STATE OF NEW MEXICO
BEFORE THE WATER QUALITY CONTROL COMMISSION

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WATER QUALITY
CONTROL COMMISSION

In the Matter of:

PROPOSED AMENDMENTS TO
*STANDARDS FOR INTERSTATE
AND INTRASTATE SURFACE
WATERS,* 20.6.4 NMAC

No. WQCC 14-05(R)

FREEPORT-McMoRan CHINO MINES COMPANY'S PETITION TO AMEND THE SURFACE WATER QUALITY STANDARDS (20.6.4 NMAC) AND REQUEST FOR HEARING

INTRODUCTION

Freeport-McMoRan Chino Mines Company ("Chino") hereby petitions the Water Quality Control Commission ("Commission") to amend the Commission's regulations in Title 20, Chapter 6, Part 4 of the New Mexico Administrative Code ("NMAC") titled "*Standards for Interstate and Intrastate Surface Waters*" ("Rules"). This petition is filed in accordance with the Scheduling Order for this matter dated July 10, 2014 and the Procedural Order of the same date.

The proposed amendment would add site-specific criteria for copper for certain surface waters located within the Mimbres River Closed Basin (hydrologic unit code HUC8-13030202) near the towns of Bayard and Hurley, New Mexico and also located within an area known as the Chino Mines Site Smelter Tailings Soil Investigation Unit (STSIU waters).

PROPOSED AMENDMENT

Add a new Section, 20.6.4.902 NMAC stating as follows:

20.6.4.902 SITE-SPECIFIC STANDARDS

A. A site-specific adjustment to copper criteria for the applicable aquatic life designated use for a segment of Lampbright Draw and certain of its tributaries and certain tributaries of Whitewater Creek located in the Mimbres River Closed Basin shall be applied as described in this subsection.

(1) the criteria adjustment for copper described in paragraph (2) of this subsection shall apply only to the portions of the surface waters located within an area known as the Chino Mines Site Smelter Tailings Soil Investigation Unit (“STSIU”) and described as follows:

(a) the mainstem of Lampbright Draw beginning at the confluence of Lampbright Draw with Rustler Canyon to the intersection of Lambright Draw with the southern STSIU boundary and all tributaries thereof that originate west of Lampbright Draw, including Rustler Canyon and Martin Canyon;

(b) Lucky Bill Canyon and all tributaries thereof;

(c) Chino Mines property Subwatershed Drainages A, B, C, D-1, D-2, D-3 and all tributaries thereof; and

(d) Chino Mines property Subwatershed Drainages E-1, E-2, and E-3.

(2) For the waters listed in paragraph (1) of this subsection, the aquatic life criteria for copper as set forth in Subsection I of 20.6.4.900 NMAC shall be adjusted by multiplying the applicable acute or chronic aquatic life criterion set forth in Subsection I of this section by the Water Effect Ratio (“WER”) adjustment expressed by the following equation:

$$WER = \frac{[10^{\,0.588+(0.703\ \times \log DOC)+(0.395\ \times \log Alkalinity)}] \times (\frac{100}{Hardness})^{0.9422}}{19.31}$$

For purposes of this paragraph, alkalinity is expressed in units of mg/L as $CaCO_3$. In waters that contain alkalinity concentrations greater than 250 mg/L, a value of 250 mg/L shall be used in the equation. No lower bound (or limit) for alkalinity concentrations shall be used in the equation. DOC is dissolved organic carbon, expressed in units of mg C/L. In waters that contain DOC concentrations greater than 16 mg C/L, a value of 16 mg C/L shall be used in the equation. No lower bound (or limit) for DOC concentrations shall be used in the equation. Hardness is expressed in units of mg/L as $CaCO_3$. In waters that contain hardness concentrations greater than 400 mg/L, a value of 400 mg/L shall be used in the equation. No lower bound (or limit) for hardness concentrations shall be used in the equation. The alkalinity, hardness and DOC concentrations used to calculate the WER value are those measured in the subject water sample. The term “19.31” is a *Daphnia magna* Species Mean Acute Value (SMAV) used to represent the laboratory water toxicity endpoint value in the WER equation. The value of 19.31 is specific to the hardness concentration term of “100” in the numerator of the term “100/*Hardness*”. The term “0.9422” (the exponent to the term “100/*Hardness*”) is the acute copper criteria hardness slope and is used to normalize a subject water sample to the same hardness concentration (100 mg/L) as the 19.31 SMAV.

STATEMENT OF BASIS FOR AMENDEMNT

Chino petitions the Commission to adopt the site-specific criteria, in accordance with 20.6.4.10(D)(3) NMAC, to adjust the aquatic and wildlife criteria for copper for the portions of the surface waters identified above. The following information is provided in accordance with that provision:

(a) identify the specific waters to which the site-specific criteria would apply:

This site-specific aquatic life criteria for copper shall apply only to certain surface waters located in the Mimbres River Closed Basin and also within an area known as the Chino Mines Site STSIU and described as follows:

(a) the mainstem of Lampbright Draw beginning at the confluence of Lampbright Draw with Rustler Canyon to the intersection of Lambright Draw with the southern STSIU boundary and all tributaries thereof that originate west of Lampbright Draw, including Rustler Canyon and Martin Canyon;
(b) Lucky Bill Canyon and all tributaries thereof;
(c) Chino Mines property Subwatershed Drainages A, B, C, D-1, D-2, D-3 and all tributaries thereof; and
(d) Chino Mines property Subwatershed Drainages E-1, E-2, and E-3.

These surface waters are shown on the map attached to this Petition as Exhibit "A".

(b) explain the rationale for proposing the site-specific criteria:

The portions of the waters identified above are within a study area known as the Chino STSIU and are the subject of investigation under an Administrative Order on Consent between Chino and the New Mexico Environment Department ("NMED") dated December 23, 1994 ("AOC"). The investigation identified elevated copper in soils as the primary contaminant of concern in this area, some of which may be from a combination of historic smelter emissions and blowing copper mill tailings. Surface-water sampling conducted as part of the investigation indicated exceedances of the current hardness-based aquatic life criteria for copper in drainages located in this area. Under the AOC, NMED has conducted an ecological risk assessment with respect to copper in the soils and has issued "pre-Feasibility Study Remedial Action Criteria" ("pre-FS RAC") with respect to the soils and surface waters, including potential impacts on aquatic life in the ephemeral and non-ephemeral surface waters. The pre-FS RAC for surface waters requires compliance with the State of New Mexico Standards for Interstate and Intrastate Surface Waters, 20.6.4 NMAC, for risk to aquatic life in the drainages of the STSIU including all approaches and tools listed in the Rules which provide options for site-specific application.

In connection with the AOC investigation, Chino proposed to evaluate potential site-specific criteria for copper for surface waters in the STSIU. All of the surface waters which are the subject of this petition are "unclassified" waters subject to use designations under 20.6.4.97, .98 or .99 NMAC, as applicable. Those waters subject to 20.6.4.98 NMAC (intermittent waters) will have the relevant designated use of "marginal aquatic life", and those waters subject to 20.6.4.99 NMAC (perennial waters) will have the relevant designated use of "warmwater aquatic life." Some of the waters to which the site-specific copper criteria adjustment proposed in this petition would apply are proposed to be treated as "ephemeral" under NMED's proposed amendments to 20.6.4.97 NMAC, as set forth in NMED's petition. If the Commission adopts NMED proposed amendments to 20.6.4.97 NMAC, then the waters covered by that amendment will have the designated use, as relevant for this petition, of "limited aquatic life." The applicable use designations under 20.6.4.97, .98 and .99 NMAC are not affected by this petition. The proposed site-specific WER adjustment, however, is intended to apply regardless of the particular aquatic life use designation under 20.6.4.97, .98 or .99 NMAC.

Under the relevant criteria specified in 20.6.4.900 NMAC, numerical aquatic-life criteria for copper are derived using a formula that considers the hardness of the water. A variety of other physical and non-hardness chemical characteristics of the water and the metal can influence metal bioavailability and toxicity to aquatic organisms, as recognized by the U.S. EPA (U.S. EPA Water Quality Standards Handbook, EPA-823-B-94-005a, 2nd edition, August 1994). These parameters include suspended and dissolved solids, pH, alkalinity, organic carbon compounds, ionic strength and other characteristics, which can have equal or greater effects on copper toxicity than hardness alone.

This Petition is based upon work completed from 2011 through 2014 that has been reviewed and commented on by NMED. In September 2011, Chino submitted a proposed Study Work Plan to NMED to utilize the water effect ratio ("WER") method to develop site-specific criteria, a method identified in 20.6.4.10(D)(4)(a)-(b) NMAC. The Study Work Plan and subsequent technical documents were distributed to the NMED Surface Water Quality and Ground Water Quality Bureaus and to the U.S. Environmental Protection Agency, Region 6, AOC project managers and its Water Quality Standards Coordinator. The Study Work Plan proposed sampling locations and frequency to gather relevant chemical data, proposed laboratory methods of analysis, identified some changes in the general methodology due to the nature of the site, and proposed the development of a model to be used to derive proposed site-specific criteria. NMED provided written comments requesting the addition of more sampling locations and increased sampling frequency and acknowledged the need for methodology changes to address the site-specific circumstances. Chino incorporated the changes to the Study Work Plan recommended by NMED and initiated the study.

Chino and NMED met in March 2012 to discuss the sampling and analytical results and the initial model development, including the selection of model parameters, the methods for model application and the production of an interim report containing all of the data. A draft interim report was submitted to NMED for review in October 2012, and NMED provided comments in December 2012. In March 2013 Chino submitted a revised interim report addressing NMED's comments and subsequently submitted a draft site-specific model report in April 2013. NMED provided comments in July 2013 and Chino submitted a final report in

October 2013 entitled "Revised Site-Specific Copper Toxicity Model Report." A copy of the text of that report is attached as Exhibit "B." Copies of the complete report including tables, figures, and appendices containing data and related evaluations are available at the following web link: http://www.fcx.com/chino/pdf/2013/100313.pdf. This Petition is based upon the information presented in the final report.

The study methodology and general results were published in a peer-reviewed scientific journal, "Environmental Technology and Chemistry": *B.A. Fulton and J.S. Meyer,* "Development of a Regression Model to Predict Copper Toxicity to *Daphnia magna* and Site-Specific Copper Criteria Across Multiple Surface-Water Drainages in an Arid Landscape," Vol. 33, No. 8 pp. 1865-1873 (2014). A copy of this paper is attached as "Exhibit C."

(c) describe the methods used to notify and solicit input from potential stakeholders and from the general public in the affected area, and present and respond to the public input received:

Chino implements a public participation process according to a Community Relations Plan under the AOC. The process includes public meetings with a Community Working Group (CWG) at which NMED and Chino present and discuss activities conducted under the AOC. The CWG holds regular meetings, in Bayard or Hurley, New Mexico and is composed of interested public stakeholders. Participation in CWG is open to all interested community members. Starting in 2011, NMED informed the CWG of Chino's efforts to develop site-specific copper criteria in drainages associated with the STSIU, and this is documented in NMED's AOC document status handouts and CWG meeting minutes.

