



**FATE OF COPPER ADDED TO SURFACE WATER:  
FIELD AND MODELING STUDIES  
FINAL REPORT**

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# 1 INTRODUCTION

The Organisation for Economic Co-operation and Development (OECD) defines hazard as an inherent or intrinsic property of a substance that has the potential to cause adverse effects in a living organism. The analysis of risk relies on hazard identification as a first step but includes additional consideration of dose-response and exposure factors to assess the probability of adverse impacts under a specified set of conditions (Organisation for Economic Co-operation and Development (OECD), 2003).

Chemical substances are classified and labeled based on hazard to promote safe use of chemicals. The United Nations Globally Harmonized System (GHS) developed a harmonized classification system meant to address all types of chemicals and mixtures (United Nations, 2017). Standardized test methods are developed, e.g. by the OECD, to allow consistency in the assessment of hazard (Organisation for Economic Co-operation and Development (OECD), 2001). The GHS has been implemented under various jurisdictions. For example, the European Regulation (EC) No 1272/2008 on classification, labelling and packaging of substances and mixtures (CLP) is based on the GHS and implements some of its key provisions in the European Union (EU).

Under the GHS and EU CLP, the classification of a substance for long-term (chronic) environmental hazards depends on its long-term toxicity to aquatic organisms, degradability (or lack thereof), and potential/actual bioaccumulation of a substance. The assessment of “degradation” recognizes that, in the event of a spillage or accident, the effects of rapidly degraded substances are localized and of short duration. Therefore, less severe chronic classification entries are assigned to substances that are rapidly degraded.

The unique aspects of metal chemistry complicate the assessment of degradability as compared to that of organics. Regarding environmental degradation, the GHS (section A9.7.1.5) indicates:

"For inorganic compounds and metals, clearly the concept of degradability, as it has been considered and used for organic substances, has limited or no meaning. Rather, the

substance may be transformed by normal environmental processes to either increase or decrease the bioavailability of the toxic species... Nevertheless, the concepts that a substance... may not be rapidly lost from the environment... are as applicable to metals and metal compounds as they are to organic substances" (United Nations, 2017)

A similar statement is incorporated in the EU CLP regulation at 4.1.2.10.1 (2008). The seventh revised edition of the GHS, section A9.7.1.6, also indicates:

"Speciation of the soluble form can be affected by pH, water hardness and other variables, and may yield particular forms of the metal ion which are more or less toxic. In addition, metal ions could be made non-available from the water column by a number of processes (e.g. mineralization and partitioning). Sometimes these processes can be sufficiently rapid to be analogous to degradation in assessing chronic classification. However, partitioning of the metal ion from the water column to other environmental media does not necessarily mean that it is no longer bioavailable, nor does it mean that the metal has been made permanently unavailable" (United Nations, 2017)

Although GHS/EU CLP classification is primarily based on intrinsic properties, both the GHS (section A9.4.1.1) (United Nations, 2017) and CLP Guidance, version 5.0 (European Chemicals Agency (ECHA), 2017) recognize that "the degree of degradation depends not only on the intrinsic degradability or recalcitrance of the molecule, but also on the actual conditions in the receiving environmental compartment such as redox potential, pH, temperature, presence of suitable micro-organisms, concentration of the substance and occurrence and concentration of other substrates" (European Chemicals Agency (ECHA), 2017).

The GHS also provides detailed guidance on the tests relevant to "degradation of organic substances". For metals, only initial guidance is available (section A9.7.1.7):

“In the first instance it should be assumed that the metal ions, once in the water, are not rapidly partitioned from the water column and thus these compounds do not meet the criteria. Underlying this is the assumption that, although speciation can occur, the species will remain available under environmentally relevant conditions. This may not always be the case, as described above, and any evidence available that would suggest changes to the bioavailability over the course of 28 days, should be carefully examined. However, as a result of naturally occurring geochemical processes metal ions can partition from the water column. Data on water column residence time, the processes involved at the water – sediment interface (i.e. deposition and re-mobilization) are fairly extensive for some metals. Using the principles and assumptions discussed above, it may be possible to incorporate this approach into classification.

Such assessments are very difficult to give guidance for and will normally be addressed on a case by case approach. However, the following may be taken into account:

- a) Changes in speciation if they are to non-available forms, however, the potential for the reverse change to occur must also be considered;
- b) Changes to a metal compound which is considerably less soluble than that of the metal compound being considered” (United Nations, 2017).

Skeaff et al. (2002) have proposed an approach to assessing metal "degradability" in the context of loss from the water column using metal "half-times" (analogous to degradation half-life) as metrics and consider the permanence of the removal by looking at the extent of metal remobilization from sediment. Their work focuses on field data and they call for the development of standard set of laboratory conditions to assess partitioning half-times although no details are offered as to the nature and setup of such bench-scale tests. Following from the GHS discussed above, one potential time frame for removal is 28 days. Furthermore, in addition to "half-time" a 70% removal (i.e., 30% remaining) benchmark can be considered in analogy to the rapid degradation cutoff applied to organic substances.

The overarching goal of the research described herein was to examine the concept of removal of metal ions from the water column in the context of hazard assessment and classification in more detail, with a specific focus on copper. This assessment focused on 1) intrinsic chemical data, 2) data from field-scale studies and 3) results from a screening-level fate and transport model, TICKET-UWM. Copper removal and remobilization were assessed under environmentally relevant conditions using the field and model data in an approach consistent with that of Skeaff et al. (2002). A standard set of environmentally relevant conditions were selected for use with the TICKET-UWM. The model was validated against field data for copper removal from the water column.

## **2 FATE OF COPPER ADDED TO SURFACE WATER: INTRINSIC PROPERTIES**

Metals, by virtue of their unique chemical properties, are distinct from other elements and compounds. Trace metals such copper, zinc, and lead, as dictated by their electron configuration, possess an intrinsic propensity to react in the environment in ways that influence their bioavailability and environmental fate and, consequently, their classification. Copper, for example, interacts strongly with various functional groups present in organic matter, iron oxides (e.g. hydrous ferric oxides and goethite), and manganese oxides through surface complexation reactions (Dzombak and Morel, 1990; Flemming and Trevors, 1989; Tipping and Hurley, 1992; Tonkin et al., 2004). These interactions are largely responsible for copper's strong affinity for particulate matter and a relatively large distribution coefficient ( $K_D$ ). Furthermore, the solubility of copper in the environment can be limited through precipitation of copper hydroxides/oxides, carbonates, and, perhaps most importantly, sulfides. The ability of a given trace metal, such as copper, to form precipitates is described quantitatively with a solubility product or  $K_{sp}$ . Solubility products for each metal are unique and vary considerably between metals (Di Toro et al., 2001). Copper inherently forms highly insoluble sulfide precipitates in sulfidic environment such as anoxic sediment, as



exemplified by the extremely low  $K_{sp}$  for copper sulfide, CuS (on the order of  $10^{-39}$  to  $10^{-41}$ )<sup>1</sup> (Dyrssen and Kremling, 1990; Stumm and Morgan, 1996). Moreover, copper has been shown to have a higher affinity for sulfide than other trace metals such as nickel, cadmium, and zinc (Berry et al., 1996). The formation of copper sulfide precipitates and binding to organic matter and iron oxides limits the bioavailability of copper and that the reduced bioavailability is effectively irreversible. Affinity for particles and participation in reactions that sequester or limit bioavailability are critical to evaluation of removal from the water column and remobilization potential as further discussed below in the review of field studies and modeling analysis.

While it is true that environmental conditions in the water and sediment (e.g., pH and redox conditions) can impact the surface complexation and precipitation reactions listed above, the tendency of copper to participate in these reactions is inherent to copper, distinguishes it from other metals, and separates it from organic substances which do not undergo the same types of surface complexation and precipitation reactions.

### **3 FATE OF COPPER ADDED TO SURFACE WATER: FIELD STUDIES**

#### **3.1 Studies on Removal of Copper from the Water Column**

In this section, several field studies examining the loss of copper from the water column of different experimental systems will be assessed. Emphasis is placed upon studies in which copper is added to the water column in a "spike" load since this best resembles degradability test protocols for organic substances. The expected response is an instantaneous increase in copper concentration to the desired dose level followed by a decline in concentration as copper is lost from the water column via adsorption/precipitation/sedimentation processes, diffusion into the sediment, and washout. A single study with a continuous load of copper is assessed at the end of the water column field and laboratory study review. For a continuous load to a flow-through system, the expected water column response is an increase

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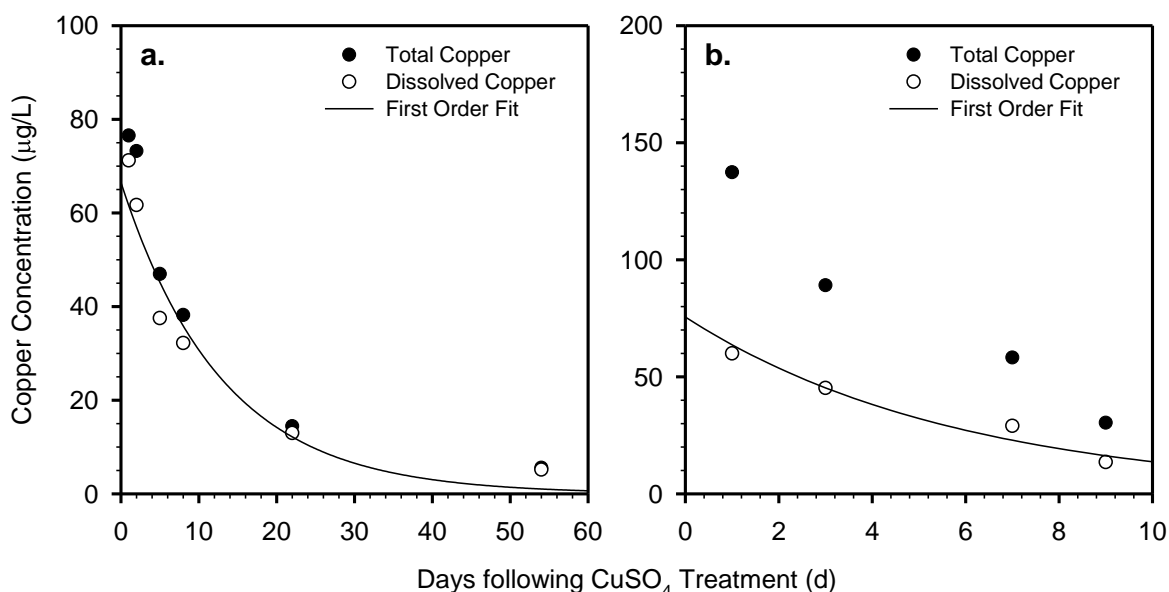
<sup>1</sup> The values in parentheses are for the  $K_{S0}$  reaction:  $\text{CuS} \leftrightarrow \text{Cu}^{2+} + \text{S}^{2-}$ . They have been estimated from  $*K_s$  values quoted in Stumm and Morgan (1996) and a range of  $K_2$  values between -17 and -19 for the reaction  $\text{HS}^- \leftrightarrow \text{S}^{2-} + \text{H}^+$ .

of copper from the initial concentration to some steady-state concentration at the influent concentration (no loss of chemical) or some fraction of the influent value (loss by reaction, settling and/or diffusion).

Van Hullebusch and colleagues assessed the fate of copper in two lakes treated with copper sulfate to control undesirable aquatic organisms (van Hullebusch et al., 2003a; Van Hullebusch et al., 2003b; Van Hullebusch et al., 2002). The first lake, Lake Courtille, is a shallow (average depth = 1.77 m), polymictic, and eutrophic lake located just outside of Guéret in the Limousin region of France. It has been dosed annually since 1998 with both aluminum sulfate and copper sulfate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) to control algal populations. In the summer of 2000, three operationally-defined fractions of copper—"truly" dissolved (10 kDa molecular weight cutoff), colloidal (less than 0.45  $\mu\text{m}$ ), and particulate copper concentrations (greater than 0.45  $\mu\text{m}$ )—were monitored near the surface and sediment interface immediately following copper sulfate addition by sampling the water column of the lake (Van Hullebusch et al., 2002). Hereafter the colloidal fraction, which contains both "truly dissolved" and colloidal copper will be referred to as simply "dissolved". The second lake, the Saint Germain les Belles Reservoir, is a mesotrophic, shallow (average depth = 1.6 m) lake also located in the Limousin region of France. In 2001, copper sulfate was added to the reservoir (van Hullebusch et al., 2003a; Van Hullebusch et al., 2003b). The operationally defined copper fractions listed above were monitored following copper sulfate application.

For both lakes, copper concentrations in the water column (near the surface) decline rapidly (Figure 1). For example, in Lake Courtille, the dissolved copper concentration at day 22 is more than 80% lower than that measured on day 1. Similarly, for Saint Germain les Belles Reservoir, the day 9 dissolved copper concentration is more than 75% lower than that measured on day 1. First-order decay fits to the data (lines in Figure 1) suggest half-time of approximately 9 days for Lake Courtille and approximately 4.1 days for Saint Germain les Belles Reservoir. As discussed above, removal of metal from the water column occurs by various processes. These include processes that transfer the metal to the sediment layer such as sorption to settling particulate matter and direct diffusion into the sediment. Dilution associated with relatively uncontaminated lake inflow can also decrease metal concentrations following dosing. The contribution of

dilution to the water column half-time can be assessed using water body's hydraulic detention time. The detention times for Lake Courtille and Saint Germain les Belles Reservoir are > 1 year and 0.25 year, respectively. The calculated half-time associated with dilution only are approximately 250 days for the lake and 63 days for the reservoir. These values are considerably larger than the half-times observed from the data. This indicates that dilution from inflow is not the major metal removal process. The primary removal mechanism is loss to the sediments via settling and/or diffusion<sup>2</sup>.



