K_D , L/kg ^b	4.07	4.07	3.93	4.07	4.07	3.94
Sediment log K_D , L/kg ^b	2.93	2.92	2.74	6.72	6.89	2.96
Time for 70% Removal, days (Approach 1)	13.2	14.7	29.1	13.2	14.4	29.0
$[0.3 \times C_T(0)] / \text{Max QSS } C_T$ ^d	14.9	14.4	10.4	16.2	16.0	11.0

^a Select simulation parameters: water column pH 7.07; sediment pH 7.56; settling velocity 2.5 m/d. For additional parameters, see Table 2.4.

^b Ranges and average are based on data from the quasi-steady state period of the simulation.

^c This number is the diffusive flux integrated over the *entire* 365-day simulation. Negative diffusive flux values are directed out of the sediment and positive diffusive flux values are directed into the sediment.

^d This quantity is the ratio of the total Ni concentration representing 70% removal ($0.3 \times C_T(0)$) to the maximum total concentration during the quasi-steady-state period (Max QSS C_T). This is meant to give an indication of where sustained water column concentrations lie relative to the 70% removal benchmark.

Table E-12. Continued ^a

Removal Approach and Output Quantity	Anoxic, AVS = 9.1 µmol/g			Oxic		
	68 µg/L	100 µg/L	1,000 µg/L	68 µg/L	100 µg/L	1,000 µg/L
Time to Quasi Steady State, days	62	65	98	62	64	98
Tot. Ni Range, µg/L ^b	1.07 - 1.26	1.60 - 1.87	20.2 - 24.9	1.10 - 1.29	1.64 - 1.94	21.2 - 26.1
Diss. Ni Range, µg/L ^b	0.912 - 1.07	1.36 - 1.59	17.8 - 22.0	0.936 - 1.10	1.39 - 1.65	18.7 - 23.1
Total Settling IN, tonnes	419	615	6020	424	622	6120
Total Resusp. OUT, tonnes	181	266	2570	181	265	2560
Total Diffusion NET, tonnes ^c	2.85	4.46	79.2	-2.17	-3.06	-32.4
Total Burial OUT, tonnes	22.3	32.7	316	22.2	32.6	315
Water column log K_D , L/kg ^b	4.07	4.07	3.95	4.07	4.07	3.94
Sediment log K_D , L/kg ^b	6.72	6.89	7.89	3.41	3.40	3.21
Time for 70% Removal, days (Approach 1)	13.2	14.4	28.9	13.2	14.4	29.0
$[0.3 \times C_T(0)] / \text{Max QSS } C_T$ ^d	16.2	16.0	12.1	15.8	15.5	11.5

^a Select simulation parameters: water column pH 7.07; sediment pH 7.56; settling velocity 2.5 m/d. For additional parameters, see Table 2.4.

^b Ranges and average are based on data from the quasi-steady state period of the simulation.

^c This number is the diffusive flux integrated over the *entire* 365-day simulation. Negative diffusive flux values are directed out of the sediment and positive diffusive flux values are directed into the sediment.

^d This quantity is the ratio of the total Ni concentration representing 70% removal ($0.3 \times C_T(0)$) to the maximum total concentration during the quasi-steady-state period (Max QSS C_T). This is meant to give an indication of where sustained water column concentrations lie relative to the 70% removal benchmark.

APPENDIX F – COBALT TABLES

Table F-1. Summary of Water Column Runs for Cobalt with the Speciation Model Method

Removal Approach and Output Quantity	pH = 6.09			pH = 7.07			pH = 8.00		
	4.9 µg/L	90.1 µg/L	1,000 µg/L	4.9 µg/L	90.1 µg/L	1,000 µg/L	4.9 µg/L	90.1 µg/L	1,000 µg/L
1: $C_D(t)/C_T(0)$									
Time for 70% removal, days	23.0	23.3	26.7	23.6	24.2	29.8	47.5	47.8	52.9
Log K_D range ^b	3.64	3.63 – 3.64	3.53 – 3.60	3.63	3.61 – 3.62	3.47 – 3.57	3.33	3.33	3.26 – 3.31
Fraction particulate range ^b	0.0613 – 0.0614	0.0598 – 0.0609	0.0486 – 0.0564	0.0596 – 0.0598	0.0574 – 0.0590	0.0424 – 0.0523	0.0313 – 0.0314	0.0308 – 0.0312	0.0264 – 0.0296
2: $C_T(t)/C_T(0)$									
Time for 70% removal, days	24.3	24.6	28.1	25.0	25.5	31.2	49.0	49.2	54.4
Log K_D range ^b	3.64	3.63 – 3.64	3.53 – 3.60	3.63	3.61 – 3.62	3.47 – 3.57	3.33	3.33	3.26 – 3.31
Fraction particulate range ^b	0.0613 – 0.0614	0.0598 – 0.0609	0.0486 – 0.0567	0.0596 – 0.0598	0.0574 – 0.0590	0.0424 – 0.0526	0.0313 – 0.0314	0.0308 – 0.0312	0.0264 – 0.0296
3: $C_D(t)/C_D(0)$									
Time for 70% removal, days	24.3	24.6	27.9	25.0	25.5	30.9	49.0	49.2	54.3
Log K_D range ^b	3.64 - 3.64	3.63 - 3.64	3.53 - 3.60	3.63 - 3.63	3.61 - 3.62	3.47 - 3.57	3.33 - 3.33	3.33 - 3.33	3.26 - 3.31
Fraction particulate range ^b	0.0613 - 0.0614	0.0598 - 0.0609	0.0486 - 0.0566	0.0596 - 0.0598	0.0574 - 0.0590	0.0424 - 0.0526	0.0313 - 0.0314	0.0308 - 0.0312	0.0264 - 0.0296

^a 70% removal occurs instantly via initial solid-solution equilibrium partitioning. Instead of log K_D and fraction particulate value ranges, the values at $t = 0$ are indicated.

^b These ranges were calculated using data prior to the time at which 70% removal was achieved

Table F-2. Summary of Water Column Runs for Cobalt with the Speciation Model Method Without Ca/Mg Competition for Sites on Organic Matter

Removal Approach and Output Quantity	pH = 6.09			pH = 7.07			pH = 8.00		
	4.9 µg/L	90.1 µg/L	1,000 µg/L	4.9 µg/L	90.1 µg/L	1,000 µg/L	4.9 µg/L	90.1 µg/L	1,000 µg/L
1: $C_D(t)/C_T(0)$									
Time for 70% removal, days	6.03	3.30	7.96	--- ^a	0.57	4.89	---	0.238	4.71
Log K_D range ^b	4.21 - 4.24	4.46 - 4.49	3.93 - 4.21	5.19	4.96 - 5.00	4.10 - 4.43	5.59	5.07 - 5.11	4.11 - 4.45
Fraction particulate range ^b	0.194 - 0.207	0.302 - 0.315	0.114 - 0.195	0.701	0.578 - 0.602	0.158 - 0.286	0.854	0.639 - 0.657	0.162 - 0.298
2: $C_T(t)/C_T(0)$									
Time for 70% removal, days	7.41	4.82	9.27	2.11	2.38	6.19	1.74	2.07	6.00
Log K_D range ^b	4.20 - 4.24	4.42 - 4.49	3.93 - 4.26	5.19 - 5.21	4.96 - 5.10	4.10 - 4.55	5.59 - 5.64	5.07 - 5.36	4.11 - 4.60
Fraction particulate range ^b	0.193 - 0.207	0.282 - 0.315	0.114 - 0.216	0.701 - 0.711	0.578 - 0.653	0.158 - 0.347	0.854 - 0.866	0.639 - 0.776	0.162 - 0.375
3: $C_D(t)/C_D(0)$									
Time for 70% removal, days	7.53	5.00	8.63	2.05	2.04	5.43	1.62	1.49	5.24
Log K_D range ^b	4.20 - 4.24	4.41 - 4.49	3.93 - 4.24	5.19 - 5.21	4.96 - 5.09	4.10 - 4.49	5.59 - 5.64	5.07 - 5.28	4.11 - 4.51
Fraction particulate range ^b	0.193 - 0.207	0.280 - 0.315	0.114 - 0.206	0.701 - 0.711	0.578 - 0.646	0.158 - 0.315	0.854 - 0.866	0.639 - 0.742	0.162 - 0.324

^a 70% removal occurs instantly via initial solid-solution equilibrium partitioning. Instead of log K_D and fraction particulate value ranges, the values at $t = 0$ are indicated.

^b These ranges were calculated using data prior to the time at which 70% removal was achieved

Table F-3. Summary of Water Column Runs for Cobalt with Lowered Settling Velocity ^a

Removal Approach and Output Quantity	Linear Partitioning	pH = 6.09	pH = 7.07	pH = 8.00
1: C_D(t)/C_T(0)				
Time for 70% removal, days	24.9	204	211	360
Log K _D range ^b	4.59	3.63 - 3.64	3.61 - 3.62	3.33
Fraction particulate range ^b	0.369	0.0598 - 0.0609	0.0574 - 0.0590	0.0308 - 0.0312
2: C_T(t)/C_T(0)				
Time for 70% removal, days	40.4	216	222	370
Log K _D range ^b	4.59	3.63 - 3.64	3.61 - 3.62	3.33
Fraction particulate range ^b	0.369	0.0598 - 0.0609	0.0574 - 0.0590	0.0308 - 0.0312

^a Initial total Ni concentration at acute ERVs: 120 (pH 6), 68 (pH 7) and 68 (pH 8)

^b These ranges were calculated using data prior to the time at which 70% removal was achieved

Table F-4. Summary of Cobalt Sediment Runs ^a

Removal Approach and Output Quantity	AVS = 0		Anoxic, AVS = 1		Anoxic, AVS = 9.1		Oxic	
	90.1 µg/L	1000 µg/L	90.1 µg/L	1000 µg/L	90.1 µg/L	1000 µg/L	90.1 µg/L	1000 µg/L
Time to Quasi Steady State, days	90	98	92	97	92	100	89	96
Tot. Co Range, µg/L ^b	4.06 – 5.38	46.1 – 61.8	3.65 – 4.77	44.4 – 60.5	3.65 – 4.86	41.1 – 55.4	3.86 – 5.12	43.9 – 59.5
Diss. Co Range, µg/L ^b	3.83 – 5.08	43.5 – 58.3	3.44 – 4.49	41.9 – 57.2	3.44 – 4.58	38.8 – 52.3	3.64 – 4.83	41.1 – 56.1
Total Settling IN, tonnes	556	6140	531	6030	531	5850	546	6050
Total Resusp. OUT, tonnes	226	2480	228	2490	228	2500	227	2490
Total Diffusion NET, tonnes ^c	-20.4	-223	8.23	-102	8.23	105	-8.39	-122
Total Burial OUT, tonnes	27.8	305	28.0	306	28.0	307	27.9	306
Water column log K_D , L/kg ^b	3.61	3.60	3.61	3.60	3.61	3.60	3.61	3.60
Sediment log K_D , L/kg ^b	2.77	2.75	4.98	2.93	4.98	6.03	3.00	2.91
Time for 70% Removal, days (Approach 1)	25.8	31.5	25.5	31.3	25.5	31.1	25.0	30.7
$[0.3 \times C_T(0)] / \text{Max QSS } C_T$ ^d	5.02	4.86	5.57	4.95	5.57	5.42	5.31	5.04

^a Select simulation parameters: water column pH 7.07; sediment pH 7.56; settling velocity 2.5 m/d. For additional parameters, see Table 2.4.