Chino provided public notice of the September 16, 2014, CWG meeting in the local newspaper of record (Silver City Daily Press) in both English and Spanish on September 2, 2014 and September 15, 2014. The public notice included information about the site-specific copper criteria presentation and the web address for Chino's online document website repository. The website contains a link to the October 2013 Revised Site Specific Copper Toxicity Model Report. NMED included copies of the same report in the Chino AOC document physical repositories located in Silver City, Bayard and Santa Fe prior to the September 16, 2014 CWG meeting. On September 11, 2014, Chino provided email notification of the CWG meeting to CWG members and NMED. At the September 16, 2014, CWG meeting held at the Bayard Community Center, Bayard, New Mexico, Chino's technical expert and consultant Barry A. Fulton of ARCADIS provided a detailed presentation to the CWG on the development of the Site-Specific Copper Toxicity Model for the STSIU drainages. At that meeting, NMED and Chino answered questions from the public, and invited public comment on the model report and proposed criteria.

(d) present and justify the derivation of the proposed criteria:

The Commission may adopt site-specific numeric criteria applicable to all or a part of a surface water of the state based upon relevant site-specific conditions under 20.6.4.10(D)(1) NMAC. The relevant site-specific conditions include "physical or chemical characteristics at a site such as pH or hardness alter the biological availability and/or toxicity of the chemical." 20.6.4.10(D)(1)(b) NMAC. Site-specific criteria must fully protect the designated use to which they apply. 20.6.4.10(D)(2) NMAC. A derivation of site-specific criteria shall rely on a scientifically defensible method, such as one of those listed in 20.6.4.10(D)(4)(a)-(e) NMAC.

Under the relevant criteria specified in 20.6.4.900 NMAC, numerical aquatic life criteria for copper are derived using a formula that considers the hardness of the water. A variety of other physical and non-hardness chemical characteristics of the water and the metal can influence metal bioavailability and toxicity to aquatic organisms, as recognized by the U.S. EPA

(U.S. EPA Water Quality Standards Handbook, EPA-823-B-94-005a, 2nd edition, August 1994). These parameters include suspended and dissolved solids, pH, alkalinity, organic carbon compounds, ionic strength and other characteristics, which can have equal or greater effects on copper toxicity than hardness alone.

To account for the effects that water chemistry has on metal toxicity, site-specific criteria may be developed using the WER procedure (20.6.4.10(D)(4)(a)-(b) NMAC). The WER procedure consists of site-water toxicity tests conducted side-by-side with laboratory-water toxicity tests, and is used to specifically account for differences between toxicity of the metal in laboratory dilution water (results of which were used to derive the copper criteria in 20.6.4.900 NMAC) and toxicity of the metal in STSIU waters that can be attributed to site-specific chemistry.

Chino used the interim WER procedure for metals (published by the U.S. Environmental Protection Agency, EPA-823-B-94-001 (February 1994)) and the streamlined WER procedure for discharges of copper (published by the U.S. Environmental Protection Agency, EPA-822-R-01-005 (March 2001)) identified in 20.6.4.10(D)(4)(a)-(b) NMAC to derive the proposed criteria. A description of the methodology used, the adjustments to reflect site-specific conditions, the basis for the methodology and the adjustments, the data collected and used to develop the proposed site-specific standard, and the calculations used to derive the proposed site-specific standard all are documented in the report attached as Exhibit "B."

The proposed WER model was selected based on statistical relations between Site chemistry and measured toxicity and by linking these relations to the dominant mechanisms of copper toxicity that occur within the specific range of STSIU water chemistries. From a statistical standpoint, the proposed model was determined as the best-fit model based on its rigorous multi-linear regression (MLR) analysis and its accuracy. The MLR model approach was determined to provide better predictions than a model using only water hardness, without systematically over- or under-predicting toxicity values, while also covering wide temporal and spatial conditions found in STSIU waters. Recommendations for using this model were also based on an understanding of the hydrology, upland properties, nature and extent of potential contamination, and surface-water chemistry that is known to occur throughout the STSIU study area.

After using the best-fit multi-linear regression (MLR) model to evaluate water samples in the STSIU study area, it was determined that the combination of DOC and alkalinity is the biggest driver in predicting copper toxicity within STSIU surface waters. The relationship between DOC and alkalinity provides a highly predictive tool for estimating site-specific copper toxicity based on using measured water chemistry values as input parameters to a predictive Site-specific copper model.

Compared to the current hardness-based copper criteria, the MLR model approach considers the effects of multiple water chemistry parameters on site-specific copper toxicity. This provides a more accurate estimate of copper toxicity across STSIU waters because other toxicity-modifying parameters than only water hardness are accounted for. As a result, the site-specific MLR approach can reduce uncertainty about the over-protectiveness or under-protectiveness of the current hardness-based criteria, or uncertainty associated with application of other site-specific criteria options such as the BLM or a traditional WER approach. Additionally, because this approach accounts for water chemistry variability by adjusting the numeric value of the site-specific criterion as a function of the water chemistry for each water sample, it is consistent with the current hardness-based approach. Further, the specific implementation steps and margin of safety incorporated into the proposed criteria for applying site-specific criteria to STSIU waters provides a technically-defensible basis to address site-specific challenges, while also providing for environmentally conservative site-specific criteria.

The results of the application of this method, based upon the site-specific data, is the formula as stated in the proposed rule language. If the Commission incorporates this language into the surface water quality standards, this formula will be used to determine numerical copper limits only for the specific waters for which the site-specific standard is adopted.

CONCLUSION

For the reasons stated above, and in accordance with 20.6.4.10(D) NMAC, Chino respectfully requests that the Commission adopt the site-specific criteria set forth in this Petition and incorporate it into 20.6.4 NMAC. Chino will present testimony and additional evidence in support of this Petition at the hearing in accordance with the Scheduling Order and the Procedural Order in this matter.

Respectfully Submitted,

GALLAGHER & KENNEDY, P.A.

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CERTIFICATE OF SERVICE

I hereby certify that a true and accurate copy of the foregoing pleading was hand-delivered to the following parties on Tuesday, September 30, 2014:

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Germaine [illegible] Chappelle
Germaine Chappelle

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Project #63524.001
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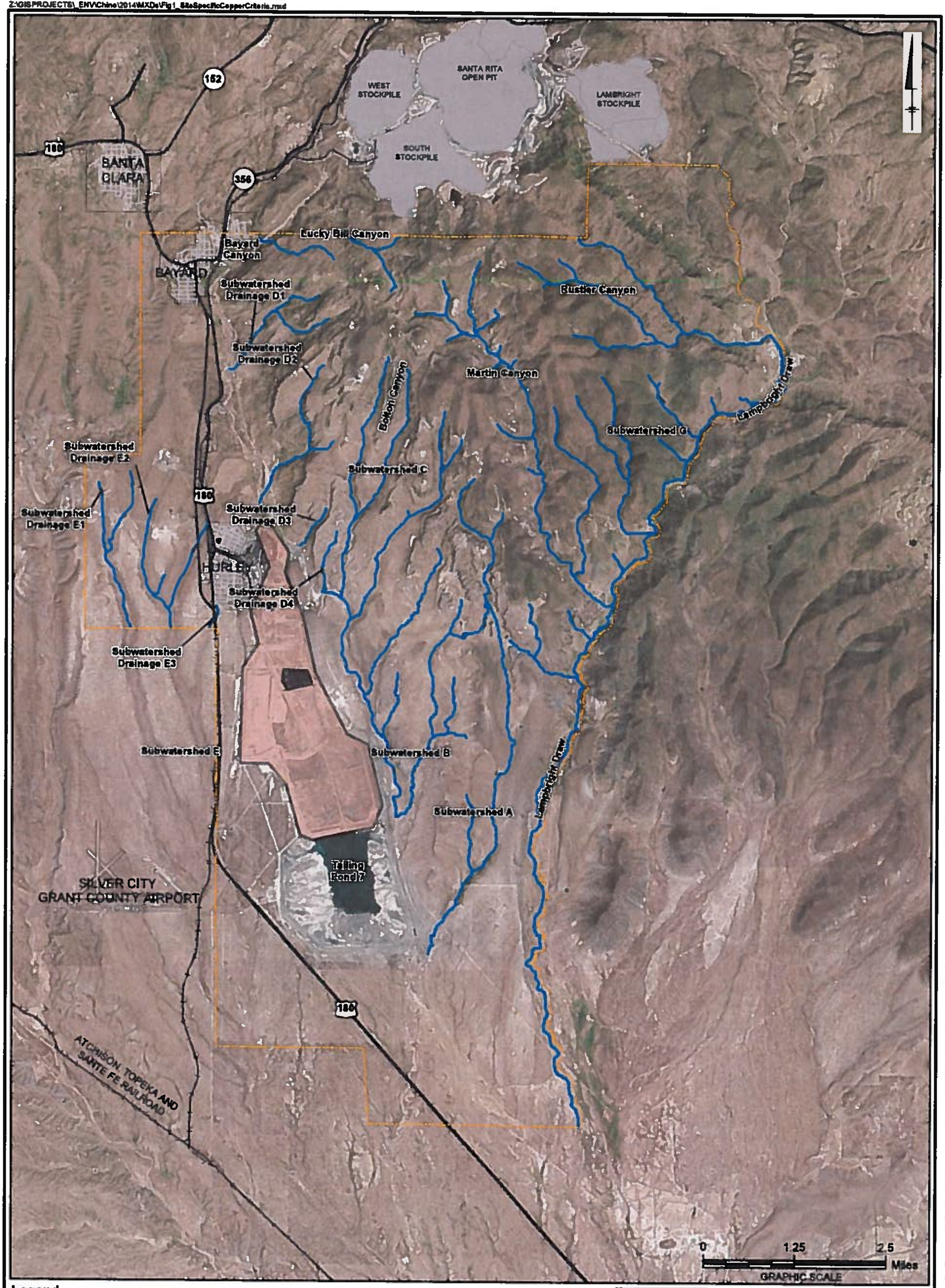

Legend

- STSIU Study Boundary
- Reclaimed Older Tailing Impoundments
- Stockpiles
- STSIU Drainages Subject to Site-Specific Copper Criteria
- Highway
- Railroad
- Town Roads

FREEPORT-MCMORAN CHINO MINES COMPANY
VANADIUM, NEW MEXICO

CHINO MINES SITE-SPECIFIC COPPER CRITERIA MAP

ARCADIS | EXHIBIT A

Layer Credits: Source: Esri, DigitalGlobe, GeoEye, i-cubed, Earthstar Geographics, CNES/Airbus DS, USDA, USGS, AEX, Getmapping, Aerogrid, IGN, IGP, swisstopo, and the GIS User Community

Exhibit
A

FREEPORT-McMoRAN
COPPER & GOLD

Chino Mines Company
Box 10
Bayard, NM 88023

October 4, 2013

Certified Mail #70122210000106174271
Return Receipt Requested

Kris Pintado, Standards Team Leader
New Mexico Environment Department
Surface Water Quality Bureau
P.O. Box 5469
Santa Fe, New Mexico 87502

Re: Revised Site-Specific Copper Toxicity Model Report
Smelter Tailings Soils IU Drainages – Chino Administrative Order on Consent

Dear Ms. Pintado:

Freeport-McMoRan Chino Mines Company (Chino) submits the attached *Revised Site-Specific Copper Toxicity Model Report* for New Mexico Environment Department (NMED) Surface Water Quality Bureau (SWQB). Chino submitted a draft of this report in April 2013 to NMED and subsequently made revisions to the report in response to comments received from SWQB in a letter dated July 1, 2013. Also attached in a separate document is Chino's response to SWQB's comments.