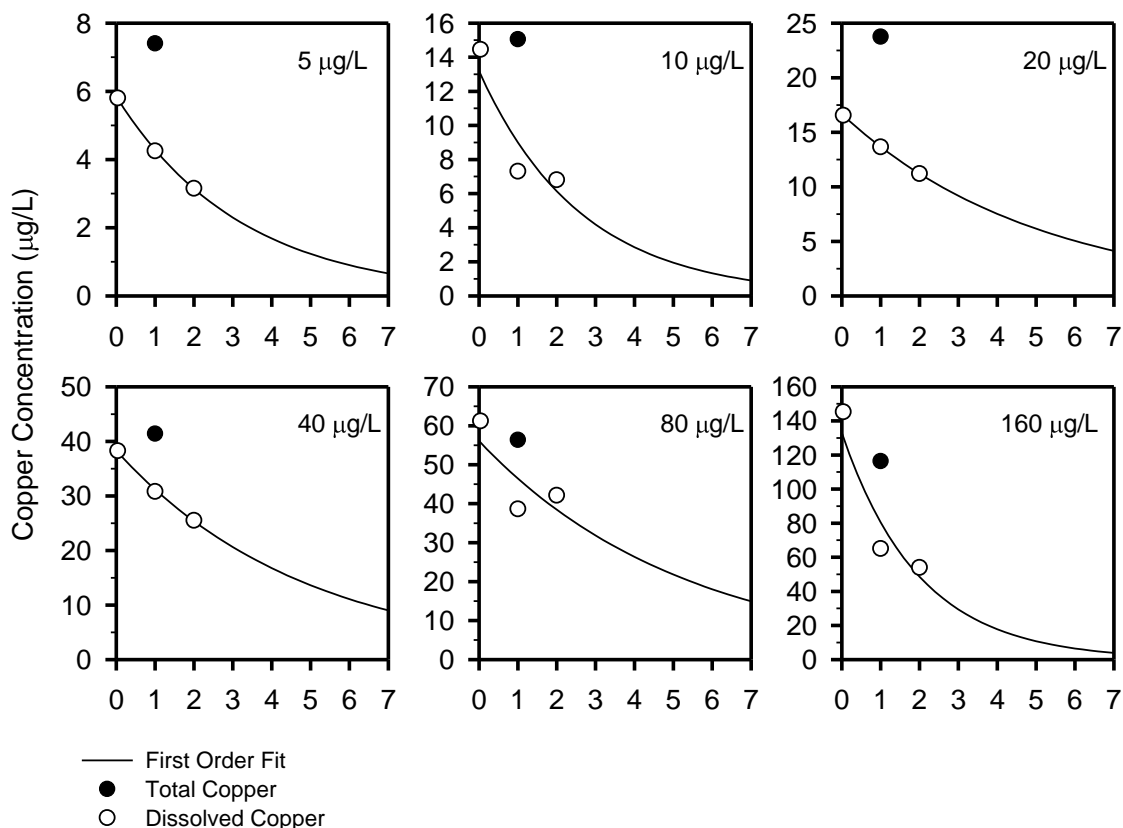
**Figure 1:** Time series of total (closed circles) and dissolved (< 0.45 µm, open circles) copper concentrations in the water column of a) Lake Courtille and b) St. Germain les Belles reservoir. The solid line is a first-order decay (i.e.,  $C = C_0 \exp[-kt]$ ) fit through the dissolved copper data.

A microcosm study was undertaken at the Fraunhofer Institute for Molecular Biology and Applied Ecology (IME) to study the effects of continuous copper exposure on aquatic organisms (Schäfers, 2003). A series of microcosms (110 cm long by 96 cm wide) were prepared with a 15- to 20-cm deep sediment layer and an overlaying water column of approximately 750 L. The depth of the water column was 0.76

<sup>2</sup> It has been assumed, for the purposes of the analyses conducted in this report, that copper added to these relatively shallow lakes mixes instantaneously throughout the water column. It is possible that some small portion of the observable copper decline in the surface water samples soon after application is due to non-instantaneous mixing of the added copper down into the deeper portions of the water column. This phenomenon, however, is expected to be minor and short-lived relative to combined removal effects of settling and diffusion into the sediment.

meters. The water and sediment were collected from a manmade pond near Schmalleberg-Oberkirchen, Germany. The microcosms were dosed with copper sulfate to achieve six nominal concentrations of copper: 5, 10, 20, 40, 80, and 160  $\mu\text{g/L}$ . The experimental setup included duplicates (i.e., two microcosms for each nominal copper concentration). Samples for total copper analysis were taken one day after dosing. Samples for dissolved copper analysis were taken at different intervals after the initial dosing including 24 and 48 hours after the initial treatment.

The researchers noted loss of dissolved copper from the water column of the microcosms. They found that supplemental copper sulfate additions every 2 - 3 days after the initial dosing were required to maintain copper concentration near the nominal values. After initial dosing, but prior to the first concentration adjustment, samples were collected from each microcosm's water column and analyzed for dissolved and total copper. Dissolved copper data indicated a marked decrease over time (Figure 2). Estimated copper half-times for the six nominal concentrations ranged between 1.4 and 3.7 days. The microcosms are not flow-through systems so the observed removal is not attributable to washout. Li et al. (2012) also had difficulty maintaining copper concentrations in their experiments because of loss from the water column.



**Figure 2:** Time series of measured total (closed circles) and dissolved (< 0.45 μm, open circles) copper in microcosms at various nominal copper concentrations. Plotted data are the arithmetic average of measurements from duplicate microcosms. The solid line is a first-order decay (i.e.,  $C = C_0 \exp[-kt]$ ) fit through the dissolved copper data.

Smolyakov and colleagues have investigated the fate of copper and other trace metals in surface water using 3-meter deep mesocosms constructed out of either transparent polyethylene film or black film mounted near the shore of the Novosibirskoye Reservoir in Russia (Smolyakov et al., 2010a; Smolyakov et al., 2010b). The reservoir water is moderately hard (Durfur and Becker, 1964) based on a hardness of approximately 70 mg/L as CaCO<sub>3</sub> (Smolyakov et al., 2010a; Smolyakov et al., 2010b). The natural suspended particulate matter (SPM) concentration and pH values are approximately 15 mg/L and 8.5., respectively. In one experiment, two separate mesocosms--one exposed to sunlight and one kept in the dark--were dosed with Cu(NO<sub>3</sub>)<sub>2</sub> to achieve initial an initial copper concentration of 500 μg/L. After 20 days, the mesocosms were dosed a second time to once again achieve a copper concentration of 500 μg/L. Copper removal in both the light and dark mesocosms was rapid. After 19 days, dissolved copper

concentrations decreased to 5% (light) and 13% (dark) of initial values. Removal rates for the second dosing were generally similar (Smolyakov et al., 2010b). The authors estimated total copper first order removal rate constant values ranging between 0.080 and 0.12 day<sup>-1</sup> for the first and second dose in the dark and light mesocosms. These rate constant values correspond to partitioning half-times of approximately 5.7 to 8.7 days. Comparable rapid copper removal was observed at a higher copper loading value of 1000 µg/L (Smolyakov et al., 2010a). In these companion experiments, floating aquatic plants (water hyacinth) were added to the mesocosms. Uptake of copper by these plants may have contributed to the copper removal. After approximately 11 days, dissolved copper concentrations decreased to 17% of the initial value and total copper decreased to 27% of the initial value. Given the elevated water pH and total copper concentrations associated with these studies, it is likely that some fraction of the particulate copper in water column was present precipitated copper hydroxide or copper oxide. Speciation calculations made using water chemistry provided in Smolyakov et al. (2010a) and Smolyakov et al. (2010b) confirm that the solubility product of copper (hydr)oxide was exceeded. This result highlights the concept that direct precipitation of trace metals (e.g., as hydroxides, oxides, and carbonates) in addition to sorption, can transfer metal to the particulate phase and result in loss from the water column via settling.

Haughey et al. (2000) assessed the fate of copper added to Lake Mathews, a drinking water reservoir in Riverside, California (USA). They found that only 20% of the copper that was exported from the reservoir during the 70-day period following the dosing. Copper added to the water column was rapidly converted to particulate forms and transported to the sediment. The time required for the total copper concentration to decline to approximately 70% of the peak observed concentration following dosing was approximately 9.5 days.

Liu et al. (2006) assessed the fate of copper applied to catfish ponds as an algacide. Results from a pilot-scale experimental pond (29 m long by 14 m wide by 0.8 - 0.9 meters deep) that greater than 90% of the copper added to the water column became strongly sorbed to particles within 2 hours. Within 2 days

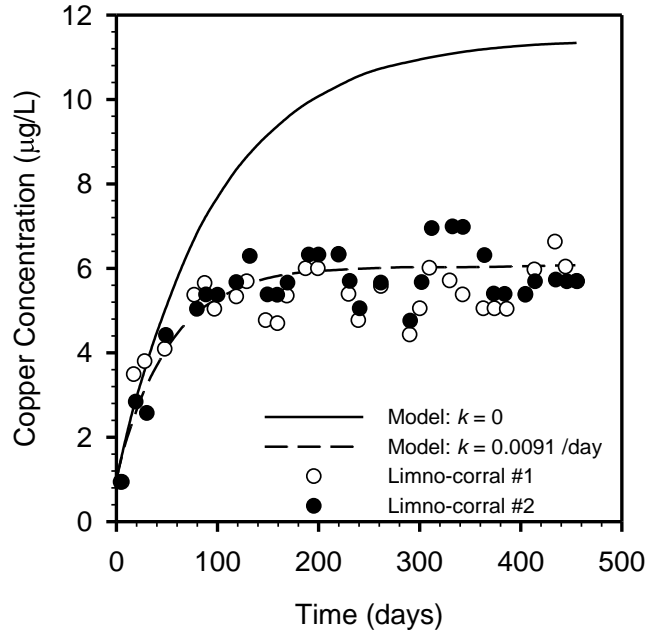
of dosing, more than 99% of the copper had been transferred to the sediment. Approximate times to reach 70% removal are 0.9 days for dissolved copper and 0.5 days for total copper.

Effler et al. (1980) examined the impact of copper sulfate treatment on Cazenovia Lake, hardwater alkaline lake in New York (USA). For dosing events in the July, August, and September of 1977, total copper concentrations immediately following application were approximately 9.2, 14, and 7.9, respectively. After pooling the data for the three events, the approximate time for 70% removal of total copper was estimated to be 33 days.

The MELIMEX (MEtal LIMnological EXperiment) study was undertaken to study the effects of increased metal loading (relative to natural levels) on lacustrine biota, assess the accumulation and distribution of metals in the food chain, and investigate the speciation, distribution and fate of added metals (Gächter, 1979). The experiment was conducted in Lake Baldegg (Lucerne, Switzerland) using large enclosures (12 meters in diameter and 10 meters deep) to isolate portions of the lake water column and sediment for study. Inflow to and outflow from the enclosures (limno-corrals) was controlled with a series of pumps. From April 1977 to June 1978, copper was added continuously to two of the three limno-corrals (one served as a control) via inflow to the enclosures at a concentration approximately equal to the maximum legally tolerated concentration of 160 nM (10.2 µg/L) at a flow rate of 11.5 m<sup>3</sup>/d (equivalent to a copper load of approximately 0.043 kg/yr) (Gächter, 1979). The actual influent concentration of 11.4 µg/L was approximately ten times higher than the initial copper concentration in the enclosures of 1.3 µg/L. Periodically during the study, the water column was sampled for several water quality parameters included dissolved copper.

As expected for continuous copper addition in a flow-through system, dissolved copper increases asymptotically to a steady-state water column concentration of approximately 6 µg/L (Figure 3). Model results from (Di Toro et al., 2001) with (dashed line) and without (solid lines) a first-order decay reaction show clearly the impact of metal removal processes. The steady-state water column concentration with

removal ( $6.2 \mu\text{g/L}$ ) is almost half the value without removal ( $11.8 \mu\text{g/L}$ ). The first order removal rate constant of  $0.0091 \text{ day}^{-1}$  corresponds to a half-time of approximately 76 days.



**Figure 3:** Time series of dissolved copper data from MELIMEX enclosure study. Data points are measured data from Gächter and Geiger (1979). The lines are model results reproduced from Di Toro et al. (2001) with and without a first order removal process included

Table 1 summarizes the water column copper removal in terms of 70% removal times. These range from approximately 0.5 days to 130 days. In general, removal rates are relatively rapid with the exception of the value associated with the MELIMEX experiment. This lake was characterized by a very low particle settling velocity ( $0.2 \text{ m/d}$ , which is more than 10 times below the value used in the EUSES system), a suspended solids concentration that is almost 3 times lower ( $5.9$  versus  $15 \text{ mg/L}$ ), and a low copper concentration in the inflow. It must also be noted that this study was conducted with a relatively low copper loading ( $11.8 \mu\text{g/L}$ ) compared to other studies. The reason for the outstanding behavior for this lake is discussed further below.



**Table 1: Summary of Estimated 70% Removal Times**

System <sup>a</sup>	70% removal time (days) <sup>b</sup>
Lake Courtille	16 (d)
St. Germain les Belles	7.1 (d)
IME Microcosms	6.0 (d)
Novosibirskoye Reservoir	10 (d) 13 (t)
Lake Mathews	9.5 (t)
Catfish Ponds	0.9 (d) 0.5 (t)
Cazenovia Lake	33 (t)
MELIMEX	130 <sup>c</sup>
TICKET-UWM (Empirical $K_D$ )	4.7
TICKET-UWM (Calculated $K_D$ )	1.6

Notes:

- a Sources: Lake Courtille and St. Germain les Belles: van Hullebusch et al. (2003a), Van Hullebusch et al. (2003b), Van Hullebusch et al. (2002); IME Microcosms: Schäfers (2003); Novosibirskoye Reservoir: Smolyakov et al. (2010a); Smolyakov et al. (2010b); Lake Mathews: Haughey et al. (2000); Catfish Ponds: Liu et al. (2006); Cazenovia Lake: Effler et al. (1980); MELIMEX: Di Toro et al. (2001); Gächter (1979)
- b Numbers in parentheses denote whether the removal basis was dissolved copper (d) or total copper (t)
- c This number was computed based on a first-order removal rate constant (see Section 3.1).

### 3.2 Studies on Resuspension of Copper from Sediments

The studies on trace metal remobilization were reviewed by Skeaff et al. (2002). These include results for copper (Table A-1 in Appendix A). While some remobilization of copper is indicated in some studies, Skeaff et al. (2002) conclude that the net flux of metals is in general directed toward the sediment. Data from more recent studies provide additional insight into the behavior of copper specifically. These studies evaluate copper remobilization at the laboratory and field scale and assess potential copper release from sediments in both lotic and lentic systems and under both oxic and anoxic conditions.

Simpson et al. (1998) conducted 8-hour oxidation studies with synthesized amorphous metal sulfides ("model metal sulfide phases") and resuspension experiments with natural sediment. Metal concentrations (including copper) were assessed using bulk sediment measurements of acid-volatile sulfide (AVS) and simultaneously extracted metal (SEM). Their results indicated that in the absence of Fe(III), the amounts of SEM (Cu) extracted from model copper sulfides--interpreted as oxidative release--is only 20% for CuS and 40% for Cu<sub>2</sub>S. This finding provides evidence that pure copper sulfide phases possess resistance to oxidative release of copper. For natural sediment, the authors state that the observed increase in SEM(Cu) is not indicative of release due to oxygenation of the system, but an analytical artifact associated with an Fe(III)-catalyzed oxidation mechanism that is favorable under the low pH conditions with the SEM extraction procedure. The authors concluded that iron sulfide (FeS) and manganese sulfide (MnS) phases, if present in excess over metal sulfide phases, can buffer bioturbation-induced trace metal sulfide oxidation. They state that trace metals associated with FeS may be released upon oxidation of the FeS carrier phase. However, they conclude that additional studies are required to assess the potential for metal release during short-term exposure to oxic conditions. Several of the studies described below address this issue.