^b Ranges and average are based on data from the quasi-steady state period of the simulation.

^c This number is the diffusive flux integrated over the *entire* 365-day simulation. Negative diffusive flux values are directed out of the sediment and positive diffusive flux values are directed into the sediment.

^d This quantity is the ratio of the total Co concentration representing 70% removal ($0.3 \times C_T(0)$) to the maximum total concentration during the quasi-steady-state period (Max QSS C_T). This is meant to give an indication of where sustained water column concentrations lie relative to the 70% removal benchmark.

Table F-5. Summary of Cobalt Sediment Runs Without Ca/Mg Competition for Sites on Organic Matter ^a

Removal Approach and Output Quantity	AVS = 0		Anoxic, AVS = 1		Anoxic, AVS = 9.1		Oxic	
	90.1 µg/L	1000 µg/L	90.1 µg/L	1000 µg/L	90.1 µg/L	1000 µg/L	90.1 µg/L	1000 µg/L
Time to Quasi Steady State, days	22	27	22	27	22	27	22	26
Tot. Co Range, µg/L ^b	0.307 – 0.341	3.46 – 3.85	0.307 – 0.341	3.45 – 3.83	0.307 – 0.341	3.43 – 3.81	0.307 – 0.341	3.46 – 3.86
Diss. Co Range, µg/L ^b	0.0882 – 0.0979	1.03 – 1.14	0.0882 – 0.0979	1.02 – 1.14	0.0882 – 0.0979	1.02 – 1.13	0.0882 – 0.0979	1.02 – 1.14
Total Settling IN, tonnes	574	6350	574	6340	574	6320	574	6350
Total Resusp. OUT, tonnes	249	2740	249	2740	249	2740	249	2740
Total Diffusion NET, tonnes ^c	-1.86	-17.0	-1.86	-7.65	-1.86	7.89	-1.85	-16.7
Total Burial OUT, tonnes	30.6	337	30.6	337	30.6	337	30.6	337
Water column log K_D , L/kg ^b	5.22	5.20	5.22	5.20	5.22	5.20	5.22	5.20
Sediment log K_D , L/kg ^b	3.93	3.86	3.93	4.05	3.93	4.95	3.93	3.87
Time for 70% Removal, days (Approach 1)	0.730	5.03	0.730	5.03	0.730	5.03	0.729	5.01
$[0.3 \times C_T(0)] / \text{Max QSS } C_T$ ^d	79.2	78.0	79.2	78.3	79.2	78.7	79.3	77.7

^a Select simulation parameters: water column pH 7.07; sediment pH 7.56; settling velocity 2.5 m/d. For additional parameters, see Table 2.4.

^b Ranges and average are based on data from the quasi-steady state period of the simulation.

^c This number is the diffusive flux integrated over the *entire* 365-day simulation. Negative diffusive flux values are directed out of the sediment and positive diffusive flux values are directed into the sediment.

^d This quantity is the ratio of the total Co concentration representing 70% removal ($0.3 \times C_T(0)$) to the maximum total concentration during the quasi-steady-state period (Max QSS C_T). This is meant to give an indication of where sustained water column concentrations lie relative to the 70% removal benchmark.

APPENDIX G – CADMIUM TABLES

Table G-1. Summary of Water Column Runs for Runs for Cadmium with the Speciation Model Method

Removal Approach and Output Quantity	pH = 6.09			pH = 7.07			pH = 8.00		
	0.21 µg/L	18 µg/L	1,000 µg/L	0.21 µg/L	18 µg/L	1,000 µg/L	0.21 µg/L	18 µg/L	1,000 µg/L
1: $C_D(t)/C_T(0)$									
Time for 70% removal, days	23.7	23.7	25.5	25.3	25.3	28.4	33.1	33.1	--- ^{a,c}
Log K_D range ^b	3.62 - 3.63	3.62	3.57 - 3.61	3.60	3.60	3.52 - 3.57	3.48	3.48	5.92
Fraction particulate range ^b	0.0594 – 0.0595	0.0593 – 0.0594	0.0530 – 0.0573	0.0560 – 0.0561	0.0558 – 0.0560	0.0468 – 0.0527	0.0436 – 0.0437	0.0436 – 0.0437	0.925
2: $C_T(t)/C_T(0)$									
Time for 70% removal, days	25.1	25.1	26.8	26.6	26.7	29.7	34.5	34.5	1.77 ^c
Log K_D range ^b	3.62 - 3.63	3.62	3.57 - 3.61	3.60	3.60	3.52 - 3.57	3.48	3.48	5.33 - 5.92
Fraction particulate range ^b	0.0594 – 0.0595	0.0593 – 0.0594	0.0530 – 0.0574	0.0560 – 0.0561	0.0558 – 0.0560	0.0468 – 0.0528	0.0436 – 0.0437	0.0436 – 0.0437	0.761 – 0.925
3: $C_D(t)/C_D(0)$									
Time for 70% removal, days	25.1	25.1	26.7	26.6	26.7	29.6	34.5	34.5	>730
Log K_D range ^b	3.62 - 3.63	3.62	3.57 - 3.61	3.60	3.60	3.52 - 3.57	3.48	3.48	3.25 - 5.92
Fraction particulate range ^b	0.0594 - 0.0595	0.0593 - 0.0594	0.0530 - 0.0574	0.0560 - 0.0561	0.0558 - 0.0560	0.0468 - 0.0528	0.0436 - 0.0437	0.0436 - 0.0437	0.0263 - 0.925

^a 70% removal occurs instantly via initial solid-solution equilibrium partitioning. Instead of log K_D and fraction particulate value ranges, the values at $t = 0$ are indicated.

^b These ranges were calculated using data prior to the time at which 70% removal was achieved

^c $CdCO_3$ (s) precipitates

Table G-2. Summary of Water Column Runs for Cadmium with the Speciation Model Method Without Ca/Mg Competition for Sites on Organic Matter

Removal Approach and Output Quantity	pH = 6.09			pH = 7.07			pH = 8.00		
	0.21 µg/L	18 µg/L	1,000 µg/L	0.21 µg/L	18 µg/L	1,000 µg/L	0.21 µg/L	18 µg/L	1,000 µg/L
1: $C_D(t)/C_T(0)$									
Time for 70% removal, days	14.4	11.5	5.57	1.06	1.01	2.86	--- ^a	--- ^a	--- ^{a,c}
Log K_D range ^b	3.84	3.90 - 4.02	4.12 - 4.33	4.87 - 4.87	4.88 - 4.89	4.34 - 4.60	5.38	5.30	5.60
Fraction particulate range ^b	0.0938 – 0.0941	0.106 – 0.135	0.164 – 0.242	0.526 – 0.527	0.534 – 0.538	0.247 – 0.376	0.782	0.749	0.856
2: $C_T(t)/C_T(0)$									
Time for 70% removal, days	15.7	12.8	6.92	2.82	2.78	4.24	1.91	1.93	2.13 ^c
Log K_D range ^b	3.84	3.89 - 4.02	4.12 - 4.38	4.87 - 4.87	4.88 - 4.89	4.34 - 4.76	5.38 - 5.38	5.30 - 5.35	4.89 - 5.60
Fraction particulate range ^b	0.0938 – 0.0941	0.105 – 0.135	0.164 – 0.263	0.526 – 0.527	0.530 – 0.538	0.247 – 0.466	0.781 – 0.782	0.749 – 0.771	0.537 – 0.856
3: $C_D(t)/C_D(0)$									
Time for 70% removal, days	15.7	13.2	6.37	2.82	2.82	3.51	1.91	1.79	3.92
Log K_D range ^b	3.84 - 3.84	3.89 - 4.02	4.12 - 4.36	4.87 - 4.87	4.88 - 4.89	4.34 - 4.68	5.38 - 5.38	5.30 - 5.35	4.89 - 5.60
Fraction particulate range ^b	0.0938 - 0.0941	0.104 - 0.135	0.164 - 0.254	0.526 - 0.527	0.530 - 0.538	0.247 - 0.420	0.781 - 0.782	0.749 - 0.769	0.537 - 0.856

^a 70% removal occurs instantly via initial solid-solution equilibrium partitioning. Instead of log K_D and fraction particulate value ranges, the values at $t = 0$ are indicated.

^b These ranges were calculated using data prior to the time at which 70% removal was achieved

^c CdCO_3 (s) precipitates

Table G-3. Summary of Water Column Runs for Cadmium with Lowered Settling Velocity
^a

Removal Approach and Output Quantity	Linear Partitioning	pH = 6.09	pH = 7.07	pH = 8.00
1: $C_D(t)/C_T(0)$				
Time for 70% removal, days	2.31	207	219	272
Log K_D range ^b	5.11	3.62 - 3.62	3.60 - 3.60	3.48 - 3.48
Fraction particulate range ^b	0.661	0.0593 - 0.0594	0.0558 - 0.0560	0.0436 - 0.0437
2: $C_T(t)/C_T(0)$				
Time for 70% removal, days	22.7	218	230	282
Log K_D range ^b	5.11	3.62 - 3.62	3.60 - 3.60	3.48 - 3.48
Fraction particulate range ^b	0.661	0.0593 - 0.0595	0.0558 - 0.0560	0.0436 - 0.0437

^a Initial total Cd at 18 µg/L

^b 70% removal occurs instantly via initial solid-solution equilibrium partitioning. Instead of log K_D and fraction particulate value ranges, the values at t = 0 are indicated.