This report contains the additional data analysis as discussed in, and as follow up to the *Development of Site-Specific Copper Criteria Interim Report* submitted to NMED on March 22, 2013. The Interim Report provides a summary of all data collected in accordance with methods described in the work plan titled *Development of Site-Specific Copper Criteria* submitted in August 2011 to NMED that described proposed studies to support development of site-specific copper criteria in the Smelter and Tailing Soil Investigation Unit (STSIU) surface waters. These reports address drainages associated with the STSIU subject to the Chino Administrative Order on Consent, supporting the development of site-specific copper criteria for surface waters. This attached revised report describes the development of a site-specific copper Water Effects Ratio model that can potentially be used to predict and derive adjusted copper criteria in STSIU surface waters.

Please contact Ned Hall at (520) 393-2292 with any questions concerning this revised report.

Sincerely,

Sherry Burt-Kested

Sherry Burt-Kested, Manager
Environmental Services

SBK:pp
Attachments
20131003-001
Attachment

c. w/ attachment
Bryan Dail, NMED SWQB
Joseph Fox, NMED GWQB
Matthew Schultz, NMED GWQB
Russell Nelson, US EPA
Ned Hall, FCX Copper & Gold Inc.
Pam Pinson, FCX,Chino

c. w/o attachment
Petra Sanchez, US EPA
James Hogan, NMED SWQB
Shelly Lemon,NMED SWQB
Dave Menzie, NMED SWQB

Exhibit
B

Similar to DOC, the TOC model range is representative of measured ranges in STSIU surface waters. Of the available surface-water data, TOC in one 2011 sample collected in Rustler Canyon (1.2 mg/L) was below the low-end of the model range (2.7 mg/L TOC). As shown on **Figure E-4**, TOC concentrations in several samples collected from different subwatersheds were greater than the samples used in the WER toxicity tests, ranging up to 20 mg/L (in a 2010 sample collected in Subwatershed D).

Figure E-5 Alkalinity: Alkalinity is an input parameter in the proposed WER model. Surface-water samples used to develop the proposed WER model (N=17) ranged in alkalinity concentrations from 27 mg/L (a Rustler Canyon sample) to 250 mg/L (a Martin Canyon sample). **Figure E-5** shows that this model range covers the majority of alkalinity concentrations measured in STSIU surface waters. As listed in **Table E-2** and shown graphically in **Figure 3**, five samples were used in Site toxicity tests that contained alkalinity concentrations less than or equal to 42 mg/L, indicating the model is well-calibrated to lower alkalinity concentrations. Although lower alkalinity concentrations have been measured in STSIU waters (**Table E-2** and **Figure E-5**), the sensitivity of the model to low alkalinity and margin of safety recommendations for model application together provide the technical basis to apply the model to lower alkalinity concentrations and derive environmentally conservative SSC (**Section 4.2.2.2**).

Figure E-6 Hardness/Alkalinity Ratio: Although not an input parameter in the proposed WER model, the hardness/alkalinity ratio was also determined to be a marginally significant predictor of Site-specific copper toxicity in this study. As shown in **Figure E-6**, the model range captures the majority of measured hardness/alkalinity ratios, and only 3 samples collected in Subwatershed D were greater than the upper model range.

Figure E-7 Total Dissolved Solids: Although not an input parameter in the proposed WER model, TDS was also determined as a marginally significant predictor of Site-specific copper toxicity in this study. **Figure E-7** shows the TDS concentrations used to develop the WER model mostly cover the range measured in STSIU surface waters. The lowest concentration of TDS from the WER toxicity test samples was 90 mg/L (a Rustler Canyon sample), and only a single 2011 sample collected in Rustler Canyon was slightly lower (80 mg/L). One 2013 sample collected in Subwatershed B (downstream of Ash Spring) contained a TDS concentration greater than the upper range of the model.

Conclusions

Overall, this evaluation shows that the ranges of chemistry parameters used to develop the WER model are representative of STSIU surface waters, based on water chemistries observed thus far in STSIU. One of the objectives of the WER study, as described in study work plan (ARCADIS 2011), was to develop a WER model over a representative range of water chemistries based on the unique hydrologic conditions and available aquatic habitats of STSIU. Comparing the range of chemistries used to develop the model with the ranges of available STSIU surface-water data clearly shows that the model was developed over a broad range relative to Site conditions (i.e., limited water). As described previously, applying the model to sample concentrations that are not in the range used to develop the model is not expected to introduce uncertainty towards the under-protectiveness of the SSC.

Freeport-McMoRan Chino Mines Company – Administrative Order on Consent Response to New Mexico Environment Department Comments dated July 1, 2013 Draft Site-Specific Copper Toxicity Model Report Smelter and Tailing Soils Investigation Unit (STSIU) Drainages

October 4, 2013

This document presents responses by Freeport-McMoRan Chino Mines Company (Chino) to comments from the New Mexico Environment Department (NMED) Surface Water Quality Bureau (SWQB) on the Draft Site-Specific Copper Toxicity Model Report for the Smelter/Tailing Soils Investigation Unit (STSIU) Drainages, dated July 1, 2013. The Draft Site-Specific Copper Toxicity Model Report, dated March 2013, was prepared to support the development of site-specific copper criteria that can be applied to STSIU surface waters, pursuant to Section 20.6.4.10 part D of the New Mexico Administrative Code (NMAC). This letter is organized to present a response to each general comment received from NMED.

NMED Comment #1: The results of regression analysis and the model proposed present a significant improvement on predicting Cu toxicity at the STISU and thus seem suitable for development of a Cu SSC. While the report is not explicit, it appears that this model was selected based primarily on the very impressive R^2. We suggest the final analysis should consider other approaches and more broadly consider what would be the most appropriate SSC. For example, it was discussed in the meeting how the model uses the ratio of hardness to alkalinity, not the measured concentrations. While the use of a ratio works for the data collected in this report, it may not apply to lower alkalinity waters which have a similar ratio as they will not have a similar protection from Cu toxicity. As such, if this model is adopted it may be appropriate to specify that it only applies to the range of alkalinity observed in this study.

Chino Response #1: Chino appreciates the feedback regarding possible approaches for deriving site-specific criteria (SSC). The initial regression model, which included total organic carbon (TOC), hardness/alkalinity ratio, and total dissolved solids (TDS) as model input parameters, was selected based primarily on its R^2 value and by considering how each parameter is mechanistically related to aqueous copper bioavailability and toxicity. **Section 3.2.4** of the revised report provides a more formal discussion of the various statistical criteria and chemistry relationships considered when evaluating and selecting a multiple-regression model.

Based on discussions with NMED SWQB during the June 10, 2013 meeting in Santa Fe, New Mexico concerning additional statistical evaluations and on the above comment regarding low alkalinity concentrations, Chino proposes a new regression model that uses dissolved organic carbon (DOC) and alkalinity as the model input parameters in the revised report. This new model is equivalent in terms of predictability compared to the initial model described above which used TOC, hardness/alkalinity, and TDS as input parameters. Additionally, this new proposed model appears to be more reliable based on the variance and model structure (i.e., similar predictive capability using fewer input parameters) and it is consistent with the NMED suggestion to not use the hardness/alkalinity ratio in the regression model. **Section 3.2.4** of the revised report describes how using measured concentrations of alkalinity instead of the hardness/alkalinity ratio addresses uncertainty about low alkalinity concentrations and/or similar hardness/alkalinity ratios that can be derived from differing alkalinity concentrations.

The revised water effect ratio (WER) model was selected based on a step-wise multiple linear regression analysis that evaluated relationships between different combinations of water chemistry parameters and copper toxicity (**Section 3.2.4** and **Table 3** of the report). Other possible approaches including the copper biotic ligand model (BLM) (**Section 3.2.5**), hardness-based criteria (**Section 3.2.1**), and application of a static WER to derive SSC (**Section 4.1**) were evaluated and compared to the proposed approach in the revised report. The general WER model approach described herein, and the specific regression model selected for this approach (DOC and alkalinity), were determined to provide the most accurate and reliable predictions of Site-specific copper toxicity based on this comparison. The margin of safety recommendations to the proposed approach (i.e., use of the *D. magna* SMAV as the WER denominator and treatment of input parameters that are either above or below the range used to develop the model described in **Section 4.2.2**) ensures that SSC are derived in an environmentally conservative way.

NMED Comment #2: Another approach discussed is to adjust the BLM which presently is systematically under-protective. Again, the suggestion here is not that one of these options is better that the model proposed in the draft report but simply that these alternatives should be evaluated to provide confidence that the proposed model is the most scientifically defensible.

Chino Response #2: As described **Section 3.2.5** of the revised report, Chino does not recommend using a modified BLM (or the BLM "out of the box") to derive site-specific copper criteria for STSIU surface waters. Currently, the options for adjusting the BLM only affect the toxicity-prediction mode application. The program files used in the BLM's criteria calculation option are not publically available. Although it is possible to request access to these files per Dr. Joe Meyer during the June 10, 2013 meeting, the acceptability of this approach is questionable since calculations would not be reproducible by others, and because these potential adjustments could be inconsistent with EPA's intended use of the BLM for copper criteria calculations. Based on the evaluations presented in the revised report and discussed during the June 10, 2013 meeting, adjusting the BLM to systematically change the predictions is not expected to provide greater predictability compared to the regression-model approach. **Section 3.2.5** of the revised report provides additional discussion of the copper BLM.

NMED Comment #3: The Cu model presented in the report addresses site specific challenges, and reduces the uncertainty associated with other approaches including hardness-based criteria and the BLM, however further detail regarding the implementation of the model to develop criteria recommendations for STSIU surface waters is also necessary. For example, given that water was only collected from perennial pools and not stormwater, the SWQB assumes that the SSC only applies to the chronic Cu criteria, and not the acute. Likewise, SWQB assumes that the geographic extent to which SSC would apply only includes those drainages from which water was collected.

Chino Response #3: **Section 4.2** of the revised report provides details regarding the implementation of the model to derive and apply SSC to STSIU waters. That section specifically describes step-by-step how to apply the proposed WER model to derive a SSC, discusses the applicability of the approach to acute and chronic SSC, and proposes the geographic extent for model application. Based on discussions provided in **Section 4.2**, a brief summary of the recommendations for model implementation and applicability follows.

- *Model Implementation*: The proposed approach for using the WER model to derive and apply SSC to STSIU waters was developed based on available WER guidance and based on current procedures for calculating and applying the current hardness-based copper criteria. The recommendation is to apply the model on a sample-by-sample basis (similar to the hardness-based criteria approach) to derive a SSC and evaluate compliance for a given sample. This is accomplished by applying the WER model to the measured DOC and alkalinity concentrations from a sample to calculate a SSC. Compliance is then evaluated by comparing the measured copper concentrations from that sample to the derived SSC.

- *Application to Acute and Chronic Criteria*: Based on USEPA WER guidance, the proposed approach can be used to derive both acute and chronic criteria. Water samples used in the WER toxicity tests were collected from ephemeral pools associated with monsoon storm water runoff and from intermittent and perennial pools; all WER toxicity tests were performed using the acute *Daphnia magna* toxicity test procedure. The USEPA WER guidance states that a WER derived from acute toxicity tests can be applied to both acute and chronic criteria. The protectiveness against toxicity (and thus the value of the WER) is determined by the water chemistry, not by the length of time surface water exists within a given drainage. **Section 4.2.1** of the revised report provides additional discussion of model application to acute and chronic criteria.