Sundelin and Eriksson (2001) studied mobility, bioavailability, and toxicity of metals in sediment from the inner archipelago of Stockholm. Specifically, they investigated the influence of oxygenation and bioturbation on metal mobility and bioavailability using un-spiked, metal-contaminated sediments. Sediments were incubated in a flow-through system with brackish water (7 ‰) for three to seven months both with and without bioturbation. They observed decreases in total sulfur which they attributed to the oxidation of sulfides as the sediment samples were exposed to oxic overlying water. Sediment copper concentrations remained constant in the surface sediment despite the effects of oxygenation and bioturbation. Furthermore, copper levels in the outflow water from the incubation chambers were not elevated compared to controls. Copper was not bioaccumulated in amphipods added to the experimental

systems. These findings provide evidence that in natural, un-spiked sediments, copper release from sulfide and other sediment binding phases during exposure to oxic conditions is very limited.

Teuchies et al. (2011) assessed the impact of increased dissolved oxygen concentrations on copper and other metal dynamics in the Zenne River in Belgium. The goal was to determine whether higher dissolved oxygen resulting from the initiation of wastewater treatment plant operations could turn the sediments into metal sources as opposed to sinks. In experimental setups mimicking anoxic, oxic, and oxic with high turbidity systems, they observed lower AVS in the oxic systems compared to the anoxic system and significantly high dissolved copper in the oxic systems relative to the anoxic system. However, sulfide oxidation and copper release were not readily observable in the field despite the large increase in DO associated with the start-up of a wastewater treatment plant. In fact, available data from a station on the Zenne River ([www.vmm.be/geoview](http://www.vmm.be/geoview); Station Number 346500) indicate an increased frequency of non-detects for dissolved copper after the plant start-up data. Dissolved copper was below the detection limit for all samples taken at this station from 2010 onward. Copper release from sediment was not able to sustain indefinitely the elevated water column concentrations occurring before wastewater treatment began. Slow oxidation rates and/or high dilution by river water are mentioned by the authors as ways metal remobilization are obscured in the field relative to what is observed in the laboratory.

van der Geest and León Paumen (2008) exposed two soils (unpolluted and polluted) from a floodplain on the River Waal for a period of 10 weeks to continuous flow of natural river water under both depositional and erosional conditions. Changes in redox conditions (Eh measurements), copper availability (diffusive gradient film measurements) and copper uptake by organisms were quantified and colonization, succession and functioning of the microphytobenthic community were evaluated. The authors found no significant relationship between sediment redox state and bioavailability within a vertical profile of a single sediment type. The polluted sediment did not show marked signs of impairment with respect to indicators such as colonization, growth and succession of algal communities. Accumulation of copper in *Tubifex*

worms was only slightly different from levels in worms placed in unpolluted sediment. This study provides an example of how low copper bioavailability can exist following significant changes in redox status.

A pair of recent studies assessed copper behavior in sediments exposed to a relatively oxic water column (Costello et al., 2014; De Jonge et al., 2012). De Jonge et al. (2012) monitored changes in redox status, sediment geochemistry, and metal bioavailability over a 54-day period in experimental flow through set-ups containing metal-contaminated sediment and overlying surface water with dissolved oxygen at either 40% or 90% of saturation. Over the study period, the Eh of the upper sediment layer increased markedly and the AVS decreased by 70% in the treatment with high oxygen. Labile copper concentrations in pore water did not increase over time, which supports the conclusion that it remained bound to the sediment. Furthermore, after 54 days, no significant release of copper to the overlying water was found. The authors attribute the limited metal release to the overlying water to the presence of remaining excess AVS and additional metal binding by iron and manganese (hydr)oxides and organic carbon.

Costello et al. (2014) studied copper dynamics during sediment aging. Sediments from the Ocoee River (Benton, TN, USA) and Dow Creek (Midland, MI, USA) were spiked with copper, incubated for 28 days under a nitrogen atmosphere, and then aged for 213 days in recirculation flumes where the water column water well-oxygenated. Over the course of the study, oxygen penetration into the sediment was evident and AVS declined in the surface layer of the sediment that initially had high AVS. Although the total amount of sediment copper did not change during the study, the pore water and labile copper concentrations rapidly decreased. The authors attribute the loss of pore water copper to binding to iron oxides. They also noted a shift in copper associated with hydrous ferric oxides to more crystalline ferric oxides. In general, older sediment was found to be less toxic than freshly-spiked sediment. Finally, the authors found very little copper was released from the sediment to the overlying water. Copper efflux rates from sediment range from 2.2 to 20  $\mu\text{g}/\text{m}^2/\text{hr}$  (Ocoee) and from 4.4 to 57  $\mu\text{g}/\text{m}^2/\text{hr}$  (Dow). The corresponding amount of copper lost from the sediment on an annual basis is less than 0.7% for the Ocoee River sediment and less than 3% for the Dow Creek sediment.

Haughey et al. (2000) estimate the rate of copper release from the sediment of Lake Mathews at  $620 \mu\text{g}/\text{m}^2/\text{d}$  or  $26 \mu\text{g}/\text{m}^2/\text{hr}$ . This is orders of magnitude lower than indicated in batch desorption kinetic experiments conducted with sediment. It is, however, generally consistent with the efflux rates observed by Costello et al. (2014). Based on the observation that a significant portion of sediment copper is associated with the oxidizable and carbonate-bound, the authors conclude that significant release of copper from the key binding phases in sediment would require large changes in pH and redox conditions.

Liu et al. (2006) performed a mass balance analysis using the catfish pond data they collected. They found that essentially all the copper added to the ponds ended up in the sediment where bioturbation helped transport it to the deeper sediment layers.

van den Berg et al. (2001) assessed the potential for dredging-related mobilization of metals in a freshwater tidal marsh area in the lower delta of the rivers Rhine and Meuse in the Netherlands. The authors found that, while the release of dredge spoils to the water column was manifested as an observable increase in the metal content of the SPM, the dissolved metal concentrations in the water column were not markedly affected by the dredging activities.

Fetters (2013) studied mobilization of zinc, copper, cadmium, lead, nickel and chromium during short-term (i.e., four-hour) resuspension events for both freshwater and marine sediments. Metal-contaminated sediment from Lake Depue (LD) in Illinois (USA) and Portsmouth Naval Shipyard (PNS) in Maine (USA) were resuspended in sediment flux exposure chambers (SeFEC). Sediments from both locations had elevated copper levels with concentrations ranging between  $364$  and  $575 \mu\text{g}/\text{g}$ . Upon resuspension, dissolved copper concentrations in the water column of this experiment remained below the practical limit of quantification of  $8 \mu\text{g}/\text{L}$ . In the PNS experiments, resuspension resulted in minimal release of dissolved metals. Dissolved copper was detected initially at a concentration of  $4 \mu\text{g}/\text{L}$  and then was below detect limits for the other two samples taken during the 4-hour resuspension. For another PNS sediment sample (MS04), dissolved copper was not detected during the four-hour resuspension.

## **4 FATE OF COPPER ADDED TO SURFACE WATER: A MODEL STUDY**

### **4.1 Description of the Model**

Unit World Models (UWMs) are screening level models used to assess the fate and effects of chemicals through simultaneous consideration of chemical partitioning, transport, reactivity, and bioavailability (Mackay, 1979, 1991; Mackay and Paterson, 1991). A UWM for metals (TICKET-UWM) 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 (Farley et al., 2011). Additional details on the TICKET-UWM are provided in the Appendix B.

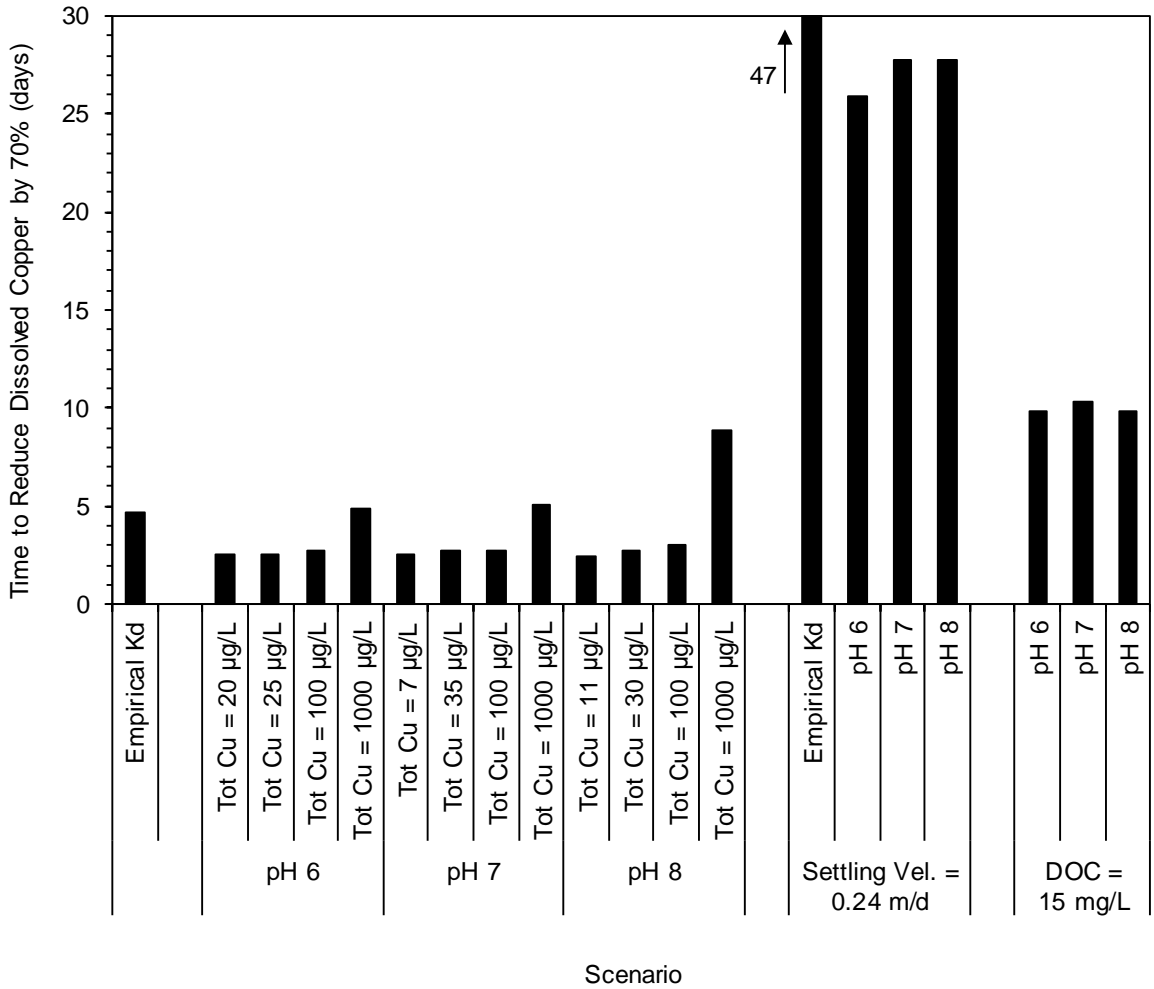
### **4.2 Application of the TICKET-UWM to the EUSES Model Lake: Water Column**

Application of fate and transport models, such the TICKET-UWM, allows detailed examination of the chemical and physical processes responsible for metal transport and fate under standardized conditions. Once established the standardized test environment or generalized lake can be further used to examine parameter sensitivities and a compare removal and remobilization rates among different metals and other substances.

A generalized lake scenario based upon the EUSES model was developed to assess metal partitioning half-times and remobilization potential in a standardized environment. Hereafter this generalized lake will be referred to as the EUSES Model Lake. The goal is to provide a computational method to (i) assess the "degradability" of metals ion (copper ions from copper salts in the present case) and (ii) ranking the hazard of metals relative to themselves and organics.

The physical and chemical parameters of the EUSES Model Lake were based on Globally Harmonized System of Classification and Labelling of Chemicals (GHS) Transformation/Dissolution (T/D) testing protocols (United Nations, 2011), risk assessment technical guidance documents (European Chemicals Bureau, 2003), and CLP testing guidance and the EUSES model (EC, 2004). Additional details regarding model parameters are provided in the Appendix B.

Metal sorption to SPM was described in the model by either 1) specifying water and sediment distribution coefficient ( $K_D$ ) values based on empirical data from a copper partition coefficient review (Heijerick and Van Sprang, 2005) ("Empirical  $K_D$ " values, see Appendix B) or 2) having the model calculate the water and sediment  $K_D$  values at each time step with a WHAM VII speciation calculation ("Calculated  $K_D$ " values). The EUSES model lake simulations were made using both Empirical and Calculated  $K_D$  values (Figure 4). For the simulations with the Empirical  $K_D$  values, total and dissolved copper concentrations decrease to half of their initial values approximately 2.7 days after copper addition and decrease to 30% of their initial values approximately 4.7 days after dosing (Figure 4 and Figure B-2 in Appendix B). After 28 days, the dissolved copper concentration in the water column was 0.22  $\mu\text{g/L}$  which is approximately 160 times lower than the starting concentration of 35  $\mu\text{g/L}$ . For the Calculated  $K_D$  simulation at pH 7 with the same initial copper concentration, log  $K_D$  values vary between 4.85 and 4.88 in the water column. WHAM VII predicts that greater than 51 % of the copper will be bound to particles. This is somewhat greater than the value from the Empirical  $K_D$  simulation of 31%. Consequently, copper removal from the water column is faster than in the Empirical  $K_D$  simulation (Figure 4 and Figure B-2 in Appendix B). Dissolved copper concentration decreases to 30% of its initial value in 2.75 days. Detailed model output from these simulations is presented in Table B-3 and Table B-4 in Appendix B.



**Figure 4:** Results of EUSES Model Lake water column analysis.

Sensitivity analysis simulations were performed to assess:

1. the effect of copper loading with initial total copper concentrations, and the two chronic classification cutoff values of 0.1 mg/L, and 1 mg/L (European Chemicals Agency (ECHA), 2011);
2. the effect of water chemistry was using the pH 6, 7, and 8 water chemistries from the GHS T/D testing protocols (United Nations, 2011) (see Appendix B for details);
3. the impact of decreasing the settling velocity from the EUSES Model Lake value of 2.5 m/d to 0.24 m/d (lower end of the POC range from (Burns and Rosa, 1980)); and
4. the impact of increasing DOC 2 mg/L to 15 mg/L to reflect the 10:1 DOC to POC ratio found in some lakes (Wetzel, 2001).



Model-predicted times required to reduce initial dissolved copper concentrations by 70% vary to a limited extent (range = 2.5 to 8.9 days) in the simulations where initial total copper concentration and water chemistry are varied (Figure 4). Modeled-predicted 70% removal times increase with an increase in DOC from 2 mg/L to 15 mg/L, but the change is relatively small. The formation of copper-DOC complexes reduces the distribution coefficient, decreases the fraction of copper sorbed to particles and, consequently, reduces the rate of water column copper removal via settling. The increase in removal times associated with the settling velocity decreased from the EUSES value of 2.5 m/d to 0.24 m/d is relatively large compared to the changes associated with variation of other parameters (Figure 4). The maximum 70% removal time in the sensitivity analysis of 47 days occurs for the scenario using the Empirical  $K_D$  value and a settling velocity of 0.24 m/d. Detailed model output from the sensitivity analysis simulations is presented in Table B-4, Table B-5, and Table B-6 in Appendix B.