^c These ranges were calculated using data prior to the time at which 70% removal was achieved

Table G-4. Summary of Cadmium Sediment Runs ^a

Removal Approach and Output Quantity	AVS = 0 µmol/g			Anoxic, AVS = 1 µmol/g		
	18 µg/L	100 µg/L	1,000 µg/L	18 µg/L	100 µg/L	1,000 µg/L
Time to Quasi Steady State, days	88	89	93	93	93	95
Tot. Cd Range, µg/L ^b	0.862 – 1.16	4.79 - 6.40	48.1 – 64.5	0.742 - 0.986	4.12 - 5.50	44.0 – 59.3
Diss. Cd Range, µg/L ^b	0.814 – 1.09	4.52 - 6.04	45.5 – 60.9	0.700 - 0.931	3.89 - 5.20	41.5 – 56.0
Total Settling IN, tonnes	113	626	6210	106	588	5990
Total Resusp. OUT, tonnes	45.0	250	2480	45.5	252	2500
Total Diffusion NET, tonnes ^c	-6.03	-33.3	-301	1.71	9.57	-50.2
Total Burial OUT, tonnes	5.53	30.7	305	5.59	31.0	307
Water column log K_D , L/kg ^b	3.60	3.60	3.59	3.60	3.60	3.59
Sediment log K_D , L/kg ^b	2.61	2.62	2.63	10.8	11.5	3.05
Time for 70% Removal, days (Approach 1)	26.1	26.4	29.0	25.9	26.1	28.9
$[0.3 \times C_T(0)] / \text{Max QSS } C_T$ ^d	4.66	4.69	4.65	5.48	5.45	5.06

^a Select simulation parameters: water column pH 7.07; sediment pH 7.56; settling velocity 2.5 m/d. For additional parameters, see Table 2.4.

^b Ranges and average are based on data from the quasi-steady state period of the simulation.

^c This number is the diffusive flux integrated over the *entire* 365-day simulation. Negative diffusive flux values are directed out of the sediment and positive diffusive flux values are directed into the sediment.

^d This quantity is the ratio of the total Cd concentration representing 70% removal ($0.3 \times C_T(0)$) to the maximum total concentration during the quasi-steady-state period (Max QSS C_T). This is meant to give an indication of where sustained water column concentrations lie relative to the 70% removal benchmark.

Table G-4. Continued ^a

Removal Approach and Output Quantity	Anoxic, AVS = 9.1 µmol/g			Oxic		
	18 µg/L	100 µg/L	1,000 µg/L	18 µg/L	100 µg/L	1,000 µg/L
Time to Quasi Steady State, days	93	93	97	91	92	95
Tot. Cd Range, µg/L ^b	0.742 - 0.986	4.12 - 5.50	41.6 – 55.6	0.784 - 1.05	4.36 - 5.82	44.9 - 60.2
Diss. Cd Range, µg/L ^b	0.700 - 0.931	3.89 - 5.20	39.2 – 52.5	0.740 - 0.993	4.12 - 5.49	42.4 - 56.9
Total Settling IN, tonnes	106	588	5860	108	602	6050
Total Resusp. OUT, tonnes	45.5	252	2510	45.3	251	2500
Total Diffusion NET, tonnes ^c	1.71	9.57	101	-1.10	-6.57	-110
Total Burial OUT, tonnes	5.59	31.0	309	5.57	30.9	307
Water column log K_D , L/kg ^b	3.60	3.60	3.59	3.60	3.60	3.59
Sediment log K_D , L/kg ^b	10.8	11.5	12.5	3.07	3.05	2.92
Time for 70% Removal, days (Approach 1)	25.9	26.1	28.9	26.0	26.2	29.0
$[0.3 \times C_T(0)] / \text{Max QSS } C_T$ ^d	5.48	5.45	5.39	5.14	5.15	4.98

^a Select simulation parameters: water column pH 7.07; sediment pH 7.56; settling velocity 2.5 m/d. For additional parameters, see Table 2.4.

^b Ranges and average are based on data from the quasi-steady state period of the simulation.

^c This number is the diffusive flux integrated over the *entire* 365-day simulation. Negative diffusive flux values are directed out of the sediment and positive diffusive flux values are directed into the sediment.

^d This quantity is the ratio of the total Cd concentration representing 70% removal ($0.3 \times C_T(0)$) to the maximum total concentration during the quasi-steady-state period (Max QSS C_T). This is meant to give an indication of where sustained water column concentrations lie relative to the 70% removal benchmark.

Table G-5. Summary of Cadmium Sediment Runs Without Ca/Mg Competition for Sites on Organic Matter ^a

Removal Approach and Output Quantity	AVS = 0 $\mu\text{mol/g}$			Anoxic, AVS = 1 $\mu\text{mol/g}$		
	18 $\mu\text{g/L}$	100 $\mu\text{g/L}$	1,000 $\mu\text{g/L}$	18 $\mu\text{g/L}$	100 $\mu\text{g/L}$	1,000 $\mu\text{g/L}$
Time to Quasi Steady State, days	25	25	26	25	25	26
Tot. Cd Range, $\mu\text{g/L}$ ^b	0.0840 - 0.0941	0.467 - 0.522	4.64 - 5.19	0.0824 - 0.0923	0.457 - 0.512	4.59 - 5.13
Diss. Cd Range, $\mu\text{g/L}$ ^b	0.0398 - 0.0446	0.221 - 0.247	2.19 - 2.44	0.0390 - 0.0437	0.217 - 0.242	2.16 - 2.41
Total Settling IN, tonnes	115	639	6380	114	634	6350
Total Resusp. OUT, tonnes	49.6	276	2750	49.6	276	2750
Total Diffusion NET, tonnes ^c	-0.912	-5.10	-48.9	0.0974	0.520	-15.0
Total Burial OUT, tonnes	6.09	33.9	338	6.10	33.9	338
Water column log K_D , L/kg ^b	4.87	4.87	4.88	4.87	4.87	4.88
Sediment log K_D , L/kg ^b	3.55	3.55	3.54	9.45	10.2	3.94
Time for 70% Removal, days (Approach 1)	1.23	0.987	3.00	1.23	0.987	3.00
$[0.3 \times C_T(0)]/\text{Max QSS } C_T$ ^d	57.4	57.5	57.8	58.5	58.6	58.5

^a Select simulation parameters: water column pH 7.07; sediment pH 7.56; settling velocity 2.5 m/d. For additional parameters, see Table 2.4.

^b Ranges and average are based on data from the quasi-steady state period of the simulation.

^c This number is the diffusive flux integrated over the *entire* 365-day simulation. Negative diffusive flux values are directed out of the sediment and positive diffusive flux values are directed into the sediment.

^d This quantity is the ratio of the total Cd concentration representing 70% removal ($0.3 \times C_T(0)$) to the maximum total concentration during the quasi-steady-state period (Max QSS C_T). This is meant to give an indication of where sustained water column concentrations lie relative to the 70% removal benchmark.

Table G-5. Continued ^a

Removal Approach and Output Quantity	Anoxic, AVS = 9.1 µmol/g			Oxic		
	18 µg/L	100 µg/L	1,000 µg/L	18 µg/L	100 µg/L	1,000 µg/L
Time to Quasi Steady State, days	25	25	26	25	25	26
Tot. Cd Range, µg/L ^b	0.0824 - 0.0923	0.457 - 0.512	4.55 - 5.09	0.0840 - 0.0941	0.466 - 0.522	4.64 - 5.19
Diss. Cd Range, µg/L ^b	0.0390 - 0.0437	0.217 - 0.242	2.14 - 2.39	0.0398 - 0.0445	0.221 - 0.247	2.19 - 2.44
Total Settling IN, tonnes	114	634	6330	115	639	6380
Total Resusp. OUT, tonnes	49.6	276	2750	49.6	276	2750
Total Diffusion NET, tonnes ^c	0.0974	0.520	7.72	-0.902	-5.04	-48.2
Total Burial OUT, tonnes	6.10	33.9	338	6.10	33.9	338
Water column log K_D , L/kg ^b	4.87	4.87	4.88	4.87	4.87	4.88
Sediment log K_D , L/kg ^b	9.45	10.2	11.2	3.55	3.55	3.55
Time for 70% Removal, days (Approach 1)	1.23	0.987	3.00	1.23	0.987	3.00
$[0.3 \times C_T(0)] / \text{Max QSS } C_T$ ^d	58.5	58.6	59.0	57.4	57.5	57.8

^a Select simulation parameters: water column pH 7.07; sediment pH 7.56; settling velocity 2.5 m/d. For additional parameters, see Table 2.4.

^b Ranges and average are based on data from the quasi-steady state period of the simulation.

^c This number is the diffusive flux integrated over the *entire* 365-day simulation. Negative diffusive flux values are directed out of the sediment and positive diffusive flux values are directed into the sediment.

^d This quantity is the ratio of the total Cd concentration representing 70% removal ($0.3 \times C_T(0)$) to the maximum total concentration during the quasi-steady-state period (Max QSS C_T). This is meant to give an indication of where sustained water column concentrations lie relative to the 70% removal benchmark.