- *Geographic Extent of Model Application:* Chino believes the proposed regression-based model can be applied to all of the STSIU drainages, provided the water chemistry is similar to the water chemistry range from which the model was developed (see discussions in **Section 4.2.2.3** of the revised report). Chino does not believe that a model developed for STSIU waters should be applied to the adjacent Hanover-Whitewater Creek (HWC) drainage system because water chemistry in HWC differs from water chemistry in the STSIU waters, and because the geomorphology, hydrology and surrounding uplands also differ from the STSIU study area. In contrast, because the model is developed from only STSIU samples collected from locations with relatively similar hydrology, geomorphology and upland vegetation characteristics, it can be applied to all drainages in the STSIU study area. Given the strong statistical relationship demonstrated between water chemistry and toxicity results, there is high confidence that "predicted" results derived from the model are applicable to all of STSIU drainage locations. Furthermore, the evaluation of STSIU chemistry ranges presented in **Appendix E** shows that chemistry ranges used to develop the proposed model are representative of surface water chemistry ranges measured to date in the STSIU area.

<u>NMED Comment #4:</u> We also recommend the final report address not only the adjustment of the Cu criteria based on SSC – but also consider specific aquatic species that are present in the watershed, and their sensitivity to Cu to ensure that the revised standard is sufficiently protective. The final report should consider the results of the 2008 USGS study by Little and Calfee, submitted to the US Fish and Wildlife Service, which examined the toxicity of metals to the Chiricahua leopard frog. The study recorded Lowest Observed Effect Concentrations from the 60-day "chronic" tests for copper at 0.047 mg/L for development and length, and 0.007 mg/L for weight. Therefore, the Chino Mines study

should consider whether the proposed regression model is consistent with these results, or otherwise address whether the regression model, if applied to these waters, would be protective of developmental stages of Chiricahua leopard frog. It is noted that while the Little and Calfee (2008) report does not provide information on TOC concentrations the TDS, alkalinity and hardness values are all within the range of waters collected from the STISU.

Chino Response #4: **Appendix** F of the revised report evaluates the protectiveness of the proposed WER model approach to the Chiricahua leopard frog (CLF), based on the copper effect concentrations reported in Little and Calfee (2008). In summary, **Appendix F** shows that the proposed approach is protective of CLF developmental stages. This conclusion is based on applying the proposed model to the water chemistry values measured during the 60-day copper exposures and determining that the derived SSC is less than all effect concentrations reported by Little and Calfee (2008). Although organic carbon concentrations were not measured or reported in Little and Calfee (2008), Little et al. (2011) reported DOC concentrations of 0.2 to 0.5 mg/L from the same laboratory and during the same time period for a similar mixture of well water and deionized water. Therefore, these DOC concentrations were used to calculate SSC from the new proposed model (which uses DOC and alkalinity to predict toxicity and thus WERs) to compare to the reported CLF effect concentrations. This comparison is the primary basis for concluding that the proposed approach will be protective of developmental stages of the CLF. In **Appendix F**, Chino also provides an evaluation of the study design and applicability of reported effect concentrations in Little and Calfee (2008) to identify possible uncertainties associated with the reported effect concentration in order to fully compare the protectiveness of the proposed WER model to the sensitivity of the CLF. This evaluation further supports Chino's conclusion that the proposed approach is protective to the CLF.

NMED Comment #5: Finally, Chino Mines suggested that they may submit the final report for external scientific review and publication. Given the unique approach presented in the draft report, SWQB supports publication in peer reviewed scientific literature as it will strengthen the basis for SSC in the STISU.

Chino Response #5: Chino plans to submit the study results and the proposed WER model report for scientific review and publication by the end of 2013, following SWQB's review of this revised report. Based on this schedule, Chino expects final approval from the journal in April 2014.

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Revised Site-Specific Copper Toxicity Model Report

Chino Mine, Vanadium, New Mexico

October 2013

ARCADIS

Revised Site-Specific Copper Toxicity Model Report

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Tables

Figures

Appendices

Acronyms and Abbreviations

ACZ	ACZ LABORATORIES, INC.
AOC	Administrative Order on Consent
AWWQRP	Arid West Water Quality Research Project
BLM	Biotic Ligand Model
CCC	Criterion Continuous Concentration
COC	Chain of Custody
Chino	Freeport-McMoRan Chino Mines Company
CMC	Criterion Maximum Concentration
DOC	Dissolved Organic Carbon
DOM	Dissolved Organic Matter
EC50	Median Effect Concentration
FS	Feasibility Study
GEI	GEI Consultants, Inc.
IA	Investigation Area
LA50	Lethal Accumulation Concentration
LC50	Median Lethal Concentration
MDL	Method Detection Limit
MLR	Multiple Linear Regression
NMAC	New Mexico Administrative Code
NMED	New Mexico Environment Department
pH	Negative of the logarithm of the hydrogen ion concentration (standard units)
RAC	Remedial Action Criteria
RI	Remedial Investigation
SSC	Site-Specific Criteria
SWQB	Surface Water Quality Bureau
STSIU	Smelter/Tailing Soil Investigation Unit
TDS	Total Dissolved Solids
TOC	Total Organic Carbon
TSS	Total Suspended Solids

UAA	Use Attainability Analysis
USEPA	United States Environmental Protection Agency
VIF	Variance Inflation Factor
WER	Water-Effect Ratio
WQC	Water Quality Criteria

1. Introduction and Background

On December 23, 1994, Freeport-McMoRan Chino Mines Company (Chino) and the New Mexico Environment Department (NMED) Surface Water Quality Bureau (SWQB) entered into an Administrative Order on Consent (AOC) to investigate historical releases of potentially hazardous substances within the Chino Mine Investigation Area (IA), Grant County, New Mexico (the Site). The Smelter and Tailing Soil Investigation Unit (STSIU) is one of the investigation units within the defined IA. By letter dated September 16, 2010, NMED specified the Pre-Feasibility Study (FS) Remedial Action Criteria (RAC) for the STSIU. As one of the Pre-FS RAC, NMED required compliance with New Mexico Standards for Interstate and Intrastate Surface waters, 20.6.4 New Mexico Administrative Code (NMAC) for risk to aquatic life for drainages within the STSIU. The letter states that Pre-FS RAC for all constituents equal 20.6.4 NMAC, including all approaches and tools listed in the Code that provide options for site-specific application.

Copper is the primary contaminant of concern in STSIU, and surface water in some STSIU drainages has been determined to exceed the aquatic life water quality criteria in 20.6.4 NMAC before consideration of the approaches and tools that provide for site-specific application. In particular, in accordance with Section 20.6.4.900 NMAC, water quality criteria for copper (and other divalent cationic metals) are calculated using a standard equation based exclusively on site-specific water hardness. Previous Site investigations, including the Site-wide ERA (Newfields 2005) and STSIU Remedial Investigation (RI) indicated exceedances of current hardness-based copper criteria in sub-drainage basins within the STSIU area. However, a variety of other physical and non-hardness chemical characteristics of the water and the metal can influence metal bioavailability and toxicity to aquatic organisms (U.S. Environmental Protection Agency [USEPA] 1994, 2001, 2007). Multiple studies have demonstrated other water quality parameters such as suspended and dissolved solids, pH, alkalinity, organic carbon compounds, ionic strength and other characteristics have equal or greater effects on copper toxicity than hardness alone (AWWQRP 2006, Meyer et al. 2007).

To account for the effects water chemistry has on metal toxicity, site-specific criteria (SSC) may be developed using scientifically defensible methods that are described in Section 20.6.4.10 part D of NMAC, which includes the Water-Effect Ratio (WER) procedure. The WER procedure consists of site-water toxicity tests conducted side-by-side with laboratory-water toxicity tests, and is used to specifically account for differences between toxicity of the metal in laboratory dilution water and toxicity of the metal in Site water that can be attributed to site-specific water chemistry. If there is a difference in toxicity and it is not taken into account, the aquatic life criteria for the tested body of water might be either more or less protective than intended by EPA's

Guidelines for Deriving Numerical National Water Quality Criteria for the Protection of Aquatic Organisms and Their Uses (USEPA 1994).

1.1 Historical Background of STSIU WER Studies

In August 2011 on behalf of Chino, ARCADIS submitted a work plan titled *Development of Site-Specific Copper Criteria* (ARCADIS 2011) to the NMED Surface Water Quality Bureau (SWQB) that described proposed WER studies to support the development of site-specific copper criteria in STSIU surface waters. SWQB provided comments to the work plan in a letter dated September 1, 2011. The WER studies were subsequently conducted, and a summary of preliminary results and the WER multiple-regression model approach described in the work plan was presented to NMED SWQB during a March 23, 2012 meeting in Albuquerque, NM. These results were further evaluated against USEPA (1994, 2001) WER acceptability criteria and fully reported in the draft Criteria Adjustment Interim report that was submitted to NMED SWQB in October 2012 (ARCADIS 2012). Chino received NMED comments to that report in December 2012, and submitted responses to those comments and a revised Interim Report to NMED SWQB in March 2013 (ARCADIS 2013a).

As described in the above work plan and Interim Report, and acknowledged by NMED comments to the work plan, a modified approach is required to develop and apply SSC to STSIU surface waters because the site-specific hydrologic conditions and contaminant sources at STSIU are not explicitly addressed in the available USEPA WER guidance. The use of multiple-regression analysis of co-located toxicity and water chemistry data explicitly accounts for the effects of site-specific water chemistry on copper bioavailability and toxicity and can also address the site-specific challenges described in the work plan. The technical basis of this approach, including statistical evaluations, application of available USEPA guidance, and consideration of the mechanisms of copper bioavailability and toxicity, was initially described in the draft Copper Toxicity Model report submitted to NMED SWQB in April 2013. Chino and NMED SWQB subsequently met in Santa Fe, NM on June 10, 2013 to discuss the WER model approach described in that report. The current report has been updated based on discussions with NMED SQWB during the June 10, 2013 meeting and based on comments received from NMED SWQB to the draft Copper Toxicity Model report in a letter dated July 1, 2013.

1.2 Study Objectives

This report describes the development of a site-specific copper WER model that can potentially be used to predict and derive adjusted copper criteria in STSIU surface waters. As described previously, a modified approach is required to develop and apply SSC to STSIU surface waters because site-specific STSIU conditions are not specifically covered in the available USEPA WER guidance documents (USEPA 1994, 2001). These site-specific conditions include diffuse, nonpoint-source copper contamination to multiple ephemeral drainage channels that typically flow only in direct response to monsoonal precipitation. As a result, almost all aquatic habitats in STSIU consist entirely of isolated pools located in predominately bedrock sections of drainage channels. Additionally, water chemistry has been observed to be variable across the numerous STSIU sub-watersheds because of localized differences in geology, geomorphology, hydrology, and surrounding upland landscapes among the sub-watersheds.

The interim report (ARCADIS 2013a) established that toxicity and chemistry data collected during WER sampling in 2012 were acceptable for use in the development of SSC for copper. WERs determined during that sampling and analysis effort were mostly greater than 1, indicating that the current hardness-based copper criteria are overprotective of aquatic life uses in the STSIU samples used for WER testing. Additionally, the Interim Report demonstrated that site-specific copper toxicity and copper WERs were variable across the STSIU watersheds. It was hypothesized in the Interim Report that the toxicity variability could be largely explained by the variability in water chemistry samples used for testing.