#### **4.3 Application of the TICKET-UWM to the EUSES Model Lake: Sediment**

Important chemical processes in the sediment include complexation to inorganic ligands and organic ligands—including dissolved organic carbon (DOC)—in the sediment pore water; sorption to metal-binding phases on sediment particles such as particulate organic carbon (POC), hydrous ferric oxides (HFO), and hydrous manganese oxides (HMO); and precipitation as metal carbonate and metal sulfide solids. Research has shown that the reaction of copper with sulfide in the form of acid volatile sulfide (AVS) to form insoluble copper sulfide is a key process that mitigates the bioavailability and toxicity of this trace metal in sediments and influences its fate in natural systems (Berry et al., 1996; Di Toro et al., 2001; Di Toro et al., 1992). Settling represents the primary metal source to the sediment layer. Resuspension and diffusion are the transport processes associated with metal remobilization from the sediment to the water column. In the model, burial of metal from the active sediment layer of the sediment is an irreversible process that removes metal from the system.

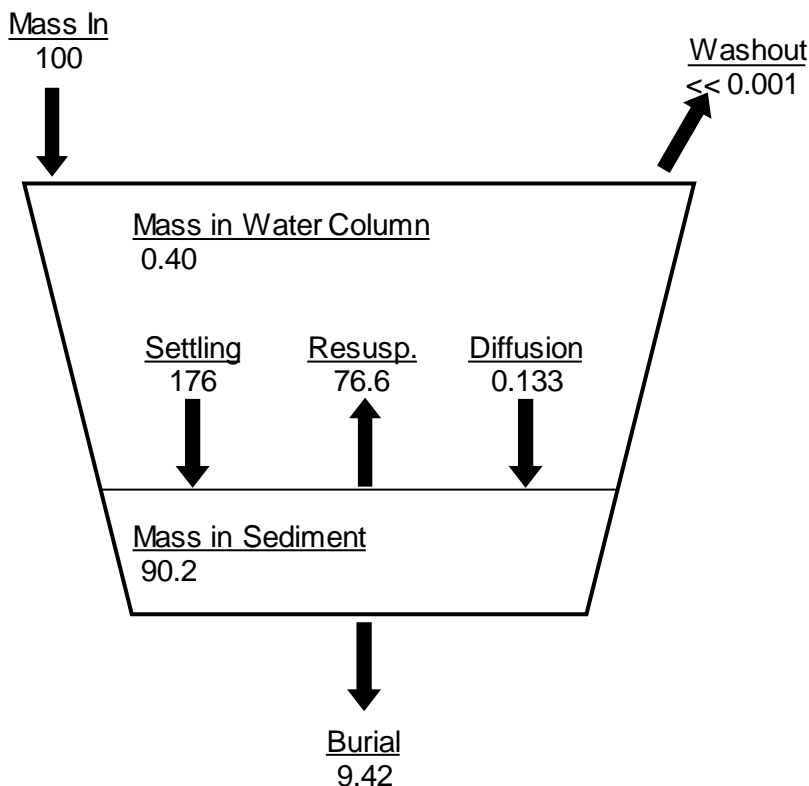
A series of model simulations were performed to assess copper speciation in sediment and the potential for copper remobilization from the sediment to the water column. Sediment simulations were 1-

year in duration and examined various chemistries and redox conditions (see Appendix B for details of the sediment simulation approach and parameters used). Key findings from the model simulations are summarized below.

#### **4.3.1 Anoxic sediment simulations**

Based on model results from day 20 of the simulation, almost all copper in the sediment is present in the particulate phase. Of the very small amount dissolved in the porewater, more than 99% of the copper is present as copper-DOC complexes. Ionic copper ( $\text{Cu}^{2+}$ ) makes up less than 0.1% of the dissolved copper. Particulate copper speciation in the sediment simulation is dominated the copper-sulfide solid  $\text{CuS(s)}$ . A more detailed summary of speciation data is provided in Table B-8 (Appendix B).

At the end of the 1-year simulation, greater than 99% of the copper added to the system is in the sediment or has been buried as  $\text{CuS(s)}$  (Figure 5). The magnitude of the settling, resuspension, and diffusion terms indicate that, based on the transport parameters in the model (Table B-7 in Appendix B), copper mass transfer between the water column and sediment is dominated by transport on solids. Diffusion plays a minor role, but integrated over the 1-year simulation (i.e. hereafter referred to as the integrated diffusive flux), it is directed into the sediment layer. This is a consequence of the highly insoluble nature of the  $\text{CuS(s)}$  precipitate and the associated very low pore water copper concentration. Resuspension does transfer copper back to the water column but this is counterbalanced by the effect of settling. Anoxic simulation results with  $\text{Cu}_2\text{S(s)}$  were almost identical to those with  $\text{CuS(s)}$  (i.e., the quantities present in Figure 5). One difference between the two cases is that the model-predicted sediment  $\log K_D$  for  $\text{Cu}_2\text{S(s)}$  (13.5) is considerably lower than the value for  $\text{CuS(s)}$  (16.0).



**Figure 5:** Mass balance results for TICKET-UWM sediment simulation. Mass values from the model have been normalized to an input mass of 100 kg. The relevant conditions of the simulation are as follows: Anoxic sediment with AVS = 9.1  $\mu\text{mol/g}$ , total initial water column Cu concentration of 35  $\mu\text{g/L}$ .

#### 4.3.2 Oxic sediment simulations

Pore water copper speciation is predicted to be dominated by copper-DOC complexes. The model indicates that greater than 95% of the particulate copper is associated with POC; 4.3% is associated with HFO and about 0.36% is associated with HMO. The model-predicted  $\log K_D$  for the sediment layer of 3.53 is considerably lower than the anoxic case value of 16.0, which is because no  $\text{CuS(s)}$  or  $\text{Cu}_2\text{S(s)}$  are formed in the oxic scenario. A more detailed summary of speciation data is provided in Table B-8.

Mass balance results from the oxic simulations are very similar to those for the anoxic simulation (Figure 5) with the exception of the diffusive flux. The oxic simulation copper diffusive flux is directed out of the sediment, but only results in the transfer of 1.5% of the total copper load back to the water column.

### 4.3.3 Sensitivity Analyses

A series of sensitivity analyses were conducted to assess effect of (i) low AVS (1  $\mu\text{mol/g}$  versus base case value of 9.1  $\mu\text{mol/g}$ ), (ii) variation in water column/sediment pH (6/7, 7/7, and 8/7.5 versus the base case combination of 7.07/7.56), (iii) low sediment solids concentration (150  $\text{g/L}_{\text{bulk}}$  versus the base case value of 500  $\text{g/L}_{\text{bulk}}$ ), (iv) variation in hardness (factor of 2 about the base value of 516  $\text{mg/L}$  as  $\text{CaCO}_3$ ), (v) variation in resuspension rate (0.1, 1, 3.2, and 10 times the default rate of 2.44  $\text{cm/yr}$ ), and (vi) variation in copper loading (initial copper concentrations of 10, 100, and 1000  $\mu\text{g/L}$ ).

Despite minor differences in the model results, the key findings of greater than 70% removal from the water column in 28 days, sustained dissolved water column concentrations much less than that representing 70% removal, and strong copper binding in the sediment through precipitation as copper sulfide are observed across all sensitivity analysis simulations. The integrated diffusive flux is directed into the sediment, with the exception of the simulation with the highest initial copper concentration and the low AVS concentration. In that simulation, the AVS binding capacity of the sediment was exceeded by the very high copper concentration. A more detailed discussion of these sensitivity analysis simulations can be found in Appendix B.

### 4.3.4 Empirical $K_D$ simulations

These indicate total and dissolved copper concentrations at the end of the 1-year simulation that are more than 30 times lower than the 70% removal concentration. Although the water column  $\log K_D$  was greater than the sediment  $\log K_D$ , the integrated diffusive flux was directed into the sediment.

In summary, detailed sediment model simulations indicate that in anoxic sediments, precipitation of copper sulfide significantly enhances copper binding in the sediment. Consequently, the diffusive copper flux integrated over 365 days was directed into the sediment. Furthermore, for all test conditions considered—including oxic sediments and sediments with high resuspension rates—water column copper concentrations resulting from sediment feedback were markedly lower than that corresponding to 70%

removal. The detailed sediment model simulations provide evidence that the potential for copper remobilization from sediment is limited and sequestration in the sediment is effectively irreversible.

## 5 SYNTHESIS OF FIELD AND MODEL DATA

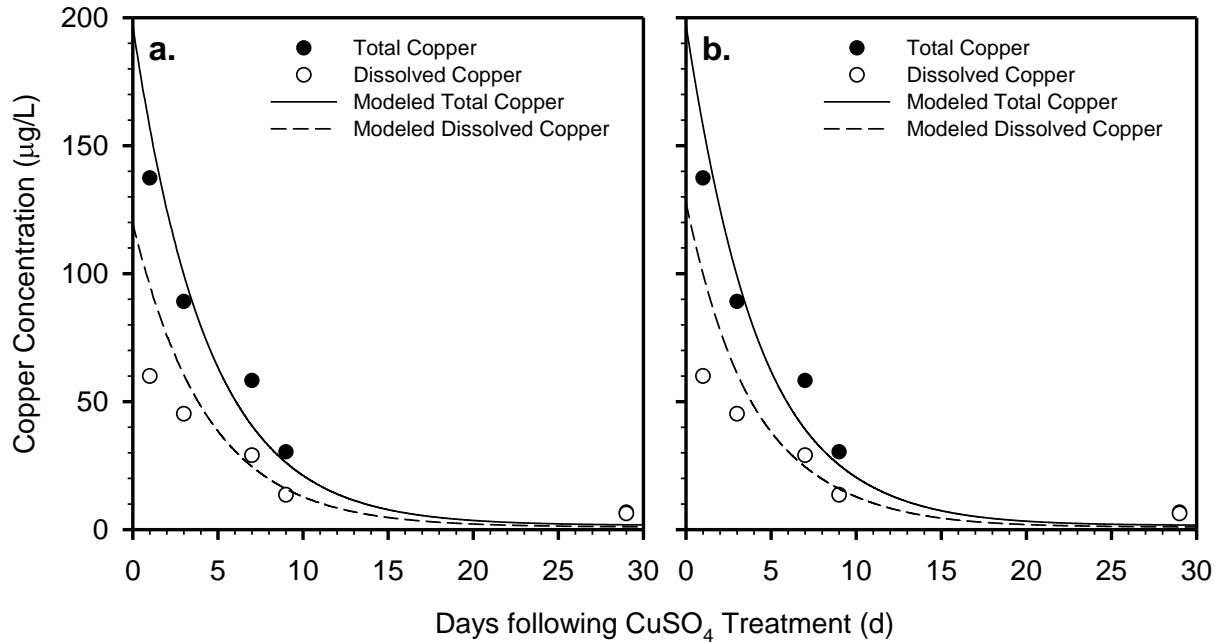
### 5.1 Modeling of the Field Study at the Saint Germain les Belles Reservoir

Water column copper concentration data from the Saint Germain les Belles Reservoir (van Hullebusch et al., 2003a; Van Hullebusch et al., 2003b) were used to test the ability of the TICKET-UWM to describe copper fate in lakes. Metal sorption to SPM was described in the model by either 1) specifying a distribution coefficient ( $K_D$ ) based on measurements in the water column and sediment ("Empirical  $K_D$ " values) or 2) having the model calculate the  $K_D$  value at each time step with a WHAM VII speciation calculation ("Calculated  $K_D$ " values). The water column Empirical  $K_D$  was based on measurements in the Saint Germain les Belles Reservoir. The sediment Empirical  $K_D$  was based the copper partition coefficient review of Heijerick and Van Sprang (2005). Additional details related to these model simulations can be found in Appendix B.

For the Empirical  $K_D$  simulation with a log  $K_D$  of 4.56 in the water column, a settling velocity of 0.90 m/d resulted in an optimal fit to the total copper data (Figure 6a). The copper behavior at day 29 is influenced by resuspension caused by heavy rains. Since this acute resuspension event is not included in the model it is understandable that the model results do not pass through this point.

For the Calculated  $K_D$  simulation, water column log  $K_D$  values increased over the 30-day simulation from 4.49 to 4.57. This highlights the non-linear, metal concentration dependent sorption predicted by the WHAM speciation model within TICKET-UWM. The model-calculated log  $K_D$  values are generally consistent with the average measured value of approximately 4.56. As a result, the calibrated settling velocity associated with the Calculated  $K_D$  simulation (0.96 m/d) is similar to that from the Empirical  $K_D$  simulation (0.90 m/d) (Figure 6b).

This application of TICKET-UWM demonstrates that the model can describe copper removal from the surface water with reasonable accuracy.



**Figure 6:** Time series of measured (points) and modeled (lines) copper in St. Germain les Belles reservoir. Model results are from simulation with water column and sediment  $K_D$  values a) specified at the measured/empirical values (surface water:  $10^{4.56}$  L/kg; sediment:  $10^{4.39}$  L/kg) and b) calculated at each time step using a WHAMVII speciation calculation.

## 5.2 Removal of Copper from the Water Column

Water column copper data from lakes, microcosms, and mesocosms provide an expanded picture of copper removal from the water column. A summary of water column removal times, expressed as 70% removal times, are presented in Table 1. Removal times vary from approximately 0.5 to 33 days, with one exception of 130 days. The work of Santschi (1984) provides a means of understanding the variation seen in the removal times. Assuming removal of metals by settling particles in a well-mixed water column, an expression for the first order removal rate ( $k$ ) for total metal (dissolved plus particulate) is as follows:

$$k = \frac{S \times K_D}{H \times (1 + K_D m)} \quad (1)$$

where  $S$  is the particle flux (equal to the settling velocity  $v_s$  times the suspended particulate matter (SPM) concentration  $m$ ),  $K_D$  is the distribution coefficient (assumed constant),  $H$  is the average depth, and  $m$  is the SPM concentration. The variables in this equation are the key parameters impacting loss from the water column via settling. There are two important limiting cases based on the value of  $K_D m$ . For  $K_D m \gg 1$ , Equation 1 simplifies to the following:

$$k = \frac{S}{H \times m} = \frac{v_s}{H} \quad (2)$$

In this limiting case, essentially all the metal is present on the particles and the metal removal rate depends only at the rate at which the particles settle out water column via settling. For  $K_D m \ll 1$ , Equation 1 simplifies to the following:

$$k = \frac{S \times K_D}{H} = \frac{v_s \times m \times K_D}{H} \quad (3)$$

Here the metal removal rate depends on the rate at which the particles settling out of the water column ( $v_s/H$ ) and the extent to which the metal is associated with the particles ( $K_D m$  or the ratio of metal on the particles to metal in the dissolved phase).