APPENDIX H – SILVER TABLES**Table H-1. Summary of Water Column Runs for Silver with the Speciation Model Method**

Removal Approach and Output Quantity	pH = 6.09		pH = 7.07		pH = 8.00	
	120 ng/L	220 ng/L	120 ng/L	220 ng/L	120 ng/L	220 ng/L
1: $C_D(t)/C_T(0)$						
Time for 70% removal, days	133	133	63.1	63.1	79.8	79.8
Log K_D	2.93	2.93	3.22	3.22	3.12	3.12
Fraction particulate	0.0126	0.0126	0.0241	0.0241	0.0195	0.0195
2: $C_T(t)/C_T(0)$						
Time for 70% removal, days	135	135	64.6	64.6	81.4	81.4
Log K_D	2.93	2.93	3.22	3.22	3.12	3.12
Fraction particulate	0.0126	0.0126	0.0241	0.0241	0.0195	0.0195
3: $C_D(t)/C_D(0)$						
Time for 70% removal, days	135	135	64.6	64.6	81.4	81.4
Log K_D	2.93	2.93	3.22	3.22	3.12	3.12
Fraction particulate	0.0126	0.0126	0.0241	0.0241	0.0195	0.0195

Table H-1. Continued

Removal Approach and Output Quantity	pH = 6.09		pH = 7.07		pH = 8.00	
	100 µg/L	1000 µg/L	100 µg/L	1000 µg/L	100 µg/L	1000 µg/L
1: C_D(t)/C_T(0)						
Time for 70% removal, days	128	--- ^a	41.9	--- ^a	53.3	--- ^a
Log K _D range ^b	2.93 - 3.79	5.82	3.21 - 4.68	6.03	3.12 - 4.67	6.03
Fraction particulate range ^b	0.0126 - 0.0844	0.908	0.0239 - 0.418	0.942	0.0194 - 0.410	0.941
2: C_T(t)/C_T(0)						
Time for 70% removal, days	130	1.85	43.5	1.70	55.0	1.71
Log K _D range ^b	2.93 - 3.79	5.20 - 5.82	3.21 - 4.68	5.44 - 6.03	3.12 - 4.67	5.44 - 6.03
Fraction particulate range ^b	0.0126 - 0.0844	0.702 - 0.908	0.0239 - 0.418	0.806 - 0.942	0.0194 - 0.410	0.804 - 0.941
3: C_D(t)/C_D(0)						
Time for 70% removal, days	143	>720	82.5	>365	109	>365
Log K _D range ^b	2.93 - 3.79	3.14 - 5.82	3.21 - 4.68	3.45 - 6.03	3.12 - 4.67	3.44 - 6.03
Fraction particulate range ^b	0.0126 - 0.0844	0.0203 - 0.908	0.0239 - 0.418	0.0404 - 0.942	0.0194 - 0.410	0.0401 - 0.941

^a 70% removal occurs instantly via initial solid-solution equilibrium partitioning. Instead of log K_D and fraction particulate value ranges, the values at t = 0 are indicated.

^b These ranges were calculated using data prior to the time at which 70% removal was achieved

Table H-2. Summary of Water Column Runs for Silver with the Speciation Model Method Without Ca/Mg Competition for Sites on Organic Matter

Removal Approach and Output Quantity	pH = 6.09		pH = 7.07		pH = 8.00	
	120 ng/L	220 ng/L	120 ng/L	220 ng/L	120 ng/L	220 ng/L
1: $C_D(t)/C_T(0)$						
Time for 70% removal, days	40.8	40.7	10.9	10.9	6.53	6.53
Log K_D	3.40	3.40	3.96	3.96	4.18	4.18
Fraction particulate	0.0360	0.0360	0.120	0.120	0.186	0.186
2: $C_T(t)/C_T(0)$						
Time for 70% removal, days	42.2	42.2	12.2	12.2	7.90	7.90
Log K_D	3.40	3.40	3.96	3.96	4.18	4.18
Fraction particulate	0.0360	0.0360	0.120	0.120	0.186	0.186
3: $C_D(t)/C_D(0)$						
Time for 70% removal, days	42.2	42.2	12.2	12.2	7.90	7.90
Log K_D	3.40	3.40	3.96	3.96	4.18	4.18
Fraction particulate	0.0360	0.0360	0.120	0.120	0.186	0.186

Table H-2. Continued

Removal Approach and Output Quantity	pH = 6.09		pH = 7.07		pH = 8.00	
	100 µg/L	1000 µg/L	100 µg/L	1000 µg/L	100 µg/L	1000 µg/L
1: $C_D(t)/C_T(0)$						
Time for 70% removal, days	39.5	--- ^a	10.1	--- ^a	6.31	--- ^a
Log K_D range ^b	3.40 - 3.41	5.75	3.93 - 4.55	5.98	4.14 - 4.61	6.00
Fraction particulate range ^b	0.0367 - 0.0374	0.894	0.112 - 0.345	0.934	0.173 - 0.381	0.938
2: $C_T(t)/C_T(0)$						
Time for 70% removal, days	41.0	1.91	11.4	1.73	7.67	1.72
Log K_D range ^b	3.40 - 3.41	5.09 - 5.75	3.93 - 4.55	5.39 - 5.98	4.14 - 4.61	5.42 - 6.00
Fraction particulate range ^b	0.0366 - 0.0374	0.650 - 0.894	0.112 - 0.345	0.786 - 0.934	0.173 - 0.381	0.796 - 0.938
3: $C_D(t)/C_D(0)$						
Time for 70% removal, days	41.0	>730	14.7	54.6	9.61	18.9
Log K_D range ^b	3.40 - 3.41	3.41 - 5.75	3.93 - 4.55	3.93 - 5.98	4.14 - 4.61	4.14 - 6.00
Fraction particulate range ^b	0.0366 - 0.0374	0.0370 - 0.894	0.112 - 0.345	0.112 - 0.934	0.173 - 0.381	0.173 - 0.938

^a 70% removal occurs instantly via initial solid-solution equilibrium partitioning. Instead of log K_D and fraction particulate value ranges, the values at $t = 0$ are indicated.

^b These ranges were calculated using data prior to the time at which 70% removal was achieved

Table H-3. Summary of Water Column Runs for Silver with Binding to Cr-Reducible Sulfide (CRS)

Removal Approach and Output Quantity	Particulate CRS = 22 nM; Dissolved CRS = 29 nM			
	120 ng/L	220 ng/L	100 µg/L	1000 µg/L
1: $C_D(t)/C_T(0)$				
Time for 70% removal, days	1.84	1.84	16.1	--- ^a
Log K_D range ^b	4.70	4.70	3.55 - 4.62	6.01
Fraction particulate range ^b	0.429	0.429	0.0508 - 0.387	0.939
2: $C_T(t)/C_T(0)$				
Time for 70% removal, days	3.45	3.45	17.4	1.72
Log K_D range ^b	4.70	4.70	3.55 - 4.62	5.42 - 6.01
Fraction particulate range ^b	0.429	0.429	0.0508 - 0.387	0.798 - 0.939
3: $C_D(t)/C_D(0)$				
Time for 70% removal, days	3.45	3.45	21.8	>60
Log K_D range ^b	4.70	4.70	3.55 - 4.62	3.55 - 6.01
Fraction particulate range ^b	0.429	0.429	0.0508 - 0.387	0.0508 - 0.939

Table H-3. Continued

Removal Approach and Output Quantity	Particulate CRS = 14 nM; Dissolved CRS = 37 nM			
	120 ng/L	220 ng/L	100 µg/L	1000 µg/L
1: $C_D(t)/C_T(0)$				
Time for 70% removal, days	3.83	3.83	22.1	--- ^a
Log K_D range ^b	4.41	4.41	3.42 - 4.61	6.00
Fraction particulate range ^b	0.279	0.279	0.0381 - 0.379	0.938
2: $C_T(t)/C_T(0)$				
Time for 70% removal, days	5.27	5.27	23.4	1.72
Log K_D range ^b	4.41	4.41	3.42 - 4.61	5.41 - 6.00
Fraction particulate range ^b	0.279	0.279	0.0381 - 0.379	0.796 - 0.938
3: $C_D(t)/C_D(0)$				
Time for 70% removal, days	5.27	5.27	30.4	>60
Log K_D range ^b	4.41	4.41	3.42 - 4.61	3.42 - 6.00
Fraction particulate range ^b	0.279	0.279	0.0382 - 0.379	0.0381 - 0.938

^a 70% removal occurs instantly via initial solid-solution equilibrium partitioning. Instead of log K_D and fraction particulate value ranges, the values at $t = 0$ are indicated.

^b These ranges were calculated using data prior to the time at which 70% removal was achieved

Table H-4. Summary of Water Column Runs for Silver with Lowered Settling Velocity ^a

Removal Approach and Output Quantity	Linear Partitioning	pH = 6.09	pH = 7.07	pH = 8.00	Particulate CRS = 14 nM	Particulate CRS = 22 nM
1: $C_D(t)/C_T(0)$						
Time for 70% removal, days	--- ^a	675	436	504	38.3	18.6
Log K_D range ^b	5.28	2.93	3.22	3.12	4.41	4.70
Fraction particulate range ^b	0.741	0.0126	0.0241	0.0195	0.279	0.429
2: $C_T(t)/C_T(0)$						
Time for 70% removal, days	20.3	682	445	513	52.6	34.7
Log K_D range ^b	5.28	2.93	3.22	3.12	4.41	4.70
Fraction particulate range ^b	0.741	0.0126	0.0241	0.0195	0.279	0.429

^a 70% removal occurs instantly via initial solid-solution equilibrium partitioning. Instead of log K_D and fraction particulate value ranges, the values at $t = 0$ are indicated.

^b These ranges were calculated using data prior to the time at which 70% removal was achieved

Table H-5. Summary of Silver Sediment Runs

Removal Approach and Output Quantity	AVS = 0 $\mu\text{mol/g}$			Anoxic, AVS = 1 $\mu\text{mol/g}$		
	Acute ERV	100 $\mu\text{g/L}$	Chronic Cutoff	Acute ERV	100 $\mu\text{g/L}$	Chronic Cutoff
Time to Quasi Steady State, days	106	85	12	111	90	12
Tot. Ag Range, $\mu\text{g/L}$ ^a	0.0218 - 0.0402	9.87 - 18.5	60.5 - 61.4	0.0199 - 0.0369	9.01 - 16.9	60.4 - 61.3
Diss. Ag Range, $\mu\text{g/L}$ ^a	0.0213 - 0.0392	9.63 - 18.0	58.2 - 58.2	0.0194 - 0.0360	8.79 - 16.5	58.2 - 58.2
Total Settling IN, tonnes	1.21	564	5980	1.17	545	5930
Total Resusp. OUT, tonnes	0.487	232	2610	0.492	234	2610
Total Diffusion NET, tonnes ^c	-0.00594	-7.99	6.31	0.0450	16.5	61.2
Total Burial OUT, tonnes	0.0598	28.5	321	0.0605	28.8	321
Water column log K_D , L/kg ^a	3.22	3.22	3.44	3.22	3.22	3.43
Sediment log K_D , L/kg ^a	2.82	2.82	3.53	4.92	7.57	8.60
Time for 70% Removal, days (Approach 1)	64.6	44.39	--- ^c	63.8	43.6	--- ^c
$[0.3 \times C_T(0)] / \text{Max QSS } C_T$ ^d	1.64	1.63	4.89	1.79	1.77	4.89

^a Ranges and average are based on data from the quasi-steady state period of the simulation

^b This number is the diffusive flux integrated over the *entire* simulation time. Negative diffusive flux values are directed out of the sediment and positive diffusive flux values are directed into the sediment

^c 70% removal occurs instantly via initial solid-solution equilibrium partitioning.