The primary objective of this report is to further evaluate site-specific copper toxicity and water chemistry data reported in ARCADIS (2013a) by performing statistical evaluations of the chemistry and toxicity variability to determine specific chemical parameters that are most correlated with the observed toxicity. Based on these evaluations, the second objective of this report is to describe a site-specific copper WER model that can explicitly account for this variability, and thus can potentially be used to develop and apply SSC to STSIU watersheds.

2. Methods

Field and laboratory methods employed in this study were described in ARCADIS (2013a) and were consistent with methods described in the available WER guidance documents. A brief summary of the field and laboratory methods as reported in ARCADIS (2013a) follows.

Field sampling and laboratory testing occurred twice during the wet season in 2011. WER samples were collected in eight different sub-watersheds; these samples were collected during two separate sampling rounds in 2011. The first round of field sampling was performed during 29 August – 2 September, 2011 and included 12 WER samples; the second round of field sampling was conducted during 19 – 20 September 2011 and included six WER samples. **Figure 1** presents the location of all samples collected during both rounds of WER sampling. Flow was not observed in any drainage during the field sampling; all water samples were collected from isolated, surface-water pools present in bedrock or primarily bedrock sections of drainage channels. In total, 18 WER samples were collected from 12 distinct sampling locations located across eight sub-watersheds (**Figure 1**). In addition to subsamples of those waters, six additional water samples were submitted for chemical analyses (i.e., these six additional samples were not used in the WER toxicity tests) during the two rounds of sampling. As noted in ARCADIS (2013a), sample locations were limited to drainage areas containing surface water. The majority of drainage areas surveyed were dry during each sampling round. At each of the 12 water-sampling locations for WER toxicity tests, surface-water samples were split at the time of collection and a portion of each split sample was sent directly from the field to ACZ Laboratories, Inc. (ACZ) in Steamboat Springs, Colorado, for chemical analyses; the other portion of the split sample was sent directly from the field to GEI Consultants, Inc. (GEI) in Denver, Colorado, for WER toxicity tests. Samples were collected, shipped, and stored according to methods described in ARCADIS (2011) and USEPA (1994, 2001), which included "clean sampling techniques", chain-of-custody (COC) forms and USEPA protocols for toxicity testing.

WER toxicity tests were conducted by GEI using less than 24-hour-old neonates of the freshwater cladoceran *Daphnia magna* (an invertebrate) as the primary test species. WER toxicity tests were also conducted on a subset of samples using less than 24-hour-old larvae of the fathead minnow (*Pimephales promelas*; a freshwater fish) as the secondary test species. The major use of the secondary species, as described by USEPA (1994), is confirmation of toxicity results obtained with the primary species. Use of a secondary species, however, was omitted from the more recent USEPA Streamlined WER Guidance because "the additional test has not been found to have value" (USEPA 2001: p. 5). Instead, the Streamlined Procedure requires that either *Ceriodaphnia dubia* (another freshwater cladoceran) or *D. magna* be used as the tested taxon because "experience has shown that the daphnids, which are quite sensitive to copper, have been the most useful test organisms for WER studies" (USEPA 2001: p. 5). As described in ARCADIS (2013a), results from the secondary test species (the fathead minnow) confirmed results obtained with the primary test species (*D. magna*) according to WER acceptability criteria presented in USEPA (1994). This report therefore focuses evaluations on the *D. magna* copper toxicity endpoints because it was identified, and validated, as the primary test organism.

Toxicity test procedures followed methods described in USEPA WER guidance (USEPA 1994, 2001) and general whole-effluent acute-toxicity testing methodology (USEPA 2002). Test conditions are listed in **Appendix A**. Stock solutions of copper were prepared by dissolving $CuCl_2{\cdot}2H_20$ in deionized water. A separate stock solution was prepared for each round of WER testing, but the same stock solution was used to spike all laboratory and STSIU waters in each round of testing. Results from 24-hour range-finding toxicity tests (conducted for each STSIU water sample) were used to select the copper exposure concentrations in the WER toxicity tests. Total recoverable and dissolved concentrations of copper were measured in each exposure treatment required to calculate the toxicity endpoint, consistent with USEPA (1994, 2001) WER protocols. Total and dissolved copper were measured at the beginning and end of each 48-hour *D. magna* toxicity test. WER guidance requires dissolved metal analysis at the beginning and end of toxicity tests, but only requires total metal analysis for exposure water samples collected at the beginning of tests. Total copper was measured on samples collected at the beginning and end of toxicity tests to provide an additional verification of copper exposure concentrations. Samples for dissolved-metals analyses were filtered in GEI's laboratory using a 0.45-micrometer (µm) filter. The samples were preserved after filtration and shipped to ACZ for analysis.

Toxicity tests using STSIU surface waters were conducted side-by-side with toxicity tests using standardized laboratory dilution water according to USEPA protocol (USEPA 1994, 2001). As described by USEPA (1994), more than one toxicity test using site water may be conducted side-by-side with a single laboratory dilution water. However, multiple laboratory dilution-water toxicity tests were conducted in this study to encompass the range of water hardness in STSIU waters and because toxicity tests were staggered across multiple days in each round of WER testing. For WER calculations, STSIU surface-water samples were matched to a laboratory dilution water toxicity test based on the hardness concentrations in each water type according to USEPA (1994). Hardness concentrations for all laboratory-water toxicity tests were selected based on the hardness of STSIU samples measured when the water samples arrived at GEI. The intent was to match water hardness between field and laboratory samples as close as possible while meeting WER testing requirements, including equal or lower water hardness in matched laboratory dilution water (unless hardness in site water is less than 50 mg/L as $CaCO_3$; USEPA 1994). Consistent with USEPA guidance, all laboratory dilution-water toxicity tests were conducted at water hardness between 40 and 220 mg/L as $CaCO_3$.

2.1 Data Analysis

Acute toxicity of contaminants to aquatic organisms is usually evaluated in terms of the concentration needed to kill or cause adverse effects to 50% of the tested organisms [i.e., median effect concentrations (EC50 values)]. In this WER study, EC50s values were calculated based on total and dissolved copper concentrations using maximum likelihood probit analysis in ToxCalc™ version 5.0 software (Tidepool Scientific Software, McKinleyville, California). One-half the detection limit was used in all samples for which copper concentration was below the method detection limit (MDL). The toxicity results for *D. magna* are reported as EC50 values because immobilization was used as a surrogate for death in those organisms (as discussed in USEPA 2002).

In accordance with USEPA (1994, 2001) guidance, the WER for each sample was calculated from the EC50 values in STSIU site water and the laboratory water, as follows:

$$\text{WER} = \frac{\text{Site-Water EC50}_{\text{hardness-normalized}}}{\text{Lab-Water EC50}_{\text{hardness-normalized}}} \qquad \text{(Eqn. 1)}$$

where:

Site-Water EC50 $_{\text{hardness-normalized}}$ = the copper EC50 obtained in STSIU site water, adjusted to a standard hardness using the copper-criteria hardness slope and equation 2 (shown below), and

Lab-Water EC50 $_{\text{hardness-normalized}}$ = the copper EC50 obtained in laboratory water, adjusted to a standard hardness using the copper-criteria hardness slope and equation 2 (shown below).

Normalization of each EC50 value used in a WER calculation is intended to account for the differing hardness concentrations of site and laboratory water and is a requirement specified in each WER guidance document (USEPA 1994, 2001). In this WER study, all EC50 values were normalized to a hardness of 100 mg $CaCO_3$/L, as follows:

$$\text{EC50}_{\text{hardness-normalized}} = \text{EC50}_{\text{at sample hardness}} \cdot \left(\frac{\text{Std H}}{\text{Sample H}}\right)^{0.9422} \qquad \text{(Eqn. 2)}$$

where:

EC50$_{\text{hardness-normalized}}$ = the copper EC50 adjusted to a standard hardness concentration (i.e., the predicted EC50 if the sample hardness had equaled the standard hardness),

Std H = a standard hardness concentration to which all EC50 values are normalized (a hardness of 100 mg/L as $CaCO_3$ was used to normalize all EC50 values in this study),

Sample H = the hardness of the laboratory water, the site water, or the species mean acute value (SMAV), 0.9422 = the log-log regression slope for the 1984/1985 and 1995 USEPA acute copper criteria, which is also the slope currently used for the copper criteria in the New Mexico Water Quality Standards.

2.2 Statistical Evaluations

The following sections describe statistical evaluations and copper biotic ligand model (BLM) analyses performed on the chemistry and toxicity data presented in ARCADIS (2013a).

All statistical evaluations of the toxicity and chemistry data, including linear correlation and regression analyses, were performed using SigmaPlot™ version 12.1 software (SYSTAT Software, Inc., San Jose, California). A Pearson Correlation analysis was performed on all the chemical and toxicity variables to calculate correlation coefficients (*r*-values) and the level of significance (i.e., *p*-value) between pairs of the variables, to help understand the degree and direction of the linear relationship between pairs of variables (including comparisons of a toxicity endpoint versus a water chemistry parameter, or comparisons of pairs of water chemistry parameters). Results from this correlation analysis were considered when selecting parameters to include in additional regression analyses. For regression analyses, data were log-transformed with the exception of pH data (which already is the negative logarithm of the hydrogen-ion concentration). Toxicity endpoints were then regressed against individual water chemistry parameters (i.e., using univariate linear regression). Based on the above analyses, in conjunction with knowledge of the mechanisms of copper toxicity and bioavailability, step-wise multiple linear regression (MLR) analyses were performed using various combinations of water chemistry parameters to determine the best subset of parameters for predicting the observed toxicity. The best-fit model was based on the coefficient of determination (i.e., R^2) of the regression, the *p*-value, and evaluation of the significance level of each variable's coefficient (for the MLR analyses).

2.3 Statistical Criteria

The *a priori* specified level of significance of $\alpha = 0.05$ was used as a basis for identifying statistically significant relationships. Thus, correlation and regression *p*-values of ≤ 0.05 are considered significant, although *p*-values that approached this specified level of significance were also considered when interpreting results. For the MLR analyses, care was taken to limit co-linearity of water chemistry parameters selected for the toxicity-prediction model, as judged by the variance inflation factor (VIF). Co-linearity between two chemistry parameters was determined to be significant (and thus might potentially confound results) if the calculated VIF value was ≥ 4, and only the more significant variable (based on univariate correlation) was potentially used in the model.

2.4 Copper Biotic Ligand Model (BLM) Evaluations

The copper BLM (version 2.2.3; available at http://hydroqual.com/wr_blm.html) was used to predict copper EC50 values for *D. magna.* Measured pH, alkalinity, and concentrations of dissolved organic carbon (DOC), calcium (Ca), magnesium (Mg), sodium (Na), potassium (K), chloride (Cl^-), and sulfate (SO_4^{2-}) were used as model input parameters for all site-water toxicity tests. In addition, default values for percent humic acids (10%) and sulfide (0.01 µM) were used, consistent with recommendations in the BLM User's Manual (HydroQual 2007).