Equation 1 can be recast to provide characteristics times (either half-time or time for 70% removal):

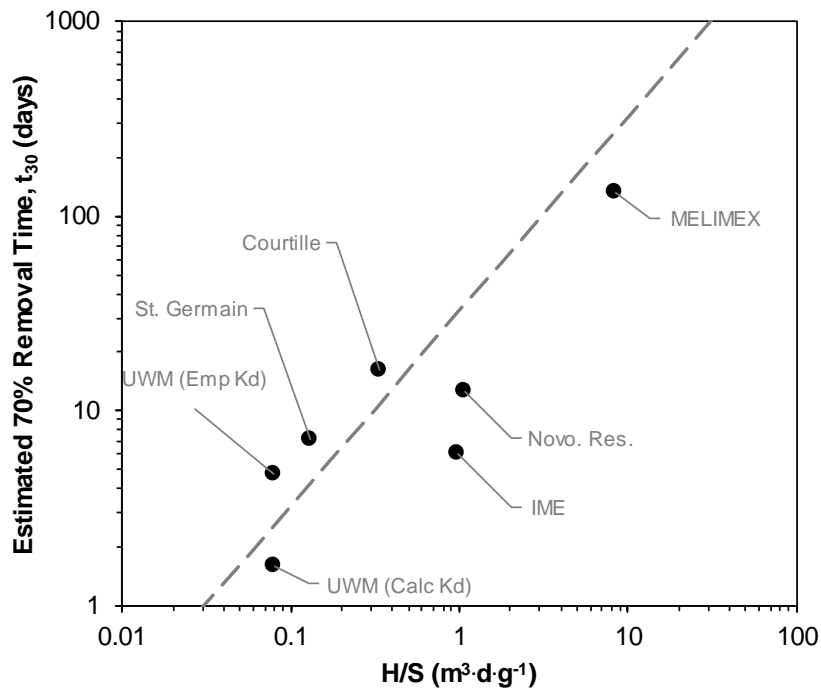
$$t_x = \ln\left(\frac{100}{x}\right) \frac{H \times (1 + K_D m)}{S \times K_D} \quad (4)$$

$$t_x = \ln\left(\frac{100}{x}\right) \frac{H \times m}{S} = \ln\left(\frac{100}{x}\right) \frac{H}{v_s} \quad \text{for } K_D m \gg 1 \quad (5)$$

$$t_x = \ln\left(\frac{100}{x}\right) \frac{H}{S \times K_D} = \ln\left(\frac{100}{x}\right) \frac{H}{v_s \times m \times K} \quad \text{for } K_D m \ll 1 \quad (6)$$

where  $x$  is the percent remaining (i.e., 50 for half-time and 30 for 70% removal). Plots of removal time  $t_x$  versus  $H/S$ —the analog of the plots of Santschi (1984)—are useful in interpreting the data in Table

1. Plots of the 70% removal time ( $t_{30}$ ) versus  $H/S$  are shown in Figure 7 for systems which were dosed with copper and for which the information was available to calculate  $t_{30}$  and  $H/S$ <sup>3</sup>. For most lakes in Figure 7, the  $t_{30}$  value was calculated using data on the reduction in copper concentration with time. For the MELIMEX dataset, a theoretical  $t_{30}$  value was calculated from the first order removal rate constant of 0.0091 day<sup>-1</sup>. Also plotted is a theoretical line that was generated from Equation 4 using average  $m$  and  $K_D$  values from the seven systems (Appendix C).



**Figure 7:** Time required for removal of 70% of the added copper to natural lakes and enclosures, plotted against the ratio of lake depth ( $H$ ) over the settling flux of suspended particulate matter ( $S$ ). The dashed line is a theoretical line generated using Equation 4 and average  $m$  and  $K_D$  values of 10.5 mg/L and  $10^{4.78}$  L/kg, respectively.

The data generally follow the behavior predicted by Equation 4 (Figure 7). Removal times increase with increasing  $H/S$  values. Intuitively, one would expect long removal times required for deeper lakes (higher  $H$ ) and lakes with lower particle fluxes to the sediment (lower  $S$ ). Most lakes in this study, including

<sup>3</sup> Particle flux ( $S$ ) data was not available for Lake Mathews, the catfish ponds, or Cazenovia Lake. These waterbodies therefore do not appear in Figure 7.



the TICKET-UWM generalized lake scenarios, have such  $H/S$  values that the time required to attain 70% removal of copper from the water column is less than 30 days. In contrast, the MELIMEX lake is very specific and different from the other lakes, with considerably greater depth and lower particle flux ( $S$ ) values compared to the other lakes (Appendix C). These observations also set it apart from the TICKET-UWM generalized lake scenario.

Some of the scatter in  $t_{30}$  data is caused by differences in metal partitioning behavior ( $m$  and  $K_D$ ) between the studied systems. However, it should be noted that the equations in this section were derived considering only metal loss from settling. Diffusion into the sediment and washout are additional processes that serve to decrease metal concentrations in the water column. Furthermore, for shallow systems, direct adsorption to the sediment layer has been indicated as an additional metal removal mechanism (Bird and Evenden, 1996; Nyffeler et al., 1986).

### **5.3 Resuspension of Copper from Sediments**

Collectively, the field data assembled on copper behavior in sediments indicate that while release/remobilization of sediment copper to the water column is possible, there is data to support that the extent and impact of the release is limited. Some studies in marine/estuarine systems have observed metal release, but the overall impact on water column dissolved copper concentrations is minor. Teuchies et al. (2011) observed a release of dissolved copper upon aeration in laboratory systems, but the effect was not observable in the field. There has been evidence presented that once copper precipitates with sulfide in sediment, it is not readily released upon exposure to oxic conditions (Costello et al., 2014; De Jonge et al., 2012; Simpson et al., 1998; Sundelin and Eriksson, 2001). This may be due to the buffering effect of iron and manganese oxides when these are present in excess (Simpson et al., 1998). The work of Costello et al. (2014) highlights the importance of iron oxides as binding phases for copper in oxic sediment. Further, it demonstrates that, while the present study focuses on lentic systems, long-term sequestration of copper also occurs in the sediment of lotic systems. In the extreme short-term resuspension cases associated with dredging and prop wash events, dissolved copper concentrations in the water column were not markedly

affected (Fetters, 2013; van den Berg et al., 2001) supporting the conclusion of minimal release of copper to the dissolved phase. The detailed sediment simulations conducted with TICKET-UWM further add to the weight of evidence that indicates minimal copper remobilization from the sediment. The available modeling and field data support the hypothesis that this is related to copper precipitation in sediment with sulfide ligands. In summary, due to the strong binding of copper in sediments, oxidation of anoxic sediments or resuspension events do not generally lead to significant remobilization of copper from sediments.

## 6 CONCLUSIONS

Field studies and modeling studies provide evidence of copper removal from the water column. Dissolved copper is sorbed in the water column and transported to sediments where it is sequestered. This process generally represents a transfer of copper to less bioavailable and less toxic forms. Field studies and modeling studies presented above further support the removal of copper from the water column by natural processes, which is a surrogate to degradation of organic substances in the context of hazard assessment and classification.

The TICKET-UWM, used as a screening tool, can be parameterized to assess the transport and fate of metals (including copper) under various water chemistry conditions and within differing surface water systems. The selection of standardized model parameters, much like the standardized conditions of biodegradation tests for organic substances, is a critical element. The EUSES surface water system is a logical choice, since it has been used widely in the EU as a generalized system to assess the fate of chemicals. While most of the discussion in this paper has focused on copper, the model can simulate other metals and even organics. Thus, it can be applied to metals and other substances for which field data are not readily available and facilitates comparison of transport, fate and toxicity between metals substances under standard conditions for hazard ranking.

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thanks Eric Van Hullebusch for sharing additional information from his Lake Courtille and St. Germain Les Belles datasets.

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## APPENDIX A – TRACE METAL REMOBILIZATION REVIEW TABLE

**Table A-1: Metal Remobilization from Studies Discussed in Skeaff et al. (2002)**

Source	Water Body	Key Finding as Summarized in (Skeaff et al., 2002)
Diamond et al. (1990)	Enclosures in Perch Lake in Ontario, Canada	Assuming iron and cobalt are representative of first row transition metals, one would expect water-to-sediment rate constants for copper to be in the range of 200 - 300 times the reverse.
Xue et al. (1997)	Lakes Sempach and Greifen in Switzerland	No copper remobilization from Lake Greifen; partial copper release from Lake Sempach likely enhanced by artificial oxygenation. Copper released redeposited with precipitated iron/manganese oxides.
van den Berg et al. (1999)	River Meuse in the Netherlands	Degree of trace metal (including copper) remobilization less than 2% amount deposited.
Hunt and Smith (1983)	Seawater microcosms using sediments from Narragansett Bay, Rhode Island, USA	Observed a release of copper and other metal from contaminated sediments, but cautioned that extrapolation to natural systems would require consideration of additional factors.
Zwolsman et al. (1997)	Scheldt estuary in the Netherlands and Belgium.	Dissolved copper and other metals were mobilized in estuary through the reoxidation of sulfides in suspended matter upon encountering the higher oxygen concentrations associated with the lower estuary.
Shaw et al. (1990)	Sites of the coast of California, USA	Metal transport to and from the sediment is complex; sample location showing Cr, Co, Ni, and Cu release had concentrations lower than 2 µg/L
Klinkhammer et al. (1982)	two deep ocean sites in the central equatorial Pacific	Copper flux from sediment to overlying water was 5-10 greater than flux to sediment; however, copper concentrations near the sediment interface were low (0.03 - 0.45 µg/L)

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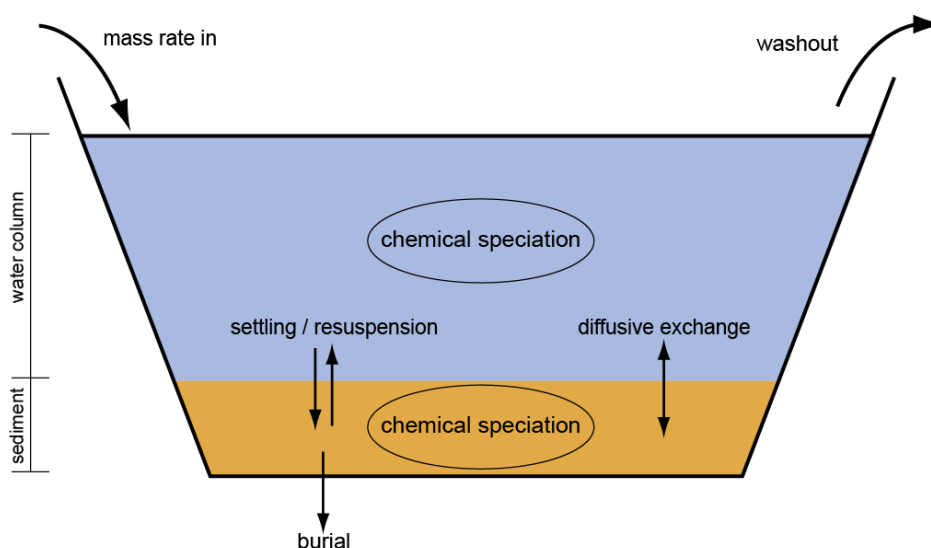
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## APPENDIX B – TICKET-UWM SIMULATIONS

### BACKGROUND INFORMATION ON THE TICKET-UWM

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, 1991; Mackay and Paterson, 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 B-1) (Farley et al., 2007; Farley et al., 2011).



**Figure B-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). The model domain consists of a single oxic water column layer and a single sediment layer. Specific processes considered in the UWM for

Metals in Lakes (hereafter referred to as the TICKET-UWM) include (i) dissolved and particulate phase transport between the overlying water and sediment; (ii) metal binding to inorganic ligands, dissolved organic carbon (DOC) and particulate organic carbon (POC) (using information from WHAM (Tipping, 1993, 1994; Tipping and Hurley, 1992), hydrous ferric oxide (HFO) (Dzombak and Morel, 1990), and hydrous manganese oxide (HMO) (Tonkin et al., 2004); (iii) metal binding to biological receptors using information from the Biotic Ligand Model (BLM) (Di Toro et al., 2001; Santore et al., 2001); (iv) metal precipitation as (hydr)oxides, carbonates, sulfates, and sulfides using information from MINEQL+ software (Schecher and McAvoy, 2003); (v) dissolution kinetics for metal powders, massives, concentrates; average-annual cycling of organic matter and sulfide production in the lake; and (vi) simplified HFO and HMO cycles.

## **DETAILS OF EUSES MODEL LAKE TICKET-UWM SIMULATIONS**

### *Water Column Simulations*

The water chemistries for the EUSES Model Lake TICKET-UWM simulations were based on directives in Annex IV of the Guidance on the Application of the CLP Criteria (European Chemicals Agency (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 in Table A10.1 from Annex 10.

Copper addition was modeled in the TICKET-UWM simulations as a single instantaneous load of a soluble copper salt (e.g.,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ). 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 the addition of copper as a salt, therefore, represents a worst-case scenario for metal release and persistence in the water column.

There exist three potential approaches for assessing copper removal in the model:

1. Copper 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 copper salt concentration (i.e. nominal or added concentration) is set equal to a relevant value. Based upon the assumption of equilibrium speciation (partitioning), the added copper immediately partitions between the suspended particles and solution phase resulting in an initial dissolved copper concentration less than the initial copper added to the computational system. This initial instantaneous copper removal from the soluble phase to the particles is counted toward the percent removal. After the initial removal, copper removal continues (non-instantaneously) as the finite amount of total copper added to the system maintains its equilibrium with suspended particles and these particles continually settle to the sediment bed. 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 copper concentration is set equal to a relevant value, and the removal of total copper (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  $t$ ,  $C_{Tot}(t)$ , by the initial total metal concentration,  $C_{Tot}(0)$ . This approach is conservative in that it assumes that copper on particles is equally bioavailable as dissolved copper. Hereafter this will be referred to as Approach 2.
  
3. The initial total copper concentration is set at the relevant value, and the removal of dissolved copper is tracked. According to this approach, removal is calculated by dividing the dissolved copper concentration at time  $t$ ,  $C_{Diss}(t)$ , by the initial dissolved copper concentration,  $C_{Diss}(0)$ . Hereafter this will be referred to as Approach 3.

Approaches 1 and 3 are more consistent with Annex IV of the CLP regulation, since they focus on soluble metal. This report focuses on simulation results from Approach 1 but includes results from Approaches 2 and 3 as well. If slow enough, the kinetics of the adsorption processes may influence the copper removal rate for Approach 1. However, this analysis is beyond the scope of the current work and is a subject for future investigations. Available data on adsorption rates in natural system indicate considerable variation in the timeframe required for copper adsorption. Estimated equilibration times (i.e.,  $4[k_f' + k_b]^{-1}$ ) range from a couple of hours to as much as three weeks (Gee and Bruland, 2002; Herzl et al., 2003; Millward et al., 1992).