^d This quantity is the ratio of the total Ag concentration representing 70% removal ($0.3 \times C_T(0)$) to the maximum total concentration during the quasi-steady-state period (Max QSS C_T). This is meant to give an indication of where sustained water column concentrations lie relative to the 70% removal benchmark.

Table H-5. Continued

Removal Approach and Output Quantity	Anoxic, AVS = 9.1 µmol/g			Oxic		
	Acute ERV	100 µg/L	Chronic Cutoff	Acute ERV	100 µg/L	Chronic Cutoff
Time to Quasi Steady State, days	111	90	12	106	86	12
Tot. Ag Range, µg/L ^a	0.0199 - 0.0369	9.01 - 16.9	60.4 - 61.3	0.0217 - 0.0401	9.86 - 18.3	60.5 - 61.4
Diss. Ag Range, µg/L ^a	0.0194 - 0.0360	8.79 - 16.5	58.2 - 58.2	0.0212 - 0.0392	9.62 - 17.8	58.2 - 58.2
Total Settling IN, tonnes	1.17	545	5930	1.21	564	5980
Total Resusp. OUT, tonnes	0.492	234	2610	0.487	232	2610
Total Diffusion NET, tonnes ^c	0.0450	16.5	61.2	-0.00526	-7.67	6.31
Total Burial OUT, tonnes	0.0605	28.8	321	0.0599	28.5	321
Water column log K_D , L/kg ^a	3.22	3.22	3.43	3.22	3.22	3.44
Sediment log K_D , L/kg ^a	4.92	7.57	8.60	2.83	2.82	3.53
Time for 70% Removal, days (Approach 1)	63.8	43.6	--- ^c	64.6	44.4	--- ^c
$[0.3 \times C_T(0)] / \text{Max QSS } C_T$ ^d	1.79	1.77	4.89	1.64	1.64	4.89

^a Ranges and average are based on data from the quasi-steady state period of the simulation

^b This number is the diffusive flux integrated over the *entire* simulation time. Negative diffusive flux values are directed out of the sediment and positive diffusive flux values are directed into the sediment

^c 70% removal occurs instantly via initial solid-solution equilibrium partitioning.

^d This quantity is the ratio of the total Ag concentration representing 70% removal ($0.3 \times C_T(0)$) to the maximum total concentration during the quasi-steady-state period (Max QSS C_T). This is meant to give an indication of where sustained water column concentrations lie relative to the 70% removal benchmark.

Table H-6. Summary of Silver Sediment Runs Without Ca/Mg Competition for Sites on Organic Matter

Removal Approach and Output Quantity	AVS = 0 $\mu\text{mol/g}$			Anoxic, AVS = 1 $\mu\text{mol/g}$		
	Acute ERV	100 $\mu\text{g/L}$	Chronic Cutoff	Acute ERV	100 $\mu\text{g/L}$	Chronic Cutoff
Time to Quasi Steady State, days	62	62	41	62	62	42
Tot. Ag Range, $\mu\text{g/L}$ ^a	0.00444 - 0.00530	2.02 - 2.41	20.5 - 24.9	0.00433 - 0.00519	1.97 - 2.36	20.0 - 24.1
Diss. Ag Range, $\mu\text{g/L}$ ^a	0.00390 - 0.00466	1.78 - 2.12	18.1 - 22.0	0.00381 - 0.00456	1.73 - 2.08	17.7 - 21.3
Total Settling IN, tonnes	1.37	622	6290	1.35	615	6220
Total Resusp. OUT, tonnes	0.584	266	2710	0.585	266	2710
Total Diffusion NET, tonnes ^c	-0.00591	-2.85	-50.8	0.00902	4.17	22.0
Total Burial OUT, tonnes	0.0719	32.7	333	0.0719	32.7	334
Water column $\log K_D$, L/kg ^a	3.96	3.96	3.95	3.96	3.96	3.95
Sediment $\log K_D$, L/kg ^a	3.43	3.43	3.42	4.96	7.62	8.62
Time for 70% Removal, days (Approach 1)	11.4	11.0	--- ^c	11.4	11.0	--- ^c
$[0.3 \times C_T(0)] / \text{Max QSS } C_T$ ^d	12.45	12.4	12.1	12.7	12.7	12.4

^a Ranges and average are based on data from the quasi-steady state period of the simulation

^b This number is the diffusive flux integrated over the *entire* simulation time. Negative diffusive flux values are directed out of the sediment and positive diffusive flux values are directed into the sediment

^c 70% removal occurs instantly via initial solid-solution equilibrium partitioning.

^d This quantity is the ratio of the total Ag concentration representing 70% removal ($0.3 \times C_T(0)$) to the maximum total concentration during the quasi-steady-state period (Max QSS C_T). This is meant to give an indication of where sustained water column concentrations lie relative to the 70% removal benchmark.

Table H-6. Continued

Removal Approach and Output Quantity	Anoxic, AVS = 9.1 µmol/g			Oxic		
	Acute ERV	100 µg/L	Chronic Cutoff	Acute ERV	100 µg/L	Chronic Cutoff
Time to Quasi Steady State, days	62	62	42	62	62	41
Tot. Ag Range, µg/L ^a	0.00433 - 0.00519	1.97 - 2.36	20.0 - 24.1	0.00444 - 0.00530	2.02 - 2.41	20.5 - 24.9
Diss. Ag Range, µg/L ^a	0.00381 - 0.00456	1.73 - 2.08	17.7 - 21.3	0.00390 - 0.00466	1.78 - 2.12	18.1 - 22.0
Total Settling IN, tonnes	1.35	615	6220	1.37	622	6290
Total Resusp. OUT, tonnes	0.585	266	2710	0.584	266	2710
Total Diffusion NET, tonnes ^c	0.00902	4.17	22.0	-0.00588	-2.84	-50.6
Total Burial OUT, tonnes	0.0719	32.7	334	0.0719	32.7	333
Water column log K_D , L/kg ^a	3.96	3.96	3.95	3.96	3.96	3.95
Sediment log K_D , L/kg ^a	4.96	7.62	8.62	3.43	3.43	3.43
Time for 70% Removal, days (Approach 1)	11.4	11.0	--- ^c	11.4	11.0	--- ^c
$[0.3 \times C_T(0)] / \text{Max QSS } C_T$ ^d	12.7	12.7	12.4	12.5	12.4	12.1

^a Ranges and average are based on data from the quasi-steady state period of the simulation

^b This number is the diffusive flux integrated over the *entire* simulation time. Negative diffusive flux values are directed out of the sediment and positive diffusive flux values are directed into the sediment

^c 70% removal occurs instantly via initial solid-solution equilibrium partitioning.

^d This quantity is the ratio of the total Ag concentration representing 70% removal ($0.3 \times C_T(0)$) to the maximum total concentration during the quasi-steady-state period (Max QSS C_T). This is meant to give an indication of where sustained water column concentrations lie relative to the 70% removal benchmark.

Table H-7. Summary of Silver Sediment Runs with Binding to Cr-Reducible Sulfide (CRS)

Removal Approach and Output Quantity	AVS = 0 $\mu\text{mol/g}$ Particulate CRS = 22 nM; Dissolved CRS = 29 nM			AVS = 0 $\mu\text{mol/g}$ Particulate CRS = 14 nM; Dissolved CRS = 37 nM		
	Acute ERV	100 $\mu\text{g/L}$	Chronic Cutoff	Acute ERV	100 $\mu\text{g/L}$	Chronic Cutoff
Time to Quasi Steady State, days	28	50	15	37	67	12
Tot. Ag Range, $\mu\text{g/L}$ ^a	0.00137 - 0.00154	0.623 - 0.694	13.5 - 62.4	0.00209 - 0.00237	0.953 - 1.07	55.9 - 65.2
Diss. Ag Range, $\mu\text{g/L}$ ^a	0.000780 - 0.000878	0.356 - 0.397	11.0 - 59.1	0.00151 - 0.00171	0.687 - 0.775	53.6 - 62.1
Total Settling IN, tonnes	1.45	651	6280	1.44	644	6000
Total Resusp. OUT, tonnes	0.603	268	2700	0.599	264	2610
Total Diffusion NET, tonnes ^c	-0.0636	-25.8	-28.8	-0.0614	-23.9	7.04
Total Burial OUT, tonnes	0.0742	32.9	332	0.0736	32.5	320
Water column $\log K_D$, L/kg ^a	4.70	4.70	3.93	4.41	4.41	3.44
Sediment $\log K_D$, L/kg ^a	2.82	2.82	3.55	2.82	2.82	3.53
Time for 70% Removal, days (Approach 1)	2.13	17.28	--- ^c	4.24	23.4	--- ^c
$[0.3 \times C_T(0)]/\text{Max QSS } C_T$ ^d	43.0	43.2	4.81	27.8	27.9	4.60

^a Ranges and average are based on data from the quasi-steady state period of the simulation

^b This number is the diffusive flux integrated over the *entire* simulation time. Negative diffusive flux values are directed out of the sediment and positive diffusive flux values are directed into the sediment

^c 70% removal occurs instantly via initial solid-solution equilibrium partitioning.

^d This quantity is the ratio of the total Ag concentration representing 70% removal ($0.3 \times C_T(0)$) to the maximum total concentration during the quasi-steady-state period (Max QSS C_T). This is meant to give an indication of where sustained water column concentrations lie relative to the 70% removal benchmark.