3. Results

All data analyses described in this report use data presented in the ARCADIS (2013a) tables, but are separate evaluations from the referenced report. Data tables presented in ARCADIS (2013a) are included in **Appendix A** for reference. Additionally:

- A summary of the Pearson Correlation analyses performed between pairs of toxicity endpoints and water chemistry parameters is provided in **Appendix B.**
- **Appendix C** provides the SigmaPlot™ statistical software output for all the univariate (i.e., single-predictor) linear regression analyses performed with pairs of parameters.
- **Appendix D** provides the SigmaPlot™ statistical software output for all the MLR analyses performed with combinations of multiple parameters.
- **Appendix E** provides an evaluation of surface-water chemistry ranges observed in STSIU.
- **Appendix F** presents an evaluation of the protectiveness of the proposed WER model to Chiricahua leopard frog.

3.1 Interim Report Results

Results presented in ARCADIS (2013a) broadly indicate that the current hardness-based copper criteria are overprotective of aquatic life uses in most STSIU surface-water samples tested. This finding is based on comparing copper toxicity endpoints measured in Site-water samples to the same copper toxicity endpoints measured in laboratory dilution-water samples. *D. magna* copper EC50, which is the concentration of copper required to cause adverse effects to 50% of the test organisms, was the toxicity endpoint used in these studies. WERs were calculated for each sample as the quotient of the site-water EC50 divided by the laboratory-water EC50; WER values greater than 1 indicate copper is less toxic in the Site water than in the laboratory dilution water.

WERs were calculated and presented in ARCADIS (2013a) using several different WER denominators that correspond to the various approaches described in the Interim WER guidance (USEPA 1994) and in the Streamlined Copper WER guidance (USEPA 2001). Based on comments received from NMED SWQB, Chino agreed that the approach described in USEPA (2001) would be used for the WER calculation. In that approach, if the hardness-normalized laboratory-water EC50 is less than the hardness-normalized species mean acute value (SMAV) presented in USEPA (2001) for *D. magna*, the SMAV should be used in the WER denominator. Normalized to a hardness of 100 mg/L as $CaCO_3$, the *D. magna* SMAV for dissolved copper is 19.31 µg/L.

Table 1 lists the measured WER values reported in ARCADIS (2013a) that were calculated using that SMAV in the denominator. Measured WERs ranged from 0.989 to 14.41, indicating that site-specific copper toxicity was variable when compared across all the surface-water samples. **Table 1** also lists:

- Dissolved copper concentrations measured in WER samples;
- The hardness-based copper criteria maximum concentration (CMC, or acute criteria) calculated from the hardness measured in each sample;
- Compliance ratios calculated by dividing the measured copper concentrations by the hardness-based copper CMC (e.g., dissolved copper / CMC), and
- Compliance ratios calculated by dividing the measured copper concentrations by their respective WER-adjusted copper CMC (e.g., dissolved copper / [CMC x WER]).

Hardness-based copper compliance ratios that are greater than 1 indicate an exceedance of the hardness-based copper CMC. As listed in **Table 1**, dissolved copper concentrations in seven samples exceeded the hardness-based CMC, with compliance ratios in those seven samples ranging from 1.2 to 7.6. However, when the WER determined for each sample is used to adjust the sample's hardness-based CMC, all of the resulting adjusted compliance ratios are less than 1. This approach is consistent with the sample-specific WER approach described in USEPA (1994: pp. 14-15), which can be used to evaluate whether metal concentrations in a sample are acceptable after accounting for the effect of site-specific water chemistry (i.e., by using the measured WER to adjust the CMC). As stated in USEPA (1994), the metal concentration of a sample is acceptable when the adjusted compliance ratio is less than 1. Based on this analysis, copper was within acceptable compliance ranges for all test samples, after applying the sample WER to account for the protective effects of site-specific water chemistry on the aquatic toxicity of copper. Broadly, this indicates copper toxicity in Site waters is less than predicted by the current hardness-based copper criteria.

One of the objectives of the WER study design, as described in ARCADIS (2011, 2013a), was to include a chemically and spatially diverse set of sample locations. The map presented in **Figure 1** shows that WER samples were collected in eight different sub-watersheds; these samples were collected during two separate sampling rounds in 2011. The variability observed in the site-specific toxicity of copper is expected to be related to the variability of water chemistry, as described in ARCADIS (2013a). In accordance with USEPA (1994), an assumption worth testing is whether the WER correlates to water quality characteristics. This assumption is statistically evaluated in Section 3.2.

3.2 Toxicity and Water Chemistry Correlations

Correlation analyses were performed using the co-located copper toxicity and water chemistry values to determine chemical parameters that were statistically associated with the measured toxicity values. Results from the Pearson Correlation analysis performed on chemistry and toxicity data are summarized in **Appendix B**. These correlation results provide a useful basis to identify water chemistry parameters that are statistically associated with copper toxicity and, therefore, parameters that might require further evaluation when considering site-specific water chemistry effects on copper toxicity. Results from the Pearson Correlation analysis are expressed as the significance level (the *p*-value) and correlation coefficient (the r-value) associated with comparisons between two variables.

3.2.1 Influence of Inorganic Water Chemistry Parameters on Observed Copper Toxicity

A greater than 12-fold difference in *D. magna* dissolved copper EC50 values was measured in Site-water samples, ranging from 14.7 µg/L in sample WER-1-12 to more than 184.7 µg/L in sample WER-2-9. An important observation is that hardness concentrations in these low- and high-WER samples were almost equal (e.g., hardness concentrations of 76 and 82 mg $CaCO_3$/L in samples WER-1-12 and WER-2-9, respectively), indicating that water chemistry parameters other than hardness can have a significant effect on site-specific copper toxicity. This has important site-specific implications because the current New Mexico numeric water quality criteria for copper are based exclusively on sample-specific hardness concentrations. The linear regression presented in **Figure 2** further illustrates the lack of relationship between hardness and copper toxicity in STSIU samples. Specifically, the coefficient of determination (R^2) for the hardness versus EC50 regression is 0.10, which implies that hardness accounts for only 10% of the variability associated with copper toxicity in these Site waters. As listed in **Figure 2**, the level of significance (i.e., the *p*-value) for the regression coefficient is 0.211, which is greater than the specified α level of 0.05, indicating that hardness is not a statistically significant predictor of copper toxicity in the tested site waters.

Other non-hardness water chemistry parameters are expected to have equal or greater influence on copper bioavailability and toxicity compared to hardness. One such parameter is alkalinity, which is a measure of the acid-neutralizing capacity of water. Alkalinity in most natural fresh waters is due to the presence of carbonate (CO_3^{2-}), bicarbonate (HCO_3^-) and hydroxyl (OH^-) anions. In some surface waters, other important non-carbonate contributors to alkalinity include organic ligands and phosphate, ammonium, silicate, sulfide, borate, and arsenate ions (Hem 1985). Alkalinity is generally recognized as influencing copper bioavailability and toxicity in aquatic systems through the formation of less toxic copper-base complexes (Wurts and Perschbacher 1994). Empirical toxicity results reported by others demonstrated that alkalinity generally decreases copper toxicity (as evidenced by increasing copper toxicity endpoints determined at increasing alkalinity concentrations; Meyer et al. 2007). Results from the current study are consistent with this general trend. As an example, **Figure 3** shows that *D. magna* EC50 values were positively correlated with alkalinity having a regression p-value of 0.004, indicating a statistically significant relationship between alkalinity and the measured *D. magna* EC50 value ($R^2 = 0.43$).

In most waters, alkalinity and hardness concentrations are similar because the anions of alkalinity (e.g., HCO_3^- and CO_3^{2-}) and the cations of hardness (e.g., Ca^{2+} and Mg^{2+}) are derived from the same carbonate minerals (Meyer et al. 2007). Any sample hardness greater than the corresponding sample alkalinity represents non-carbonate hardness (e.g., $CaSO_4$, $MgCl_2$). In contrast, in waters containing greater alkalinity than hardness, potassium and sodium carbonates/bicarbonates are expected to be a major source of the alkalinity. Although hardness and alkalinity concentrations in the Site-water toxicity samples were well-correlated (**Figure 4**; R^2=0.68), relative differences were observed between hardness and alkalinity proportions across all tested waters, which can be an important factor to consider when evaluating toxicity variability, as described below.

That copper toxicity endpoints were significantly correlated with alkalinity, but not hardness, indicates alkalinity might be a better predictor of site-specific copper toxicity than hardness. However, evaluating the relationship between copper toxicity and the relative difference between hardness and alkalinity of a sample is informative to the mechanisms of copper bioavailability and toxicity. A potential metric for this evaluation is the hardness-to-alkalinity ratio (H/A), which can be interpreted as a measure of the alkalinity deficiency of a sample (because alkalinity is typically equal to or less than the hardness of STSIU waters). As shown in **Figure 5**, copper toxicity in Site water tends to increase (i.e., lower EC50 values) when the hardness concentration is increasingly greater than the alkalinity concentration (i.e., at greater H/A values). In contrast, Site-specific copper toxicity decreases as the hardness-to-alkalinity ratio decreases. Using the hardness-to-alkalinity ratio as a predictor variable for site-specific copper toxicity provides a more statistically significant relationship (i.e., regression coefficient *p*-value < 0.001; $R^2 = 0.54$) compared to regressing the toxicity endpoint against hardness or alkalinity separately. Although the concentration difference between hardness and alkalinity might logically have also been used as a predictor of copper toxicity, it was not as strong a predictor as the hardness-to-alkalinity ratio.

Another non-hardness chemical parameter determined to be significantly correlated to site-specific copper toxicity is total dissolved solids (TDS), which refers to the amount of all inorganic and organic substances in a water sample that passes through a 0.45-µm filter. TDS measurements are not ion-specific (i.e., they do not quantify the mass concentration of a particular ion), but describe the overall mass of all dissolved inorganic and organic constituents. TDS is often correlated with electrical conductivity and the ionic strength of a sample, which have been previously shown to influence the toxicity of copper to aquatic organisms. Major ions typically responsible for the TDS content of a sample include calcium, magnesium, sodium, potassium, bicarbonate, phosphates, nitrates, chloride and sulfate. As indicated in **Figure 6**, copper toxicity generally decreased as TDS concentration increased (*p*-value = 0.04; $R^2 = 0.25$).

3.2.2 Influence of Organic Carbon on Observed Copper Toxicity

Organic carbon is well-known to have an important effect on copper bioavailability and toxicity to aquatic organisms (EPA 2007, Meyer et al. 2007). The Interim Report described how both total organic carbon (TOC) and DOC varied substantially in water samples collected throughout the STSIU drainages. This organic carbon variability explains a substantial portion of the variability of toxicity measured in the STSIU surface-water samples. As shown in **Figures 7** and **8**, both TOC and DOC were well-correlated with site-specific copper toxicity, with toxicity decreasing (i.e., EC50 values increasing) as TOC and DOC concentrations increased. Based on all statistical analyses conducted and presented herein, organic carbon (either as DOC or TOC) was the single parameter most statistically correlated to site-specific copper toxicity (TOC: $R^2 = 0.62$, *p*-value <0.001; DOC: $R^2 = 0.75$, *p*-value <0.001). Mechanistically, organic carbon decreases the free-ion (i.e., Cu^{2+}) concentrations through the formation of copper-organic carbon complexes, thereby decreasing the bioavailablity of copper to aquatic organisms and thus decreasing its toxicity (Meyer et al. 2007).