The initial total copper concentration (i.e. the spiking concentration) in the water column was the values contained in Table B-1.

**Table B-1: Summary of Initial Copper 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

All concentration in units of  $\mu\text{g/L}$

The remaining TICKET-UWM input parameters with their basis/references were obtained from the following sources:

- European Chemicals Agency REACH implementation guidance document summarizing EUSES model parameters (European Chemicals Agency (ECHA), 2010); and
- The RIVM EUSES report (EC, 2004).

A summary of TICKET-UWM parameters used for the generalized lake environment calculations is shown in Table B-2. The chemical composition associated with the three water chemistries in Table B-2 is generally consistent with summaries prepared from EU monitoring databases (ARCHE, 2013).

**Table B-2: TICKET-UWM Input for the EUSES Model Lake Simulations**

Parameter	Value		
	EUSES Model Lake		
Volume, m <sup>3</sup>	3.6 × 10 <sup>9</sup> <sup>a</sup>		
Surface area, km <sup>2</sup>	1200 <sup>a</sup>		
Average water depth, m	3		
Residence time, yr	300		
Settling rate, m/d	2.5 <sup>b</sup>		
Burial rate, cm/yr	0.3		
Resuspension rate, cm/yr	2.44		
Diffusive exchange, cm/day	0.24 <sup>a,c</sup>		
Sediment $f_{oc}$	0.05		
Sediment solids conc., g/L <sub>bulk</sub>	500		
Depth of active sediment, cm	3		
AVS, μmol/g <sub>dry</sub>	0.77 <sup>d</sup>		
Sediment HFO, mg/kg	0 (anoxic sediment)		
Sediment HMO, mg/kg	0 (anoxic sediment)		
Initial Cu conc., μg/L as Cu	35		
Initial Sed Cu conc., μg/g	0		
Suspended solids, mg/L	15 <sup>e</sup>		
Suspended solids foc	0.1 <sup>e</sup>		
POC, mg/L	1.5		
DOC, mg/L	2.0 <sup>f</sup>		
Water column pH	6.09 <sup>f</sup>	7.07 <sup>f</sup>	8.00 <sup>f</sup>
Sediment pH	6.09	7.07	8.00
Alkalinity, mg/L as CaCO <sub>3</sub>	3.85	7.47	37.2
Calcium, mg/L	8.0	32.1	80.1
Magnesium, mg/L	1.2	4.9	12.1
Sodium, mg/L	1.8	3.4	18.0
Potassium, mg/L	0.3	1.2	3.02
Sulfate, mg/L as SO <sub>4</sub>	4.8	19.2	47.9
Chloride	14.5	57.8	145

<sup>a</sup> Data from EUSES model lake (EC, 2004; European Chemicals Agency (ECHA), 2010). Surface area and volume values quoted refer to a regional scale assessment. They do not influence the removal simulations.

<sup>b</sup> Calculated using the settling velocity, suspended solids concentration, sediment bulk solid concentration, and the burial (net sedimentation) rate shown in the table using a steady-state solids balance (Chapra, 1997).

<sup>c</sup> EUSES pore water side mass transfer coefficient. Mass transfer resistance is assumed to be all on the sediment side (Di Toro et al., 1981).

<sup>d</sup> 10<sup>th</sup> percentile AVS concentration for a Flemish dataset (Vangheluwe et al., 2005)

<sup>e</sup> From (European Chemicals Bureau, 2003)

<sup>f</sup> Water chemistries for the three pH values were taken from Annex 10 of the Globally Harmonized System of Classification and Labelling of Chemicals (United Nations, 2011).

The resuspension rate (Table B-2) 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:

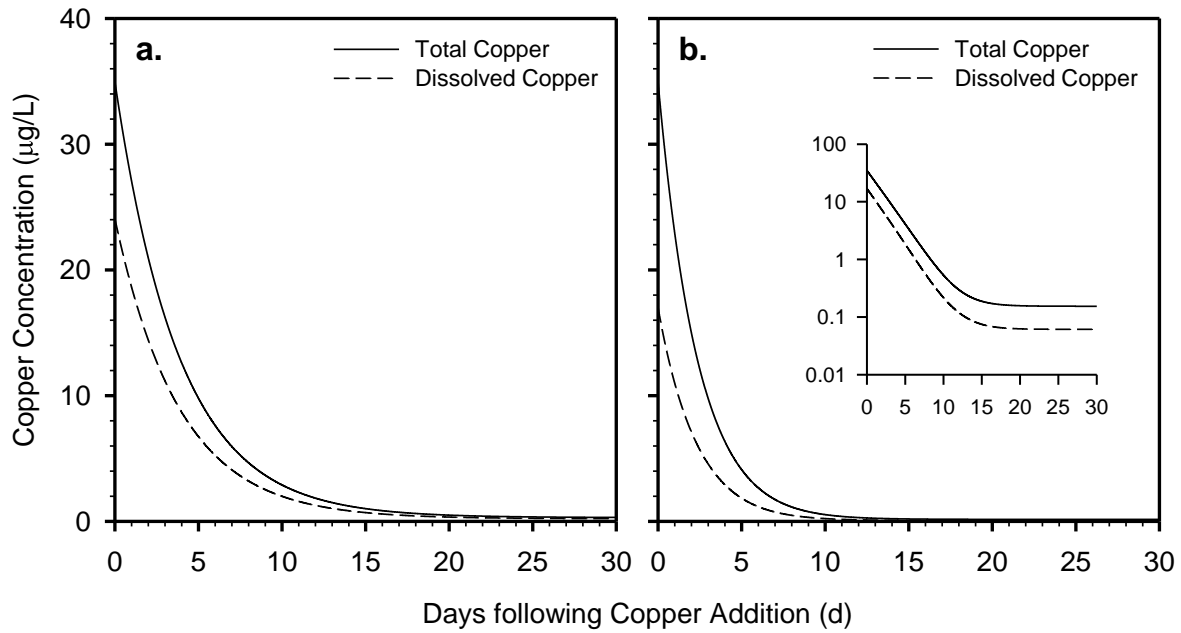
$$v_r = v_s \frac{m}{m_a} - v_b \quad (\text{B-1})$$

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.

It should be noted that the EUSES Model Lake is prescribed to have a sediment compartment that is 10% aerobic. At present, TICKET-UWM simulations utilize a single sediment layer and cannot directly reproduce this condition. The redox state (oxic or anoxic) of the sediment layer in the TICKET-UWM is specified by the user. This selection determines the sorption/precipitation reactions included in the simulation. For the generalized lake environment calculations, an anoxic sediment layer was used with the AVS concentration set to the 10<sup>th</sup> percentile value from EU monitoring data (Vangheluwe et al., 2005) (additional information from: <http://echa.europa.eu/copper-voluntary-risk-assessment-reports> [environment/Risk Characterization/Chapter 3.3.7.1.3.]). This reflects a level of conservatism with respect to the amount of copper capable of being bound by sulfide in sediments.

Simulations were made using empirical  $K_D$  values and  $K_D$  values calculated by WHAM VII. For the Empirical  $K_D$  simulation, the surface water and sediment log  $K_D$  values were specified as 4.48 and 4.39 based on the copper partition coefficient review of Heijerick and Van Sprang (2005). For the Calculated  $K_D$  simulation,  $K_D$  values at each time step were generated with WHAM VII. Copper binding to HFO and HMO in the water column was not considered.

Based on the suspended solids concentration of 15 mg/L and  $\log K_D$  of 4.48, approximately 31% of the copper added to the water column was bound to suspended particles for the Empirical  $K_D$  simulation for the EUSES Model Lake. The decrease of copper in time for the Empirical  $K_D$  and Calculated  $K_D$  simulations is shown below in Figure B-2. Summaries of EUSES Model Lake TICKET-UWM simulation results are presented in Table B-3 through Table B-6 below.



**Figure B-2:** Time series of total and dissolved copper for the EUSES Model Lake with  $K_D$  a) specified at empirical values (surface water  $\log K_D$ : 4.48; sediment  $\log K_D$ : 4.39) and b) calculated at each time step using a WHAM VII speciation calculation.



**Table B-3: Summary of EUSES  
Model Lake Empirical  $K_D$  Simulation  
Results**

<b>Removal Approach and Output Quantity</b>	<b>Result from Model</b>
<b>1: <math>C_D(t)/C_T(0)</math></b>	
Time for 70% removal, days	3.25
Log $K_D$ range <sup>b</sup>	4.48
Fraction particulate range <sup>b</sup>	0.312
<b>2: <math>CT(t)/CT(0)</math></b>	
Time for 70% removal, days	4.72
Log $K_D$ range <sup>b</sup>	4.48
Fraction particulate range <sup>b</sup>	0.312
<b>3: <math>CD(t)/CD(0)</math></b>	
Time for 70% removal, days	4.72
Log $K_D$ range <sup>b</sup>	4.48
Fraction particulate range <sup>b</sup>	0.312

<sup>a</sup> 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.

<sup>b</sup> These ranges were calculated using data prior to the time at which 70% removal was achieved.

**Table B-4: Summary of EUSES Model Lake Calculated  $K_D$  Simulation Results for Different Water Chemistries and Copper Loadings**

Removal Approach and Output Quantity	pH = 6.09		pH = 7.07		pH = 8.00	
	20 µg/L	25 µg/L	7 µg/L	35 µg/L	11 µg/L	30 µg/L
<b>1: <math>C_D(t)/C_T(0)</math></b>						
Time for 70% removal, days	0.922	0.961	0.918	1.11	1.01	1.34
Log $K_D$ range <sup>a</sup>	4.89 - 4.91	4.87 - 4.90	4.89 - 4.91	4.85 - 4.86	4.85 - 4.89	4.77 - 4.81
Fraction particulate range <sup>a</sup>	0.537 - 0.548	0.529 - 0.542	0.539 - 0.549	0.513 - 0.521	0.514 - 0.538	0.470 - 0.492
<b>2: <math>C_T(t)/C_T(0)</math></b>						
Time for 70% removal, days	2.69	2.71	2.68	2.83	2.72	2.98
Log $K_D$ range <sup>a</sup>	4.89 - 4.93	4.87 - 4.93	4.89 - 4.94	4.85 - 4.88	4.85 - 4.94	4.77 - 4.86
Fraction particulate range <sup>a</sup>	0.537 - 0.561	0.529 - 0.559	0.539 - 0.568	0.513 - 0.531	0.514 - 0.567	0.470 - 0.523
<b>3: <math>C_D(t)/C_D(0)</math></b>						
Time for 70% removal, days	2.57	2.57	2.54	2.75	2.48	2.75
Log $K_D$ range <sup>a</sup>	4.89 - 4.93	4.87 - 4.92	4.89 - 4.94	4.85 - 4.88	4.85 - 4.94	4.77 - 4.86
Fraction particulate range <sup>a</sup>	0.537 - 0.560	0.529 - 0.558	0.539 - 0.567	0.513 - 0.530	0.514 - 0.564	0.470 - 0.518

<sup>a</sup> These ranges were calculated using data prior to the time at which 70% removal was achieved.

**Table B-4. Continued**

Removal Approach and Output Quantity	pH = 6.09		pH = 7.07		pH = 8.00	
	100 µg/L	1,000 µg/L	100 µg/L	1,000 µg/L	100 µg/L	1,000 µg/L
<b>1: <math>C_D(t)/C_T(0)</math></b>						
Time for 70% removal, days	1.37	4.16	1.35	4.37	1.99	--- a
Log $K_D$ range <sup>a</sup>	4.75 - 4.80	4.21 - 4.46	4.75 - 4.81	4.18 - 4.45	4.58 - 4.69	5.82
Fraction particulate range <sup>a</sup>	0.458 - 0.489	0.194 - 0.303	0.459 - 0.492	0.186 - 0.295	0.361 - 0.425	0.908
<b>2: <math>C_T(t)/C_T(0)</math></b>						
Time for 70% removal, days	3.00	5.52	3.00	5.72	3.51	1.85
Log $K_D$ range <sup>b</sup>	4.75 - 4.86	4.21 - 4.56	4.75 - 4.85	4.18 - 4.55	4.58 - 4.77	5.19 - 5.82
Fraction particulate range <sup>a</sup>	0.458 - 0.522	0.194 - 0.353	0.459 - 0.516	0.186 - 0.345	0.361 - 0.469	0.701 - 0.908
<b>3: <math>C_D(t)/C_D(0)</math></b>						
Time for 70% removal, days	2.73	4.85	2.74	5.05	3.07	8.86
Log $K_D$ range <sup>a</sup>	4.75 - 4.85	4.21 - 4.51	4.75 - 4.85	4.18 - 4.50	4.58 - 4.75	4.42 - 5.82
Fraction particulate range <sup>a</sup>	0.458 - 0.517	0.194 - 0.327	0.459 - 0.514	0.186 - 0.320	0.361 - 0.458	0.281 - 0.908

<sup>a</sup> These ranges were calculated using data prior to the time at which 70% removal was achieved.

**Table B-5: Summary of EUSES Model Simulation Results for Settling Velocity of 0.24 m/d**

Metal Removal Approach and Output Quantity	Empirical $K_D$	Calculated $K_D$		
		pH = 6.09	pH = 7.07	pH = 8.00
<b>1: <math>C_D(t)/C_T(0)</math></b>				
Time for 70% removal, days	32.6	9.73	11.2	13.5
Log $K_D$ range <sup>a</sup>	4.48	4.87 - 4.90	4.85 - 4.86	4.77 - 4.81
Fraction particulate range <sup>a</sup>	0.312	0.529 - 0.543	0.513 - 0.521	0.470 - 0.492
<b>2: <math>C_T(t)/C_T(0)</math></b>				
Time for 70% removal, days	47.3	27.4	28.6	30.1
Log $K_D$ range <sup>a</sup>	4.48 - 4.48	4.87 - 4.93	4.85 - 4.88	4.77 - 4.87
Fraction particulate range <sup>a</sup>	0.312 - 0.312	0.529 - 0.559	0.513 - 0.531	0.470 - 0.525
<b>3: <math>C_D(t)/C_D(0)</math></b>				
Time for 70% removal, days	47.3	26.0	27.7	27.8
Log $K_D$ range <sup>a</sup>	4.48 - 4.48	4.87 - 4.93	4.85 - 4.88	4.77 - 4.86
Fraction particulate range <sup>a</sup>	0.312 - 0.312	0.529 - 0.558	0.513 - 0.531	0.470 - 0.519

<sup>a</sup> These ranges were calculated using data prior to the time at which 70% removal was achieved.