Table H-7. Continued

Removal Approach and Output Quantity	Anoxic, AVS = 1 $\mu\text{mol/g}$ Particulate CRS = 22 nM; Dissolved CRS = 29 nM			Anoxic, AVS = 1 $\mu\text{mol/g}$ Particulate CRS = 14 nM; Dissolved CRS = 37 nM		
	Acute ERV	100 $\mu\text{g/L}$	Chronic Cutoff	Acute ERV	100 $\mu\text{g/L}$	Chronic Cutoff
Time to Quasi Steady State, days	29	50	28	37	67	12
Tot. Ag Range, $\mu\text{g/L}$ ^a	0.00124 - 0.00138	0.563 - 0.629	11.0 - 54.4	0.00189 - 0.00216	0.862 - 0.973	53.3 - 65.2
Diss. Ag Range, $\mu\text{g/L}$ ^a	0.000707 - 0.000791	0.322 - 0.359	8.52 - 51.2	0.00136 - 0.00156	0.622 - 0.701	51.0 - 62.1
Total Settling IN, tonnes	1.39	623	6240	1.38	617	5960
Total Resusp. OUT, tonnes	0.605	269	2710	0.601	265	2610
Total Diffusion NET, tonnes ^c	0.00130	3.34	23.9	0.00296	4.79	59.9
Total Burial OUT, tonnes	0.0744	33.0	333	0.0738	32.6	321
Water column $\log K_D$, L/kg ^a	4.70	4.70	3.99	4.41	4.41	3.45
Sediment $\log K_D$, L/kg ^a	4.96	7.62	8.61	4.96	7.62	8.60
Time for 70% Removal, days (Approach 1)	2.13	17.2	--- ^c	4.23	23.3	--- ^c
$[0.3 \times C_T(0)] / \text{Max QSS } C_T$ ^d	47.7	47.7	5.52	30.6	30.8	4.60

^a Ranges and average are based on data from the quasi-steady state period of the simulation

^b This number is the diffusive flux integrated over the *entire* simulation time. Negative diffusive flux values are directed out of the sediment and positive diffusive flux values are directed into the sediment

^c 70% removal occurs instantly via initial solid-solution equilibrium partitioning.

^d This quantity is the ratio of the total Ag concentration representing 70% removal ($0.3 \times C_T(0)$) to the maximum total concentration during the quasi-steady-state period (Max QSS C_T). This is meant to give an indication of where sustained water column concentrations lie relative to the 70% removal benchmark.

APPENDIX I – ARSENIC TABLES

Table I-1. Arsenic(V) Complexes with Sulfide

Species	Reaction letter and log K from [2]	Operations to produce required reaction	Stoichiometry			log K	Reference
			AsO ₄ ³⁻	HS ⁻	H ⁺		
H ₃ AsO ₄ (aq)	W (-2.3)	-(W+X+Y)	1	0	3	21.09	[1]
H ₂ AsO ₄ ⁻	X (-6.99)	-(X+Y)	1	0	2	18.79	[1]
HAsO ₄ ²⁻	Y (-11.80)	-Y	1	0	1	11.80	[1]
H ₃ AsSO ₃ (aq)	J (11.0)	J-(W+X+Y)-N	1 ^a	1	4	39.1	[2]
H ₂ AsSO ₃ ⁻	Z (-3.3)	J-(W+X+Y)-N+Z	1	1	3	35.8	[3]
HAsSO ₃ ²⁻	AA (-7.2)	J-(W+X+Y)-N+Z+AA	1	1	2	25.6	[3]
AsSO ₃ ³⁻	BB (-11.0)	J-(W+X+Y)-N+Z+AA+BB	1	1	1	17.6	[3]
H ₃ AsS ₂ O ₂ (aq)	K (0.1)	J+K-(W+X+Y)-2N	1 ^a	2	5	46.2	[2]
H ₂ AsS ₂ O ₂ ⁻	CC (2.4)	J+K-(W+X+Y)-2N+CC	1	2	4	48.6	[2]
HAsS ₂ O ₂ ²⁻	DD (-7.1)	J+K-(W+X+Y)-2N+CC+DD	1	2	3	41.5	[3]
AsS ₂ O ₂ ³⁻	EE (-10.8)	J+K-(W+X+Y)-2N+CC+DD+EE	1	2	2	30.7	[3]
H ₃ AsS ₃ O(aq)	L (3.5)	J+K+L-(W+X+Y)-3N	1	3	6	56.7	[2]
H ₂ AsS ₃ O ⁻	FF (1.7)	J+K+L-(W+X+Y)-3N+FF	1	3	5	58.3	[2]
HAsS ₃ O ²⁻	GG (-1.5)	J+K+L-(W+X+Y)-3N+FF+GG	1	3	4	56.9	[2]
AsS ₃ O ³⁻	HH (-10.8)	J+K+L-(W+X+Y)-3N+FF+GG+HH	1	3	3	46.1	[3]
H ₃ AsS ₄ (aq)	M (2.6)	J+K+L+M-(W+X+Y)-4N	1	4	7	66.3	[2]
H ₂ AsS ₄ ⁻	II (2.3)	J+K+L+M-(W+X+Y)-4N+II	1	4	6	68.6	[2]
HAsS ₄ ²⁻	JJ (-1.5)	J+K+L+M-(W+X+Y)-4N+II+JJ	1	4	5	67.1	[2]
AsS ₄ ³⁻	KK (-5.2)	J+K+L+M-(W+X+Y)-4N+II+JJ+KK	1	4	4	61.9	[3]
H ₂ S(aq)	N (-6.99)	-N	0	1	1	6.99	[1]

^a Incorrectly listed as AsO₃³⁻ in Couture et al (2010)

Table I-2. Arsenic(III) Complexes with Sulfide

Species	Reaction letter and log K from [2]	Operations to produce required reaction	Stoichiometry			log K	Reference
			AsO ₄ ³⁻	HS ⁻	H ⁺		
H ₃ AsO ₃ (aq)	O (-9.17)	-(O+P-15)	1	0	3	34.2	[1]
H ₂ AsO ₃ ⁻	P (-14.1)	-(P-15.1)	1	0	2	29.2	[1]
HAsO ₃ ²⁻	Not listed	-15.0	1	0	1	15.0	[1]
H ₃ AsSO ₂ (aq)	G (0.4)	G-(O+P-15)-N	1	1	4	45.7	[2]
H ₂ AsSO ₂ ⁻	Q (-3.7)	G-(O+P-15)-N+Q	1	1	3	42.0	[2]
HAsSO ₂ ²⁻	R (-14.1)	G-(O+P-15)-N+Q	1	1	2	27.9	[2]
H ₃ AsS ₂ O(aq)	H (3.8)	G+H-(O+P-15)-2N	1	2	5	56.5	[2]
H ₂ AsS ₂ O ⁻	S (-3.7)	G+H-(O+P-15)-2N+S	1	2	4	52.8	[2]
HAsS ₂ O ²⁻	T (-8.6)	G+H-(O+P-15)-2N+S+T	1	2	3	44.2	[2]
H ₃ AsS ₃ (aq)	I (5.6)	G+H+I-(O+P-15)-3N	1	3	6	69.0	[2]
H ₂ AsS ₃ ⁻	U (-3.7)	G+H+I-(O+P-15)-3N+U	1	3	5	65.3	[2]
HAsS ₃ ²⁻	V (-8.6)	G+H+I-(O+P-15)-3N+U+V	1	3	4	56.7	[2]

Table I-3. Arsenic(V) Complexes with Cations

Species	Stoichiometry			log K	Reference
	AsO ₄ ³⁻	M ²⁺	H ⁺		
CaAsO ₄ ⁻	1	1	0	4.36 ^a	[4] (4.36)
CaHAsO ₄ (aq)	1	1	1	14.26 ^a	[4] (2.66)
CaH ₂ AsO ₄ ⁺	1	1	2	19.66 ^a	[4] (1.30)
MgAsO ₄ ⁻	1	1	0	6.34	[1]
MgHAsO ₄ (aq)	1	1	1	14.66	[1]
MgH ₂ AsO ₄ ⁺	1	1	2	20.31	[1]
FeAsO ₄ ⁻	1	1	0	7.06 ^b	[1]
FeHAsO ₄ (aq)	1	1	1	15.34 ^b	[1]
FeH ₂ AsO ₄ ⁺	1	1	2	21.47 ^b	[1]
MnAsO ₄ ⁻	1	1	0	6.13	[1]
MnHAsO ₄ (aq)	1	1	1	15.55	[1]
NiAsO ₄ ⁻	1	1	0	6.34	[1]
NiHAsO ₄ (aq)	1	1	1	14.70	[1]
NiH ₂ AsO ₄ ⁺	1	1	2	20.31	[1]
PbHAsO ₄ (aq)	1	1	1	14.84	[1]
PbH ₂ AsO ₄ ⁺	1	1	2	20.32	[1]
CuHAsO ₄ (aq)	1	1	1	15.48	[1]
ZnHAsO ₄ (aq)	1	1	1	15.01	[1]
CdHAsO ₄ (aq)	1	1	1	15.51	[1]
Species	AsO ₄ ³⁻	M ³⁺	H ⁺	log K	Reference
FeAsO ₄ (aq)	1	1	0	18.9	
FeHAsO ₄ ⁺	1	1	1	21.66	
FeH ₂ AsO ₄ ²⁺	1	1	2	22.83	
AlAsO ₄ (aq)	1	1	0	14.1	
AlHAsO ₄ ⁺	1	1	1	19.09	
AlH ₂ AsO ₄ ²⁺	1	1	2	21.6	

^a Boothe and Brown used pK_{a1}, pK_{a2} and pK_{a3} values of 2.249, 6.761, and 11.602 in their speciation model. Their reported constant is in parenthesis.