In addition to the statistical relationships described above and the mechanistic importance of organic carbon to copper bioavailability, the relationship between organic carbon and copper toxicity has important Site-specific implications because of the variability and relatively high concentrations of organic carbon measured in STSIU surface waters (**Table 2**). Dissolved organic matter (DOM) is a ubiquitous component of natural surface and ground waters, and is chemically composed of a variety of carbon-based constituents including a small proportion of identifiable, low-molecular weight compounds such as carbohydrates and amino acids, and a larger proportion of complex, higher-molecular weight compounds collectively termed humic substances. DOM is operationally defined as any organic compound passing through a 0.45-µm filter (Evans et al. 2005).

The DOC component of DOM is conventionally measured as a surrogate to DOM concentrations, and DOC is assumed to constitute approximately ½ the mass of the DOM. Concentrations of DOC in natural waters vary widely, from less than 1 to greater than 50 mg/L (Thurman 1985). Concentrations of DOC in natural waters typically vary depending on watershed hydrologic conditions, geology, soil types, land-use, climate, and aquatic life. Generally, the lowest values are observed in the oceans, groundwater, and oligotrophic lakes and rivers draining bare rock or thin, organic-poor soils (Evans et al. 2005). Concentrations are highest in organic soil porewater, and fresh water draining wetlands and peat lands, especially where runoff is low and hydrologic residence time is high (Evans et al. 2005). In ephemeral stream systems typical of the arid southwest, the limited hydrologic flushing of adjacent uplands in conjunction with longer hydrologic residence times can contribute to moderately high aqueous organic carbon concentrations. In a study that characterized organic carbon in arid stream systems in the southwest, Westeroff and Anning (2000) reported that organic carbon concentrations were greater in ephemeral streams compared to nearby perennial stream systems. In these ephemeral systems, algae growth in the channel can represent a significant source of autochthonous (i.e., internally generated) organic matter and can potentially be a more important source of organic carbon than terrestrial plants due to the relatively sparse upland plant cover.

3.2.3 Consideration of Other Water Chemistry Parameters

Other chemical parameters such as total suspended solids (TSS), pH, and other ions can potentially affect copper toxicity to aquatic organisms. Presented as Pearson Corrleation results (i.e., r-values and *p*-values), **Appendix B** provides a summary of relationships observed between measured copper EC50s and these chemical parameters (in addition to relationships between pairs of chemical parameters).

Although pH can mechanistically influence copper bioavailability and toxicity to aquatic organisms (Meyer et al. 2007), a significant relationship was not observed in the current study between pH and copper EC50 values (r-value = -0.314; *p*-value = 0.220; **Appendix C** and **Figure 9**). Additionally, pH was not significantly associated with other inorganic parameters such as hardness, alkalinity, or TDS. However, a significant relationship was observed between pH and DOC (r-value = -0.488; *p*-value = 0.047) and the relationship between pH and TOC approached the specified level of significance of α = 0.05 (r-value = -0.398; *p*-value = 0.114). Greater DOC and TOC values were associated with lower pH values, perhaps because high concentrations of humic/fulvic acids (which can dominate DOC and TOC concentrations) tend to slightly acidify natural waters.

TSS was not significantly associated with copper EC50 values (r-value = 0.266; *p*-value = 0.301). The lack of relationship between copper EC50 values and TSS is not surprising because the current EC50 values are based on the dissolved fraction of copper to be consistent with the current aquatic life standard for copper in New Mexico. Accordingly, the amount of solids dissolved in a water sample (i.e., TDS concentration) is likely to be more important than TSS when considering mechanisms of dissolved copper bioavailability and toxicity. This is supported by the significant relationship observed between TDS and copper EC50 values described in Section 3.2.1. In contrast, TSS probably would be an important determinant of the bioavailability and toxicity of total recoverable copper in STSIU waters; however, total recoverable copper is not of regulatory concern in this situation.

Other ions such as potassium, calcium, magnesium, sodium, and sulfate were either signficantly associated with copper EC50 values (i.e., *p*-values <0.05) or approached the specified level of significance of α = 0.05 (**Appendix C**). However, these ions are explicitly accounted for by other inorganic parameters described in Section 3.2.1, including hardness, alkalinity and TDS. As a result, these ions are highly correlated to hardness, alkalinity and TDS (**Appendix B**) and thus should not be included in a statistical model of copper toxicity, because their inclusion would cause concern about co-linearity with other predictor variables.

3.2.4 Influence of Multiple Water Chemistry Parameters on Observed Copper Toxicity

The effect of multiple water chemistry parameters on the aquatic toxicity of metals is widely documented in the scientific literature (e.g., see review in Meyer et al. 2007), and reflected in USEPA options for site-specific criteria derivations (i.e., WER Procedure and the USEPA Copper BLM). An important finding from the above analyses is that multiple water chemistry parameters significantly influenced copper toxicity, and the relationship between these parameters is consistent with mechanisms of copper toxicity and consistent with relationships previously reported in the scientific literature. A series of MLR analyses were therefore performed in an effort to more fully examine effects of varying Site chemistry on dissolved copper toxicity.

Chemical parameters were evaluated in MLR analyses based on the correlation results (**Appendix B**), linear regression analyses (as described in the above Section and presented in **Appendix C**), and consideration of mechanisms of copper bioavailability and toxicity. **Table 3** lists the statistical summaries of the various MLR models evaluated (see **Appendix D** for complete statistical summaries of all evaluated MLR models).

The MLR models were evaluated on a statistical basis for predictive capabilities and by considering the relationship between water chemistry parameters and copper toxicity. Specific statistical criteria and relationships considered include:

- *Overall statistical fit*: Multiple-regression coefficients (i.e., R^2 and adjusted R^2) were used to evaluate the strength of the predictive relationship between sets of water chemistry parameters and copper toxicity. The statistical significance of the multiple-regression coefficient was also considered (i.e., by examining the overall regression p-value), although most MLR models considered were highly significant (i.e., $p < 0.001$). Because different numbers of predictor variables (i.e., water chemistry parameters) were evaluated across MLR models, the adjusted R^2 value was considered the most appropriate basis to compare the predictive strength among models. The adjusted R^2 takes into account the sample size and the number of predictor variables (and uses variances instead of the variations), which provides a more relevant diagnostic measure in multiple-regression analysis, especially when additional predictor variables are added to the model. An important point is that R^2 values can only increase or stay the same when additional predictor variables are added to a MLR model, regardless of whether the added variables is a significant predictor. In contrast, the adjusted R^2 value is sensitive to the number of predictor values and can decrease as additional predictor variables are added.
- *Strength of relationship between individual predictor variables and copper toxicity*: The strength of relationships between individual water chemistry parameters and copper toxicity was evaluated by the variable's coefficient p-value (or level of statistical significance). The specified level of significance of $\alpha = 0.05$ was used as a general basis for evaluating the significance of a single parameter, or whether a single parameter improved the statistical fit of the MLR model.
- *Multicollinearity*: The degree of correlation between predictor variables (referred to as multicollinearity) was examined when evaluating MLR models. When any one predictor variable can be predicted to a high degree from one or more other predictor variables (i.e., high correlation between predictor variables), MLR model estimates are considered unstable. Therefore, only the most predictive variable in a set of highly correlated variables should be entered into an MLR model.

- *Linkage between water chemistry and copper toxicity*: Parameters were selected for MLR evaluation based on their relationship to copper bioavailability and toxicity. Care was taken to select key, individual parameters that were previously identified as being significantly correlated to measured copper toxicity (based on results presented in Section 3).

Based on these criteria, several potential predictive MLR models were identified in the step-wise multiple linear regression analysis (**Table 3**). Key predictor variables included: TOC, DOC, alkalinity, and TDS. Of the models and parameters evaluated, one of the the best-fit MLR models (based on the R^2 value, adjusted R^2 value, and coefficient p-values) combined four variables previously shown to affect copper toxicity – TOC, hardness, alkalinity, and TDS. This model had high predictive power (R^2 = 0.869, adjusted R^2 = 0.838, and regression *p*-value < 0.001), and each input parameter significantly contributed to the statistical fit of the model (i.e., regression coefficient *p*-values for each parameters was less than 0.05; Model 1 in **Table 3**). Note that replacing TOC with DOC in this model also yields a highly predictive model (adjusted R^2 = 0.838; Model 2 in **Table 3**). In both of these models, hardness and alkalinity were combined into a hardness/alkalinity ratio.

A potential limitation of using the hardness/alkalinity ratio as a predictive measure of toxicity is that alkalinity concentrations are not explicitly accounted for. Because the ratio of hardness/alkalinity is a proportional measure of the two parameters, it might not directly reflect the range of protective effects across low and high carbonate/bi-carbonate concentrations. For example, a similar hardness/alkalinity ratio is possible at low alkalinity concentrations and at higher alkalinity concentrations, but the protectiveness effects would be expected to differ (based on the relationship between alkalinity and copper toxicity discussed in Section 3). Alkalinity by itself (i.e., not as the hardness/alkalinity ratio) was therefore evaluated as an input parameter to MLR models.

Replacing the hardness/alkalinity ratio with alkalinity (but keeping TOC and TDS) provides a model with an adjusted R^2 value of 0.766 (Model 15 in **Table 3**). However, the p-value for TDS in this regression model is 0.839 indicating that TDS is not a significant predictor of toxicity when combined with TOC and alkalinity. A similar result is obtained by using DOC, alkalinity and TDS as predictor variables (i.e., adjusted R^2 = 0.829, but TDS not a significant parameter [p-value = 0.448]). These results suggest that when alkalinity is used instead of the hardness/alkalinity ratio as a model parameter, including TDS does not improve the statistical fit of the model. Additional regression analyses were therefore performed using either TOC or DOC and alkalinity as parameters and excluding TDS (**Table 3**).

The combination of DOC and alkalinity yields a MLR model with an adjusted R^2 value of 0.833 (and co-efficient p-values of less than 0.05 for DOC and alkalinity; Model 18 in

Table 3), which is almost identical to the variance accounted for by the MLR model evaluated above that incorporated TOC (or DOC), hardness/alkalinity, and TDS. As inferred from an adjusted R^2 value of 0.833, the combination of DOC and alkalinity explains 83 percent of the measured variability in copper toxicity (compared to an adjusted R^2 value of 0.838 using DOC (or TOC), hardness/alkalinity, and TDS). In multiple-regression analysis, it is desirable to limit the number of predictor variables while maximizing the predictive relationship, particularly with smaller datasets, thus making Model 18 (DOC and alkalinity) preferable over Model 1 (DOC or TOC plus hardness/alkalinity and TDS) in Table 3. Additionally, because alkalinity is used as predictor of copper toxicity in the BLM and the hardness/alkalinity ratio is not, Model 18 (DOC and alkalinity) is preferable over Model 1 (DOC or TOC plus hardness/alkalinity and TDS) from a mechanistic perspective.