**Table B-6: Summary of EUSES Model Simulation Results with DOC increased from 2 to 15 mg/L**

Metal Removal Approach and Output Quantity	Calculated $K_D$		
	pH = 6.09	pH = 7.07	pH = 8.00
<b>1: <math>C_D(t)/C_T(0)</math></b>			
Time for 70% removal, days	8.43	9.08	8.67
Log $K_D$ range <sup>a</sup>	4.07 - 4.08	4.02 - 4.06	4.02 - 4.08
Fraction particulate range <sup>a</sup>	0.149 - 0.151	0.135 - 0.146	0.137 - 0.152
<b>2: <math>C_T(t)/C_T(0)</math></b>			
Time for 70% removal, days	9.79	10.4	10.0
Log $K_D$ range <sup>a</sup>	4.06 - 4.08	4.02 - 4.06	4.02 - 4.08
Fraction particulate range <sup>a</sup>	0.148 - 0.151	0.135 - 0.148	0.137 - 0.152
<b>3: <math>C_D(t)/C_D(0)</math></b>			
Time for 70% removal, days	9.82	10.3	9.87
Log $K_D$ range <sup>a</sup>	4.06 - 4.08	4.02 - 4.06	4.02 - 4.08
Fraction particulate range <sup>a</sup>	0.148 - 0.151	0.135 - 0.148	0.137 - 0.152

<sup>a</sup> These ranges were calculated using data prior to the time at which 70% removal was achieved.

### *Sediment Simulations*

The water column in the TICKET-UWM is represented as being oxic with a negligible sulfide concentration. In accordance with the equilibrium mass action law, any copper sulfide solid resuspended from the sediment layer to the water column immediately dissolves, releasing copper to re-equilibrate between the settling particles the dissolved phase in the water column. Since the immediate redistribution supplies dissolved copper in the water column, the model calculations are closer to a worst-case scenario for dissolved copper removal.

For the detail sediment simulations, the EUSES Model Lake water chemistry (Table B-2) was used for the surface water. Model simulations used bulk and pore water sediment chemistry from several field studies (Table B-7). The base case sediment pH was 7.56. Copper  $\log K_D$  values in sediment were specified using the Calculated  $K_D$  approach (described above). Simulations were performed for an oxic sediment and an anoxic sediment to assess the two redox end members occurring in natural sediment. For the oxic sediment simulations, sulfide production and metal sulfide precipitation were not included. Metals sorb to POC, HFO, and HMO in the sediment and precipitate as carbonates and/or hydroxides. For the anoxic sediment simulations, metal binding to HFO and HMO is not considered. Metals sorb to POC and precipitate as sulfides, carbonates, and/or hydroxides.

To model the formation and dissolution of copper sulfide solid, the following reaction and solubility product from Dyrssen and Kremling (1990) were used initially:



Simpson et al. (2000) suggest  $\text{Cu}_2\text{S}$  is an important copper solid phase in anoxic sediments. The solubility of this species has been described with the following solubility product in (Dyrssen and Kremling, 1990):



Simulations were made with both copper-sulfide solid species.

**Table B-7: Bulk and Pore Water Sediment Chemistry Parameters**

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

<sup>a</sup> From a monitoring dataset on Flemish navigable waterways (de Deckere et al., 2000). For conversion of hardness to Ca<sup>2+</sup> and Mg<sup>2+</sup>, a molar ratio of Ca:Mg = 2.20 was used based on average river water in Stumm and Morgan (1996).

<sup>b</sup> Estimated using the SO<sub>4</sub><sup>2-</sup> and Cl<sup>-</sup> data from (de Deckere et al., 2000) and a seawater/river water mixing method similar to Di Toro et al. (2005).

<sup>c</sup> Unpublished data from Besser et al. (2011) study (personal communication with John Besser of the USGS, 2010)

<sup>d</sup> From 1995 sediment monitoring program (Personal communication with Marnix Vangheluwe of ARCHE, 2010)

<sup>e</sup> Personal communication with Chris Schlekot of NiPERA, John Besser of the USGS, Marnix Vangheluwe of ARCHE, 2010 and (EURAS, 2008; van den Berg et al., 2001; van den Berg et al., 1998; van den Hoop et al., 1997; Vangheluwe et al., 2005)

<sup>f</sup> 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.

<sup>g</sup> 10<sup>th</sup> and 50<sup>th</sup> percentiles

<sup>h</sup> 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, [Fe<sup>2+</sup>].

<sup>i</sup> Values from Table B-11

The water column results for the anoxic simulation indicate that around day 24 of the simulation, the total and dissolved copper concentrations leveled off. Similar behavior was noted for the water column runs (Figure B-2). For the remainder of the 365-day simulation, water column copper concentrations decreased only very slightly. Between day 24 and day 365, the ranges of water column copper concentrations were 140 to 160 ng/L (total) and 56 to 62 ng/L (dissolved) respectively. These dissolved values are greater than 150 times lower than the 70% removal concentration of 10.5  $\mu\text{g/L}$ . The relatively flat copper response between day 24 and 365 in the water column is the result of a local equilibrium established between the settling flux of copper (directed into the sediment) and the resuspension flux (directed out of the sediment). The local equilibrium can be referred to as a *pseudo steady-state*. The smaller burial flux slowly depletes copper from the system moving the water column / sediment system toward the final steady-state in which the water column and sediment copper concentrations are zero. Detailed output from anoxic and oxic simulations is shown in Table B-8.

A series of sensitivity analyses were conducted to assess effect of (i) low AVS (1  $\mu\text{mol/g}$ ), (ii) variation in water column/sediment pH (6/7, 7/7, and 8/7.5), (iii) low sediment solids concentration (150  $\text{g/L}_{\text{bulk}}$ ), (iv) variation in hardness (factor of 2), (v) variation in resuspension rate (0.1, 1, 3.2, and 10 times the default rate), and (vi) variation in copper loading (initial copper concentrations of 10, 100, and 1000  $\mu\text{g/L}$ ). Additionally, Empirical  $K_D$  sediment simulations were made using water column and sediment  $\log K_D$  values of 4.48 and 4.39, respectively.

Model results from the anoxic simulation with AVS of 1  $\mu\text{mol/g}$  were identical to those with an AVS of 9.1 (Table B-8). This is because AVS is present in excess of the total sediment copper concentration. Simulations associated with items (ii) - (iv) use an anoxic simulation with  $\text{Cu}_2\text{S(s)}$ , total initial copper of



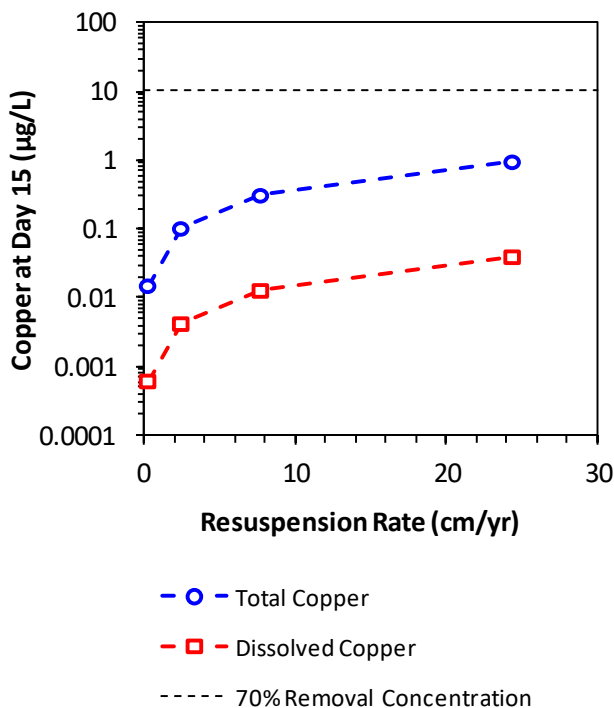
100 µg/L, and were performed with WHAM V instead of WHAM VII<sup>1</sup>. Detailed results can be found in Table B-9. For the relative pH variation sensitivity analysis, the largest change in time required to achieve 70% removal of total copper was for the 8/7.5 simulation; the predicted increase in removal time was from 1.7 days to 2.3 days. Variation of pH water column / sediment pH values had a relatively minor impact on the magnitude of the pseudo steady-state water column copper concentrations (Table B-9). Total copper concentrations at the start of pseudo steady state are within 12% of the base case. Dissolved concentrations from the pH 8/7.5 simulation are about a factor of 3.9 higher than the base case (i.e., 7.07/7.56). However, the total copper concentrations at the start of pseudo state-state conditions are at least 98 times smaller than the concentration representing 70% removal. Other than a factor of approximately 3 increase in the integrated diffusion flux into the sediment for the 8/7.5 simulation the mass balance results are similar to the base case. In all pH variation runs, particulate copper speciation in the sediment is dominated by the formation of Cu<sub>2</sub>S(s). Removal time, pseudo steady-state water column copper concentrations, and mass balance results show no sensitivity to a factor of 2 variation in sediment hardness. Though the simulations with the decreased sediment solid concentration show some departures from the base case values for pseudo steady-state water column copper concentrations as well as settling and resuspension fluxes, key outcomes remain similar to the base case. The 70% removal time is still approximately 1.7 days, the total copper concentrations at the start of pseudo state-state conditions is still significantly smaller than the concentration representing 70% removal, the integrated diffusive flux is directed into the sediment and particulate copper speciation in the sediment is dominated by the formation of Cu<sub>2</sub>S(s).

Simulations associated with item (v) used an anoxic simulation with AVS = 9.1µmol/g, CuS(s), total initial copper of 35 µg/L, and were performed with WHAM V instead of WHAM VII. Model runs with the sediment resuspension rate set (item v) at 0.1, 1, 3.2, and 10 times the default rate were made to examine the impact of enhanced resuspension on water column copper concentrations in more detail. The

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<sup>1</sup> While WHAM V and WHAM VII produce somewhat different copper speciation results with respect to organic carbon, these differences are not expected to produce significantly different results in the context of a sensitivity analysis, particularly in anoxic sediment where copper speciation is dominated by interaction with sulfide.

resuspension rate was increased by factors of 3.2 and 10 keeping the settling velocity and burial rate constant. The total and dissolved copper concentration in the water column at day 15 increased as the resuspension rate increased (Figure B-3). However, even at the highest resuspension rate (i.e., 10 times the default value), total and dissolved copper in the water remained more than 10 times lower than the concentration representing 70% removal of 10.5  $\mu\text{g/L}$ .



**Figure B-3:** Effect of resuspension rate on total and dissolved copper concentration at day 15.

Simulations associated with items (vi) used an anoxic simulation with  $\text{AVS} = 9.1 \mu\text{mol/g}$  and  $\text{CuS(s)}$ . The results indicate that total dissolved pseudo steady-state copper concentration and mass flux/balance values (except the diffusive flux) vary linearly with the initial copper concentration (Table B-10). For the sensitivity analysis simulation with initial copper concentration at  $1,000 \mu\text{g/L}$  and an  $\text{AVS}$  of  $1 \mu\text{mol/g}$ , the capacity of the sediment to bind copper as  $\text{CuS(s)}$  was exceeded. Sediment copper in excess of  $\text{AVS}$  is bound by POC. This results in a decreased sediment  $K_D$ , increased pore water copper concentration and an integrated diffusive flux directed out of the sediment. However, this change in sediment speciation does

not impact the amount of time required for 70% removal in the water column nor does it influence the pseudo steady-state concentration to an appreciable extent (compare last two columns in Table B-10). The copper loading sensitivity analysis simulations show 70% removal times that are less than 6 days and pseudo steady state water column total copper concentrations that are more than 50 times lower than that representing 70% removal.

Empirical  $K_D$  sediment simulations indicate total and dissolved copper concentrations at the onset of pseudo steady-state conditions of 0.31 and 0.21  $\mu\text{g/L}$ , respectively, which are more than 30 times lower than the 70% removal concentration of 10.5  $\mu\text{g/L}$ . Although the water column  $\log K_D$  was greater than the sediment  $\log K_D$ , the integrated diffusive flux was directed into the sediment.

<b>Table B-8: Results of Sediment Simulations</b>					
<b>Sediment Type</b>		<b>Anoxic</b>		<b>Anoxic (using Cu<sub>2</sub>S)</b>	<b>Oxic</b>
<b>AVS, μmol/g</b>		<b>9.1</b>	<b>1</b>	<b>9.1</b>	<b>0</b>
<b>Water Column Removal Data</b>					
Time for 70% Removal	days	3.4	3.4	3.4	3.4
[0.3×C <sub>T</sub> (0)]/Max QSS C <sub>T</sub> <sup>i</sup>		67	67	68	66
<b>Pseudo Steady-State Water Column Copper Concentrations</b>					
Tot. Cu Range <sup>a</sup>	ng/L	140 - 160	140 - 160	140 - 150	140 - 160
Diss. Cu Range <sup>a</sup>	ng/L	56 - 62	56 - 62	56 - 61	57 - 64
Water column log <i>K<sub>D</sub></i> <sup>a</sup>	---	5.00	5.00	5.00	5.00
<b>Mass Balance at 1 Year</b>					
Mass in the Water Column	%	0.40	0.40	0.40	0.41
Mass in the Sediment	%	90.2	90.2	90	90
Total Settling IN	%	176	176	176	178
Total Resusp. OUT	%	76.6	76.6	77	76.6
Total Burial OUT	%	9.42	9.42	9.4	9.41
Total Diffusion NET <sup>c</sup>	%	0.133	0.133	0.133	-1.47
<b>Sediment Speciation Data<sup>d</sup></b>					
Total Sediment Cu	μg/g	6.9	6.9	6.9	6.9
	μmol/g	0.11	0.11	0.11	0.11
Ionic Cu <sup>2+</sup>	ng/L <sub>pw</sub> <sup>e</sup>	1.5E-13	1.5E-13	1.7E-14	3.1E-01
	μg/g	2.4E-19	2.4E-19	2.6E-20	5.0E-07
Inorganic Cu <sup>f</sup>	ng/L <sub>pw</sub>	2.7E-12	2.7E-12	2.1E-07	4.2E+00
	μg/g	4.4E-18	4.4E-18	3.4E-13	6.7E-06
Cu-DOC	ng/L <sub>pw</sub>	7.0E-10	7.0E-10	7.8E-11	2.0E+03
	μg/g	1.1E-15	1.1E-15	1.2E-16	3.2E-03
Cu-POC	μg/g	1.7E-12	1.7E-12	1.9E-13	6.6E+00
Cu-HO&C <sup>g</sup>	μg/g	0	0	0	0
Cu-Sulfide	μg/g	6.9	6.9	6.9	0
Cu-HFO	μg/g	9.9E-23	9.9E-23	1.1E-23	3.0E-01
Cu-HMO	μg/g	6.8E-24	6.8E-24	7.5E-25	2.5E-02
Dissolved Cu	ng/L <sub>pw</sub>	7.1E-10	7.1E-10	2.1E-07	2.0E+03
	μg/g	1.1E-15	1.1E-15	3.4E-13	3.2E-03
Particulate Cu	μg/g	6.93	6.93	6.93	6.93
Sediment log <i>K<sub>D</sub></i>	---	16.0	16.0	13.5	3.53