^b Incorrectly listed as AsO₃³⁻ in Couture et al (2010)

Table I-4. Arsenic Solids in TICKET-UWM

As(III) Solid Species	AsO₃³⁻	H⁺	HS⁻	e⁻	M²⁺	log K	Reference
As ₂ S ₃ (s,orpiment)	2	9	3			122.8	[1]
As ₂ S ₃ (s,amorph)	2	9	3			121.4	[1]
As ₂ O ₃ (s,arsenolite)	2	6				77.92	[1]
As(V) Solid Species	AsO₄³⁻	H⁺	HS⁻	e⁻	M²⁺	log K	Reference
FeAsO ₄ (s,scorodite)	1				1	25.83	[5]
FeAsO ₄ (s,amorph)	1				1	23.0	[5]
Fe ₂ (AsO ₄) ₃ (s)	3				2	34.41	[6]
As ₂ O ₅ (s)	2	6				61.95	[1]
Mg ₃ (AsO ₄) ₂ (s)	2	3			3	30.02	[6]
Ca ₃ (AsO ₄) ₂ •4H ₂ O(s)	2	3			3	21.15	[4]
Ca ₅ (OH)(AsO ₄) ₃ (s)	3	-1			5	24.3	[4]
CaHAsO ₄ (s)	1	1			1	16.34	[4]
Ca ₅ (HAsO ₄) ₂ (AsO ₄) ₂ (s,ferrarisite)	4	2			5	56.61	[4]
Ca ₅ (HAsO ₄) ₂ (AsO ₄) ₂ (s,guerinite)	4	2			5	55.81	[4]
As ₂ S ₃ (s,orpiment)	2	13	3	4		122.8+2(2.17) = 127.14	[1]
As ₂ O ₃ (s,arsenolite)	2	10		4		77.92+2(2.17) = 82.26	[1]
As ₂ S ₃ (s,amorph)	2	13	3	4		121.4+2(2.17) = 125.74	[1]

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Table I-5. Summary of Task 1 Runs for Arsenic(III) – Anoxic Sediment

Removal Approach and Output Quantity	pH = 6.09			pH = 6.09 Alternate		
	40 µg/L	480 µg/L	1000 µg/L	40 µg/L	480 µg/L	1000 µg/L
1: $C_D(t)/C_T(0)$						
Time for 70% removal, days	>365 days	>365 days	>365 days	28.8	310	>365 days
Log K_D range ^b	3.72 - 3.77	3.51 - 3.57	3.33 - 3.39	3.64 - 3.77	3.51 - 3.55	3.33 - 3.39
Fraction particulate range ^b	0.0722 - 0.0815	0.0464 - 0.0528	0.0313 - 0.0359	0.0610 - 0.0805	0.0463 - 0.0510	0.0313 - 0.0358
2: $C_T(t)/C_T(0)$						
Time for 70% removal, days	>365 days	>365 days	>365 days	31.4	463	>365 days
Log K_D range ^b	3.72 - 3.77	3.51 - 3.57	3.33 - 3.39	3.64 - 3.77	3.51 - 3.56	3.33 - 3.39
Fraction particulate range ^b	0.0722 - 0.0815	0.0464 - 0.0528	0.0313 - 0.0359	0.0608 - 0.0805	0.0463 - 0.0515	0.0313 - 0.0358
3: $C_D(t)/C_D(0)$						
Time for 70% removal, days	>365 days	>365 days	>365 days	32.3	448	>365 days
Log K_D range ^b	3.72 - 3.77	3.51 - 3.57	3.33 - 3.39	3.63 - 3.77	3.51 - 3.56	3.33 - 3.39
Fraction particulate range ^b	0.0722 - 0.0815	0.0464 - 0.0528	0.0313 - 0.0359	0.0608 - 0.0805	0.0463 - 0.0514	0.0313 - 0.0358

Table I-5. Continued

Removal Approach and Output Quantity	pH = 7.07			pH = 8.00		
	40 µg/L	480 µg/L	1000 µg/L	40 µg/L	480 µg/L	1000 µg/L
1: C_D(t)/C_T(0)						
Time for 70% removal, days	>365 days	>365 days	>365 days	4.23	>365 days	>365 days
Log K _D range ^b	4.15 - 4.20	3.64 - 3.79	3.41 - 3.52	4.39 - 4.51	3.66 - 3.88	3.39 - 3.52
Fraction particulate range ^b	0.175 - 0.194	0.0620 - 0.0845	0.0371 - 0.0468	0.271 - 0.326	0.0643 - 0.102	0.0356 - 0.0468
2: C_T(t)/C_T(0)						
Time for 70% removal, days	>365 days	>365 days	>365 days	8.39	>365 days	>365 days
Log K _D range ^b	4.15 - 4.20	3.64 - 3.79	3.41 - 3.52	4.39 - 4.54	3.66 - 3.88	3.39 - 3.52
Fraction particulate range ^b	0.175 - 0.194	0.0620 - 0.0845	0.0371 - 0.0468	0.271 - 0.343	0.0643 - 0.102	0.0356 - 0.0468
3: C_D(t)/C_D(0)						
Time for 70% removal, days	>365 days	>365 days	>365 days	6.89	>365 days	>365 days
Log K _D range ^b	4.15 - 4.20	3.64 - 3.79	3.41 - 3.52	4.39 - 4.53	3.66 - 3.88	3.39 - 3.52
Fraction particulate range ^b	0.175 - 0.194	0.0620 - 0.0845	0.0371 - 0.0468	0.271 - 0.339	0.0643 - 0.102	0.0356 - 0.0468

^a 70% removal occurs instantly via initial solid-solution equilibrium partitioning. Instead of log K_D and fraction particulate value ranges, the values at t = 0 are indicated.

^b These ranges were calculated using data prior to the time at which 70% removal was achieved

Table I-6. Summary of Task 1 Runs for Arsenic(III) with the Speciation Model Method – Oxidic Sediment

Removal Approach and Output Quantity	pH = 6.09			pH = 7.07			pH = 8.00		
	40 µg/L	480 µg/L	1000 µg/L	40 µg/L	480 µg/L	1000 µg/L	40 µg/L	480 µg/L	1000 µg/L
1: $C_D(t)/C_T(0)$									
Time for 70% removal, days	16.7	24.7	34.0	6.40	15.8	25.6	3.41	13.8	25.1
Log K_D range ^b	3.77 - 3.78	3.51 - 3.67	3.33 - 3.58	4.15 - 4.21	3.64 - 3.91	3.41 - 3.74	4.39 - 4.50	3.66 - 4.01	3.39 - 3.80
Fraction particulate range ^b	0.0805 - 0.0830	0.0464 - 0.0662	0.0313 - 0.0537	0.175 - 0.196	0.0620 - 0.109	0.0371 - 0.0765	0.271 - 0.320	0.0643 - 0.134	0.0356 - 0.0858
2: $C_T(t)/C_T(0)$									
Time for 70% removal, days	18.0	26.0	35.4	7.77	17.1	26.9	4.93	15.1	26.4
Log K_D range ^b	3.77 - 3.78	3.51 - 3.68	3.33 - 3.59	4.15 - 4.22	3.64 - 3.95	3.41 - 3.76	4.39 - 4.53	3.66 - 4.07	3.39 - 3.83
Fraction particulate range ^b	0.0805 - 0.0831	0.0464 - 0.0671	0.0313 - 0.0546	0.175 - 0.199	0.0620 - 0.118	0.0371 - 0.0792	0.271 - 0.339	0.0643 - 0.149	0.0356 - 0.0912
3: $C_D(t)/C_D(0)$									
Time for 70% removal, days	18.0	25.6	34.8	7.59	16.4	26.2	4.55	14.4	25.6
Log K_D range ^b	3.77 - 3.78	3.51 - 3.68	3.33 - 3.58	4.15 - 4.22	3.64 - 3.93	3.41 - 3.76	4.39 - 4.53	3.66 - 4.03	3.39 - 3.81
Fraction particulate range ^b	0.0805 - 0.0831	0.0464 - 0.0668	0.0313 - 0.0543	0.175 - 0.199	0.0620 - 0.113	0.0371 - 0.0792	0.271 - 0.339	0.0643 - 0.139	0.0356 - 0.0880

^a 70% removal occurs instantly via initial solid-solution equilibrium partitioning. Instead of log K_D and fraction particulate value ranges, the values at $t = 0$ are indicated.

^b These ranges were calculated using data prior to the time at which 70% removal was achieved

Table I-7. Summary of Arsenic(III) Sediment Runs

Removal Approach and Output Quantity	Anoxic, AVS = 1 $\mu\text{mol/g}$			Oxic		
	Chronic ERV	Acute ERV	Chronic Cutoff	Chronic ERV	Acute ERV	Chronic Cutoff
Time to Quasi Steady State, days	17	18	14	45	60	76
Tot. As(III) Range, $\mu\text{g/L}$ ^a	15.4 - 16.1	281 - 301	682 - 744	0.476 - 0.536	5.90 - 6.68	12.8 - 14.7
Diss. As(III) Range, $\mu\text{g/L}$ ^a	12.4 - 13.3	257 - 277	716 - 779	0.380 - 0.425	4.75 - 5.36	10.4 - 11.9
Total Settling IN, tonnes	3200	25800	36600	250	2970	6110
Total Resusp. OUT, tonnes	--- ^b	--- ^b	--- ^b	108	1280	2610
Total Diffusion NET, tonnes ^c	-3110	-25100	-35500	0.614	16.2	53.7
Total Burial OUT, tonnes	--- ^b	--- ^b	--- ^b	13.3	157	321
Water column log K_D , L/kg ^a	4.16	3.78	3.51	4.23	4.21	4.19
Sediment log K_D , L/kg ^a	--- ^b	--- ^b	--- ^b	4.35	4.33	4.30
Time for 70% Removal, days (Approach 1)	>365	>365	>365	6.81	16.0	25.8
$[0.3 \times C_T(0)] / \text{Max QSS } C_T$ ^d	0.74	0.48	0.39	22.4	21.5	20.4

^a Ranges and average are based on data from the quasi-steady state period of the simulation

^b No particulate arsenic(III) in sediment

^c This number is the diffusive flux integrated over the *entire* simulation time. Negative diffusive flux values are directed out of the sediment and positive diffusive flux values are directed into the sediment

^d This quantity is the ratio of the total As(III) concentration representing 70% removal ($0.3 \times C_T(0)$) to the maximum total concentration during the quasi-steady-state period (Max QSS C_T). This is meant to give an indication of where sustained water column concentrations lie relative to the 70% removal benchmark.