<sup>a</sup> These refer to the period in the simulation from day 24 to day 365. The log *K<sub>D</sub>* values quoted are arithmetic averages for this time period

<sup>b</sup> Units of water column *K<sub>D</sub>* are L/kg

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

<sup>d</sup> Speciation data was taken from day 20 of the simulation

<sup>e</sup> pw = porewater

<sup>f</sup> Inorganic copper is the sum of ionic copper and inorganic copper complexes (e.g., with hydroxide, chloride and carbonate)

<sup>g</sup> Copper (hydr)oxide and copper carbonate precipitates

<sup>h</sup> Units of sediment *K<sub>D</sub>* are L<sub>pw</sub>/kg

- i 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-9. Results of Copper Sediment Sensitivity Analysis Runs**

Removal Approach and Output Quantity	Sensitivity Analysis Run						
	Base Case <sup>a</sup>	WC pH = 6.094 Sed pH = 7	WC pH = 7.073 Sed pH = 7	WC pH = 8.002 Sed pH = 7.5	Hardness × 2	Hardness ÷ 2	Sediment solids = 150 g/L <sub>bulk</sub>
Tot. Cu Range, µg/L <sup>b</sup>	0.252 - 0.279	0.250 - 0.277	0.252 - 0.280	0.282 - 0.313	0.252 - 0.279	0.252 - 0.279	0.905 - 1.00
Diss. Cu Range, µg/L <sup>b</sup>	0.0104 - 0.0116	0.00831 - 0.00918	0.0105 - 0.0116	0.0403 - 0.0447	0.0104 - 0.0116	0.0104 - 0.0116	0.0378 - 0.0417
Mass in the Water Column, %	0.25	0.25	0.25	0.28	0.25	0.25	0.91
Mass in the Sediment, %	90	91	91	91	91	90	90
Total Settling IN, %	177	177	177	177	177	177	375
Total Resusp. OUT, %	77	77	77	77	77	77	276
Total Diffusion NET, % <sup>c</sup>	0.01	0.01	0.01	0.03	0.01	0.01	0.02
Total Burial OUT, %	9.5	9.5	9.5	9.5	9.5	9.5	9.4
Water column log <i>K<sub>D</sub></i> , L/kg <sup>b</sup>	6.19	6.29	6.19	5.60	6.19	6.19	6.18
Sediment log <i>K<sub>D</sub></i> , L/kg <sup>b</sup>	13.8	13.8	13.8	13.8	13.8	13.7	14.4
Time for 70% Removal of Total Copper, days	1.72	2.10	2.13	2.33	1.72	1.72	1.73
[0.3× <i>C<sub>T</sub></i> (0)]/Max QSS <i>C<sub>T</sub></i> <sup>d</sup>	107	108	107	98.5	107	107	30.0

<sup>a</sup> Select simulation parameters: water column pH 7.07; sediment pH 7.56; anoxic sediment with AVS = 1 µmol/g, settling velocity 2.5 m/d; initial Cu concentration = 0.1 mg/L; Cu<sub>2</sub>S is the potential copper sulfide precipitate

<sup>b</sup> Ranges and average are based on data from the quasi-steady state period of the simulation.

<sup>c</sup> 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.

<sup>d</sup> This quantity is the ratio of the total Cu concentration representing 70% removal (0.3×*C<sub>T</sub>*(0)) to the maximum total concentration during the quasi-steady-state period (Max QSS *C<sub>T</sub>*). This is meant to give an indication of where sustained water column concentrations lie relative to the 70% removal benchmark.

**Table B-10: Results of Copper Loading Sediment Sensitivity Analysis Simulations**

Initial Total Copper, µg/L		10		100		1000	
AVS, µmol/g		9.1	1	9.1	1	9.1	1
<b>Water Column Removal Data</b>							
Time for 70% Removal	days	3.2	3.2	3.5	3.5	6.0	6.0
[0.3×C <sub>T</sub> (0)]/Max QSS C <sub>T</sub> <sup>i</sup>		68	68	66	66	61	60
<b>Pseudo Steady-State Water Column Copper Concentrations</b>							
Tot. Cu Range <sup>a</sup>	ng/L	40 - 44	40 - 44	400 - 450	400 - 450	4,400 – 4,900	4,500 - 5000
Diss. Cu Range <sup>a</sup>	ng/L	16 - 18	16 - 18	160 - 180	160 - 180	2,000 – 2,200	2,000 – 2,300
Water column log K <sub>D</sub> <sup>a</sup>	--- <sup>b</sup>	5.01	5.01	4.99	4.99	4.91	4.91
<b>Mass Balance at 1 Year</b>							
Mass in the Water Column	%	0.40	0.40	0.40	0.40	0.44	0.45
Mass in the Sediment	%	90.2	90.2	90.2	90.2	90.2	90.2
Total Settling IN	%	176	176	176	176	175	177
Total Resusp. OUT	%	76.6	76.6	76.6	76.6	76.2	76.2
Total Burial OUT	%	9.42	9.42	9.42	9.42	9.37	9.36
Total Diffusion NET <sup>c</sup>	%	0.124	0.124	0.143	0.143	0.297	-1.151
<b>Sediment Speciation Data <sup>d</sup></b>							
Total Sediment Cu	µg/g	2.0	2.0	20	20	198	198
	µmol/g	0.03	0.03	0.31	0.31	3.1	3.1
Ionic Cu <sup>2+</sup>	ng/L <sub>pw</sub> <sup>e</sup>	1.5E-13	1.5E-13	1.5E-13	1.5E-13	1.5E-13	6.1E+01
	µg/g	2.4E-19	2.4E-19	2.4E-19	2.4E-19	2.4E-19	9.8E-05
Inorganic Cu <sup>f</sup>	ng/L <sub>pw</sub>	2.7E-12	2.7E-12	2.7E-12	2.7E-12	2.7E-12	1.1E+03
	µg/g	4.4E-18	4.4E-18	4.4E-18	4.4E-18	4.4E-18	1.8E-03
Cu-DOC	ng/L <sub>pw</sub>	7.0E-10	7.0E-10	7.0E-10	7.0E-10	7.0E-10	5.3E+04
	µg/g	1.1E-15	1.1E-15	1.1E-15	1.1E-15	1.1E-15	8.5E-02
Cu-POC	µg/g	1.7E-12	1.7E-12	1.7E-12	1.7E-12	1.7E-12	1.3E+02
Cu-HO&C <sup>g</sup>	µg/g	0	0	0	0	0	0
Cu-Sulfide	µg/g	2.0	2.0	19.8	19.8	197.7	63.5
Cu-HFO	µg/g	9.9E-23	9.9E-23	9.9E-23	9.9E-23	9.9E-23	3.8E-08
Cu-HMO	µg/g	6.8E-24	6.8E-24	6.8E-24	6.8E-24	6.8E-24	1.6E-09
Dissolved Cu	ng/L <sub>pw</sub>	7.1E-10	7.1E-10	7.1E-10	7.1E-10	7.1E-10	5.5E+04
	µg/g	1.1E-15	1.1E-15	1.1E-15	1.1E-15	1.1E-15	8.7E-02
Particulate Cu	µg/g	2.0	2.0	20	20	198	198
Sediment log K <sub>D</sub>	--- <sup>h</sup>	15.4	15.4	16.4	16.4	17.4	3.56

<sup>a</sup> These refer to the period in the simulation from day 24 to day 365. The log K<sub>D</sub> values quoted are arithmetic averages for this time period

<sup>b</sup> Units of water column K<sub>D</sub> are L/kg

<sup>c</sup> 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.

<sup>d</sup> Speciation data was taken from day 20 of the simulation

<sup>e</sup> pw = porewater

<sup>f</sup> Inorganic copper is the sum of ionic copper and inorganic copper complexes (e.g., with hydroxide, chloride and carbonate)

<sup>g</sup> Copper (hydr)oxide and copper carbonate precipitates

- h Units of sediment  $K_D$  are  $L_{pw}/kg$
- i 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.



## DETAILS OF SAINT GERMAIN LES BELLES RESERVOIR TICKET-UWM SIMULATIONS

### *Parameter Selection*

Where possible, physical and chemical parameters serving as input for the TICKET-UWM were specified based on direct measurements provided in (van Hullebusch et al., 2003a; Van Hullebusch et al., 2003b) (Table B-11). Since settling rate, burial rate, and sediment solids concentration were not measured for the reservoir, these parameters were set to regional values from the EUSES model lake (EC, 2004; European Chemicals Agency (ECHA), 2010) (Table B-11). The resuspension rate was calculated based on a solids balance and assuming the solids in the system are at steady-state.

**Table B-11: TICKET-UWM Input for the Saint Germain les Belles Reservoir Simulations<sup>a</sup>**

Parameter	Value
	Saint Germain les Belles Reservoir <sup>a</sup>
Volume, m <sup>3</sup>	6.5 × 10 <sup>4</sup>
Surface area, km <sup>2</sup>	0.04
Average water depth, m	1.6
Residence time, yr	0.25
Settling rate, m/d	Calibrated
Burial rate, cm/yr	0.3 <sup>b</sup>
Resuspension rate, cm/yr	2.75 <sup>c</sup>
Diffusive exchange, cm/day	0.24 <sup>b,d</sup>
Sediment <i>f</i> <sub>oc</sub>	0.073
Sediment solids conc., g/L <sub>bulk</sub>	500 <sup>b</sup>
Depth of active sediment, cm	5
AVS, μmol/g <sub>dry</sub>	8.8 <sup>e</sup>
Sediment HFO, mg/kg	0 (anoxic sediment)
Sediment HMO, mg/kg	0 (anoxic sediment)
Initial Cu conc., μg/L as Cu	197 <sup>f</sup>
Initial Sed Cu conc., μg/g	37.7
Suspended solids, mg/L	18.0
Suspended solids <i>f</i> <sub>oc</sub>	0.1 <sup>b</sup>
POC, mg/L	1.80
DOC, mg/L	5.1
Water column pH	8.4
Sediment pH	7.5
Alkalinity, mg/L as CaCO <sub>3</sub>	49.0
Calcium, mg/L	3.4
Magnesium, mg/L	3.6
Sodium, mg/L	5.1
Potassium, mg/L	1.3
Sulfate, mg/L as SO <sub>4</sub>	4.7
Chloride, mg/L	7.5

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- <sup>a</sup> Unless otherwise noted, input parameter are taken (or estimated) from (van Hullebusch et al., 2003a; Van Hullebusch et al., 2003b)
- <sup>b</sup> Data from EUSES model lake (EC, 2004; European Chemicals Agency (ECHA), 2010). Surface area and volume values quoted refer to a regional scale assessment. They do not influence the removal simulations.
- <sup>c</sup> Calculated using the settling velocity, suspended solids concentration, sediment bulk solid concentration, and the burial (net sedimentation) rate shown in the table using a steady-state solids balance (Chapra, 1997).
- <sup>d</sup> EUSES pore water side mass transfer coefficient. Mass transfer resistance is assumed to be all on the sediment side (Di Toro et al., 1981).
- <sup>e</sup> Median AVS concentration for a Flemish dataset (Vangheluwe et al., 2005)
- <sup>f</sup> This was calculated by adding the theoretical dose value to the measured pre-dose background copper concentration of 1.28 µg/L.

#### *Distribution Coefficients - Empirical $K_D$*

According to measured total and dissolved copper and SPM concentrations in the reservoir, log  $K_D$  values spanned the range 3.66 to 4.87 (i.e.,  $K_D = 10^{3.66}$  to  $10^{4.87}$  L/kg). The Empirical  $K_D$  simulation used the average log  $K_D$  value of 4.56. Based on the average SPM concentration over the study period of 18.0 mg/L, the average fraction particulate was 0.39. The distribution coefficient in the sediment of the reservoir was not measured. Therefore, for the Empirical  $K_D$  simulation the sediment log  $K_D$  was set at 4.39 based upon the copper partition coefficient review of Heijerick and Van Sprang (2005).

#### *Distribution Coefficients - Calculated $K_D$*

WHAM VII (Tipping et al., 2011) was used to calculate copper  $K_D$  values based on pH, DOC, cations, anions, and the concentration of 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 copper concentration in the water column as well as competition between copper, protons and hardness cations (Ca and Mg) for binding sites. The concentrations of particulate and colloidal HA and FA were calculated from POM and DOC as follows: For both particulate organic matter (POM) and dissolved organic matter (DOM),  $f_{OC} = 0.58$  g org C/g OM (van Hullebusch et al., 2003a; Van Hullebusch et al., 2003b); POM is 100% active with 50% HA and 50% FA (Lofts and Tipping, 2000); DOM is 63.5% active with 0% HA and 100% FA (Bryan et al., 2002; Lofts and Tipping, 2011).

Concentrations of HFO and HMO in the water column were estimated from measured total sediment particulate iron and manganese concentrations (Saint Germain les Belles Reservoir), and the water column suspended solids concentrations for the reservoir (Table B-11). The following specifications were used to determine the amount of HFO and HMO from measured total iron and manganese, respectively.

- Approximately 40% and 18% of the total particulate iron and manganese in the water column were specified to be HFO and HMO, respectively (HydroQual and Manhattan College, 2010)
- HFO-iron was assigned a formula weight of 89 g HFO/mol Fe (Dzombak and Morel, 1990)
- HMO-manganese Mn was assigned a formula weight of 119 g HMO/mol Mn (Tonkin et al., 2004).

The AVS of the sediment in the reservoir was not measured, so it was set at the average AVS value of 8.8  $\mu\text{mol/g}$  dry weight from (Vangheluwe et al., 2005).

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## APPENDIX C – REMOVAL OF COPPER FROM THE WATER COLUMN

**Table C-1: Parameters Used for Summary of Copper Removal from the Water Column**

ID	m	v <sub>s</sub>	S	H	log K <sub>D</sub>	H/S	t <sub>30</sub>
	(mg/L)	(m/d)	(g/m <sup>2</sup> /d)	(m)		(m <sup>3</sup> ·d/g)	(days)
Lake Courtille	6.94	0.750	5.21	1.77	4.44	0.340	16.0
St. Germain les Belles	18.0	0.680	12.2	1.60	4.78	0.131	7.10
IME Mesocosms	2.20	0.350	0.770	0.76	4.99	0.987	6.00
MELIMEX	5.91	0.200	1.18	10.0	4.12	8.46	132
Novosibirskoye Reservoir	15.0	0.184	2.76	3.00	5.07	1.09	12.6
TICKET-UWM (Emp K <sub>d</sub> )	15.0	2.50	37.5	3.00	4.48	0.0800	4.70
TICKET-UWM (Calc K <sub>d</sub> )	15.0	2.50	37.5	3.00	4.90	0.0800	1.60

Averages (from highlighted cells):  $m = 10.5 \text{ mg/L}$ ;  $K_D = 10^{4.78} \text{ L/kg}$