Table I-8. Summary of Task 1 Runs for Arsenic(V) with the Speciation Model Method – Anoxic sediment

Removal Approach and Output Quantity	pH = 6.09			pH = 7.07			pH = 8.00		
	40 µg/L	480 µg/L	1000 µg/L	40 µg/L	480 µg/L	1000 µg/L	40 µg/L	480 µg/L	1000 µg/L
1: $C_D(t)/C_T(0)$									
Time for 70% removal, days	0.314	29.2	62.3	0.715	67.7	136	1.18	>730 days	--- ^a
Log K_D range ^b	4.96 - 5.08	3.66 - 4.11	3.36 - 3.82	4.77 - 4.99	3.56 - 4.01	3.26 - 3.72	4.62 - 4.88	3.85 - 5.02	5.47
Fraction particulate range ^b	0.575 - 0.646	0.0643 - 0.162	0.0330 - 0.0898	0.469 - 0.592	0.0516 - 0.134	0.0264 - 0.0736	0.384 - 0.530	0.0960 - 0.613	0.814
2: $C_T(t)/C_T(0)$									
Time for 70% removal, days	2.07	33.6	66.3	2.43	79.4	145	2.88	>730 days	2.47
Log K_D range ^b	4.96 - 6.62	3.66 - 4.19	3.36 - 3.86	4.77 - 6.06	3.56 - 4.08	3.26 - 3.76	4.62 - 5.66	3.85 - 5.02	4.64 - 5.47
Fraction particulate range ^b	0.575 - 0.984	0.0643 - 0.189	0.0330 - 0.0982	0.469 - 0.945	0.0516 - 0.153	0.0264 - 0.0789	0.384 - 0.874	0.0960 - 0.613	0.393 - 0.814
3: $C_D(t)/C_D(0)$									
Time for 70% removal, days	0.851	30.6	63.6	1.26	71.4	139	1.72	>730 days	>730 days
Log K_D range ^b	4.96 - 5.39	3.66 - 4.14	3.36 - 3.83	4.77 - 5.20	3.56 - 4.04	3.26 - 3.73	4.62 - 5.08	3.85 - 5.02	3.87 - 5.47
Fraction particulate range ^b	0.575 - 0.785	0.0643 - 0.171	0.0330 - 0.0927	0.469 - 0.704	0.0516 - 0.140	0.0264 - 0.0752	0.384 - 0.642	0.0960 - 0.613	0.101 - 0.814

^a 70% removal occurs instantly via initial solid-solution equilibrium partitioning. Instead of log K_D and fraction particulate value ranges, the values at $t = 0$ are indicated.

^b These ranges were calculated using data prior to the time at which 70% removal was achieved

Table I-9. Summary of Task 1 Runs for Arsenic(V) with the Speciation Model Method – Oxidic Sediment

Removal Approach and Output Quantity	pH = 6.09			pH = 7.07			pH = 8.00		
	40 µg/L	480 µg/L	1000 µg/L	40 µg/L	480 µg/L	1000 µg/L	40 µg/L	480 µg/L	1000 µg/L
1: $C_D(t)/C_T(0)$									
Time for 70% removal, days	0.308	12.5	25.7	0.687	15.9	32.5	1.11	6.43	--- ^a
Log K_D range ^b	4.96 - 5.09	3.66 - 4.11	3.36 - 3.82	4.77 - 4.96	3.56 - 3.97	3.26 - 3.71	4.62 - 4.90	3.81 - 5.02	5.47
Fraction particulate range ^b	0.575 - 0.647	0.0643 - 0.162	0.0330 - 0.0897	0.469 - 0.576	0.0516 - 0.124	0.0264 - 0.0720	0.384 - 0.542	0.0891 - 0.613	0.814
2: $C_T(t)/C_T(0)$									
Time for 70% removal, days	1.82	13.8	27.0	2.11	17.2	33.8	2.46	7.69	2.47
Log K_D range ^b	4.96 - 6.66	3.66 - 4.19	3.36 - 3.86	4.77 - 6.07	3.56 - 4.07	3.26 - 3.74	4.62 - 5.66	3.81 - 5.02	4.64 - 5.47
Fraction particulate range ^b	0.575 - 0.986	0.0643 - 0.188	0.0330 - 0.0979	0.469 - 0.947	0.0516 - 0.151	0.0264 - 0.0758	0.384 - 0.873	0.0891 - 0.613	0.393 - 0.814
3: $C_D(t)/C_D(0)$									
Time for 70% removal, days	0.811	13.0	26.1	1.18	16.3	32.9	1.57	13.0	15.3
Log K_D range ^b	4.96 - 5.41	3.66 - 4.13	3.36 - 3.83	4.77 - 5.19	3.56 - 4.02	3.26 - 3.71	4.62 - 5.05	3.81 - 5.02	3.81 - 5.47
Fraction particulate range ^b	0.575 - 0.796	0.0643 - 0.170	0.0330 - 0.0927	0.469 - 0.697	0.0516 - 0.136	0.0264 - 0.0720	0.384 - 0.629	0.0891 - 0.613	0.0887 - 0.814

^a 70% removal occurs instantly via initial solid-solution equilibrium partitioning. Instead of log K_D and fraction particulate value ranges, the values at $t = 0$ are indicated.

^b These ranges were calculated using data prior to the time at which 70% removal was achieved

Table I-10. Summary of Arsenic(V) Sediment Runs

Removal Approach and Output Quantity	Anoxic, AVS = 1 $\mu\text{mol/g}$			Oxic		
	Chronic ERV	Acute ERV	Chronic Cutoff	Chronic ERV	Acute ERV	Chronic Cutoff
Time to Quasi Steady State, days	11	105	10	18	38	62
Tot. As(V) Range, $\mu\text{g/L}$ ^a	4.31 - 4.34	68.5 - 110	113 - 862	0.0968 - 0.107	1.17 - 1.28	2.44 - 2.68
Diss. As(V) Range, $\mu\text{g/L}$ ^a	0.0227 - 0.0292	48.3 - 88.4	91.3 - 836	0.000173 - 0.000186	0.00289 - 0.00310	0.00875 - 0.00977
Total Settling IN, tonnes	4800	23100	25500	254	3000	6130
Total Resusp. OUT, tonnes	--- ^b	569	1450	111	1290	2610
Total Diffusion NET, tonnes ^c	-4670	-21100	-20900	0.0299	14.8	64.8
Total Burial OUT, tonnes	--- ^b	70.0	178	13.6	159	320
Water column $\log K_D$, L/kg ^a	7.01	4.41	3.85	7.57	7.43	7.26
Sediment $\log K_D$, L/kg ^a	--- ^b	0.354	0.512	7.10	6.93	6.71
Time for 70% Removal, days (Approach 1)	0.81	68.8	137	0.75	16.0	32.6
$[0.3 \times C_T(0)] / \text{Max QSS } C_T$ ^d	2.76	1.31	0.35	112	112	112

^a Ranges and average are based on data from the quasi-steady state period of the simulation

^b No particulate arsenic(V) in sediment

^c This number is the diffusive flux integrated over the *entire* simulation time. Negative diffusive flux values are directed out of the sediment and positive diffusive flux values are directed into the sediment

^d This quantity is the ratio of the total As(V) concentration representing 70% removal ($0.3 \times C_T(0)$) to the maximum total concentration during the quasi-steady-state period (Max QSS C_T). This is meant to give an indication of where sustained water column concentrations lie relative to the 70% removal benchmark.

APPENDIX J – ORGANIC CHEMICAL TABLES**Table J-1. Summary of Water Column Runs for Organic Chemicals**

Removal Approach and Output Quantity	Log K_D	Fraction particulate	Time for 70% removal, days $C_D(t)/C_T(0)$	Time for 70% removal, days $C_T(t)/C_T(0)$	Time for 70% removal, days $C_D(t)/C_D(0)$
4,4'-DDT	4.59	0.366	2.49	4.03	4.03
Hexachlorobenzene	4.10	0.160	7.83 (5.76) ¹	9.19 (6.75)	9.19 (6.74)
Heptachlor	3.88	0.102	13.2 (8.68)	14.5 (9.54)	14.5 (9.54)
Endrin	3.11	0.0190	83.3 (65.8)	85.1 (67.0)	85.1 (67.0)
Acenaphthene	2.54	0.00520	1,550 (38.8)	1,580 (39.0)	1,580 (39.0)
Lindane	2.31	0.0037	4,550 (781)	4,580 (785)	4,580 (785)

¹ Removal times were initially calculated with volatilization excluded. Times in parentheses reflect are from follow-up calculations with volatilization included.

Table J-2. Summary of Water Column Runs for Selected Organic Chemicals with Lowered Settling Velocity ^a

Removal Approach and Output Quantity	Hexachlorobenzene	Heptachlor	Endrin
1: $C_D(t)/C_T(0)$			
Time for 70% removal, days	76.5	124	566
Log K_D range ^b	4.10	3.88	3.11
Fraction particulate range ^b	0.160	0.102	0.0190
2: $C_T(t)/C_T(0)$			
Time for 70% removal, days	89.5	137	576
Log K_D range ^b	4.10	3.88	3.11
Fraction particulate range ^b	0.160	0.102	0.0190

^a Initial total concentration of organic chemical at 1 µg/L

^b 70% removal occurs instantly via initial solid-solution equilibrium partitioning. Instead of log K_D and fraction particulate value ranges, the values at t = 0 are indicated.

Table J-3. Summary of Sediment Runs for Organic Chemicals ^a

Removal Approach and Output Quantity	4,4'-DDT	Hexachlorobenzene	Heptachlor	Endrin	Acenaphthene	Lindane
Time to Quasi Steady State, days	32	46	58	114	173	---
Tot. POP Range, µg/L ^b	0.00661 – 0.00742	0.00673 – 0.00928	0.00819 - 0.0121	0.0816 - 0.169	0.00702 – 0.0169	0.436 – 0.996
Diss. POP Range, µg/L ^b	0.00419 – 0.00470	0.00565 – 0.00780	0.00736 - 0.0108	0.0800 - 0.166	0.00699 – 0.0168	0.435 – 0.993
Total Settling IN, tonnes	6.32	3.98	3.42	4.21	0.551	2.07
Total Resusp. OUT, tonnes	2.74	1.81	1.58	1.74	0.264	0.735
Total Diffusion NET, tonnes ^c	-0.0114	-0.0130	-0.0161	-0.0569	-0.0466	-0.0513
Total Burial OUT, tonnes	0.337	0.223	0.194	0.213	0.0325	0.0903
Water column log K_D , L/kg ^b	4.59	4.10	3.88	3.11	2.54	2.31
Sediment log K_D , L/kg ^b	3.95	3.60	3.40	2.67	2.11	1.88
Time for 70% Removal, days (Approach 1)	2.84	8.32	13.7	84.7	>365	>365
$[0.3 \times C_T(0)] / \text{Max QSS } C_T$ ^d	40.4	16.9	10.3	1.08	0.30	0.30

^a Initial total concentration of organic chemical at 1 µg/L

^b Ranges and average are based on data from the quasi-steady state period of the simulation

^c This number is the diffusive flux integrated over the *entire* simulation time. Negative diffusive flux values are directed out of the sediment and positive diffusive flux values are directed into the sediment

^d This quantity is the ratio of the total organic concentration representing 70% removal ($0.3 \times C_T(0)$) to the maximum total concentration during the quasi-steady-state period (Max QSS C_T). This is meant to give an indication of where sustained water column concentrations lie relative to the 70% removal benchmark.