To further validate the accuracy of these MLR models and to understand any potential bias in model-predicted values, a residual-based analysis was performed. **Figure 10** graphically depicts the accuracy of model-predicted toxicity values when compared to measured toxicity values. In this approach, copper toxicity is predicted by applying the MLR model equation to the water chemistry values measured in the toxicity test sample to derive a model-predicted toxicity value. In effect, this residual-based analysis quantitatively compares measured toxicity values to model-predicted toxicity values which are derived by applying the MLR equation to measured water chemistry. **Figure 10** shows that MLR-predicted copper toxicity values from each model were strongly correlated with measured toxicity. The solid diagonal line on **Figure 10** represents perfect agreement between the observed and predicted values (i.e., predicted values equal observed values), while the dotted lines represent two-fold deviations of the observed toxicity from the predicted toxicity. A two-fold variation in a measured toxicity endpoint is a commonly-used range to represent the natural variability considered to be inherent in toxicity testing procedures (Di Torro et al. 2001, Esbaugh et al. 2011). Importantly, **Figure 10** shows that the model-predicted copper toxicity values from each model are highly accurate (relative to the observed values), and a bias is not evident in either model. That is, neither model appears to systematically over- or under-predict toxicity when evaluated across the range of observed toxicity values. Predicted values are within two-fold of the observed values, which provides a strong indication of accuracy for each MLR model.

3.2.5 Copper BLM Comparisons

The copper BLM offers a computational tool to evaluate the protective impact of water chemistry on copper toxicity by systematically combining the complexation and competitive properties of water chemistry parameters (Di Toro et al. 2001, Paquin et al.

2002). Input parameters for the BLM calculations are temperature, pH, alkalinity, and concentrations of Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-}, SO_4^{2-}, and DOC. Although the current USEPA-promulgated water quality criteria (WQC) for copper are based on the BLM (USEPA 2007), to date no state has adopted the Cu-BLM as a primary basis for a state copper criterion. Recent studies have indicated disparities in BLM-predicted and empirical toxicity endpoints, suggesting variable BLM performance in different water types relative to the waters used to develop the BLM. One potential explanation for this discrepancy is that the BLM is based on one possible composition of organic matter (i.e., assumed 10 percent fulvic acid), which may differ chemically from the types of DOM in Site waters. Another potential explanation is that the sensitivity of the organisms used in those toxicity tests differed from the sensitivity of the organisms used in the toxicity tests to which the BLM is calibrated. However, in this study the BLM performed reasonably well in predicting toxicity in Site waters. **Figure 11** shows that the BLM-predicted copper EC50s were well-correlated to the observed copper EC50s ($R^2 = 0.66$; *p*-value < 0.001), but were biased high, indicating the BLM under-predicts copper toxicity (i.e., predicts greater EC50s) when compared to observed values (i.e., measured EC50 values). The majority of BLM-predicted EC50 values (11 out of 17) were more than two-fold greater than actual observed copper EC50 values (**Figure 11**). However, as indicated by the correlation statistics, the BLM predictions generally agreed with observed values, with the lowest predicted EC50 values corresponding to the lowest observed EC50 values and the highest BLM-predicted EC50 values corresponding to the highest observed EC50 values (i.e., a positive relationship between BLM-predicted and observed EC50s). This finding is consistent with the above observations concerning the effects of variable water chemistry on site-specific toxicity, with the range of BLM predictions corresponding overall to the range of water chemistry.

Comparing the MLR model predictions and the BLM predictions to the observed toxicity values (**Figures 10** and **11**, respectively) indicates the MLR model provides a more accurate prediction of site-specific copper toxicity than the BLM. This finding is based on the regression statistics and by considering whether either model over- or under-predicts toxicity over the relatively wide range of water chemistry and observed toxicity values. Given the above trends, it follows that BLM-predicted EC50s were also well-correlated with the EC50s obtained with the MLR model. As shown on **Figure 12**, the BLM EC50s were strongly correlated with the MLR model EC50s, but were biased high (i.e., BLM-predicted EC50s were consistently greater than the MLR model-predicted EC50s). Although BLM-predicted EC50s were consistently greater than MLR model-predicted EC50s, the strong correlation between the two models further highlights the effect of water chemistry on site-specific toxicity and further corroborates the MLR model structure and performance.

To provide additional context to the BLM, a brief description of the various BLM applications follows. The BLM offers separate applications to evaluate copper toxicity (i.e., the toxicity-prediction mode option) and copper speciation (i.e., the chemical speciation mode option). When run in speciation mode, the BLM predicts the chemical speciation of dissolved copper including complexation with inorganic and organic ligands, and the biotic ligand. When run in toxicity-prediction mode, the BLM predicts the median lethal or effect concentration (i.e., LC50 or EC50) based on the user-selected organism and the site-specific water chemistry parameters. In addition to these applications, the BLM can be used to predict site-specific copper water quality criteria by selecting the *Cu WQC Calculation* option.

The BLM-based evaluations and figures presented herein and discussed during the June 10, 2013 meeting were performed by using the BLM in toxicity prediction mode (i.e., comparing the BLM-predicted EC50s to the measured EC50s). These BLM predictions were made by using the BLM "out-of-the-box", which refers to running the BLM with the default sensitivity parameters. As discussed during that meeting, the BLM can be adjusted to potentially improve these toxicity predictions by modifying the median lethal accumulation concentration (LA50) in the program file for the user-selected organism. The LA50 value is the concentration of copper accumulated on the biotic ligand that results in 50% mortality in a toxicological exposure (i.e., the amount of metal accumulated on the biotic ligand that results in the water column EC50).

As shown on Figure 11, the BLM systematically over-predicted the EC50 values when compared to the measured EC50 values. Therefore, the default LA50 value listed in the program file could be decreased to predict lower EC50 values, which would result in better agreement between the BLM-predicted and measured EC50 values. However, this adjustment would only affect the BLM's toxicity predictions (i.e., predicted EC50 values), and would not impact the predicted site-specific copper criteria derived from the *Cu WQC Calculation* option. This option is EPA's recommended approach for using the BLM to derive site-specific criteria. The program files used to make the BLM's Cu WQC predictions are not publicly available, and ARCADIS does not currently have access to these. During the June 10, 2013 meeting, ARCADIS discussed the possibility of obtaining these parameterization files from the developers of the BLM (Hydroqual) to perform such modifications. Although this approach might be feasible, these files are not accessible to the public or scientific community, and could therefore limit the general acceptance of this approach since criteria predictions would not be reproducible by others. Additionally, modifying the parameterization of the BLM's Cu WQC calculations could be inconsistent with EPA's current BLM-based criteria approach, and would thus need to be fully evaluated in conjunction with EPA and BLM developers.

With this background, Chino does not recommend using a modified BLM (or the BLM "out of the box") to derive site-specific copper criteria for STSIU surface waters. The proposed regression-based approach, which has been developed from empirical toxicity tests conducted in site water, provides a more accurate and technically-defensible approach for deriving site-specific copper criteria *for the STSIU surface waters* (i.e., the proposed approach is highly specific to STSIU surface waters) and is consistent with the approach adopted by Esbaugh et al. (2011). Based on the evaluations presented in this report and discussed during the 6/10/13 meeting, adjusting the BLM to systematically change the predictions is not expected to provide greater predictability compared to the regression model approach.

4. Discussion

4.1 Technical Basis of a WER Model

Section 3.1 describes the USEPA (1994) sample-specific WER approach where the WER value determined in a tested sample is used to adjust the hardness-based copper criteria to evaluate whether copper concentrations are acceptable when the effects of water chemistry are considered. This analysis indicated copper concentrations were within acceptable ranges (when applied according to USEPA [1994]); **Table 1**). Although this approach is informative to understanding copper compliance for a sample, it would be cost-prohibitive and logistically impracticable to perform WER testing to evaluate compliance for all surface waters within the expansive and somewhat remote study area (recognizing that the copper in STSIU waters originates from non-point sources). Therefore, this study evaluated an alternative approach based on statistical relationships between these empirical toxicity results and Site-water chemistry.

One of the primary findings from the Interim Report (ARCADIS 2013a) was that the measured WERs were variable, reflecting the influence of variable Site-specific water chemistries on copper toxicity. This finding highlighted the need to further understand the influence of site-specific water chemistry on observed copper toxicity. Statistical evaluations (presented in Section 3) were thus performed to better understand the statistical association between measured toxicity and chemistry parameters. Based on the best-fit MLR model, the combination of DOC and alkalinity explained 83% of the variability in the observed copper toxicity values. This relationship provides a highly predictive tool for estimating site-specific copper toxicity based on using measured water chemistry values as input parameters to a predictive Site-specific copper model.

In addition to providing a statistically robust option to derive Site-specific copper criteria, a Site-specific MLR model approach can address the challenges associated with the Site conditions described previously. Because the model was developed from toxicity tests conducted in actual site water, which covered a relatively wide range of values of a variety of chemical parameters, the model is expected to perform very well in water chemistries that are typical of surface water at the Site (i.e., the model is highly specific to Site-water chemistries).

The Site-specific MLR approach can reduce uncertainty about the over-protectiveness or under-protectiveness of the current hardness-based criteria, or uncertainty associated with application of other site-specific criteria options such as the BLM or a traditional WER approach.

- First, compared to the current hardness-based copper criteria, the MLR-model approach considers the effects of multiple water chemistry parameters on Site-specific copper toxicity. This provides a more accurate estimate of copper toxicity across Site waters because other toxicity-modifying parameters are accounted for. Although hardness was not determined as a strong predictor variable in the best-fit MLR model, the proposed WER model approach still accounts for hardness by normalizing the site and laboratory water to the same hardness.
- Second, compared to the BLM, the MLR-model approach predicts toxicity based on the relationship between measured Site toxicity and chemistry values. Because the BLM approach does not include empirical toxicity tests to confirm its computational-based predictions, the MLR-model approach can reduce uncertainty associated with default BLM assumptions and/or take into account how other water chemistry parameters that are not incorporated into the BLM affect toxicity characteristics of a water (such as other co-occurring metals and type or quality of organic matter).
- Third, compared to the traditional WER approach in which a single or set of static site-specific criteria are applied to a water body, the MLR-model offers a way to evaluate copper compliance on a sample-specific basis, similar to the BLM and hardness-based options.

Another important consideration when evaluating the technical basis of this MLR-model approach is that regression analyses are commonly used to derive WQC. For example, the current hardness-based WQC for a number of divalent metals (including copper) are based on regressions between laboratory-water toxicity endpoints and water hardness. The current WQC for these select divalent metals are thus expressed as univariate linear regression equations, using hardness as the single predictor variable to determine the numeric WQC value. Further, the current USEPA ammonia WQC are based on a multivariate regression model that uses temperature and pH as input variables. With this background, the MLR-model approach described in this report is conceptually consistent to current approaches used to calculate WQC values.

Applying this type of MLR-model approach to the WER procedure framework should therefore provide a robust and technically-defensible basis to develop and apply SSC.

4.2 WER Model Implementation

The proposed approach to applying the MLR-model to derive site-specific copper criteria that can be applied to STSIU surface waters is described below:

1. Input a sample's measured water chemistry values into the MLR-model equation to calculate a predicted Site copper EC50 value;
2. Normalize the predicted EC50 value to a standard hardness (e.g., 100 mg/L as $CaCO_3$), using Equation 2 presented in Section 2.1. This value becomes the numerator to the WER equation;
3. Divide the normalized predicted Site EC50 value by the hardness-normalized *D. magna* SMAV for copper (normalized to the same hardness used in Step 2) to calculate a sample WER.
4. Multiply the sample WER by the hardness-based copper standard (calculated at the hardness of the water sample) to derive a site-specific standard for the sample.

Table 4 provides a step-by-step example of how to apply this approach to derive a site-specific standard for a sample (using measured water chemistry from sample WER-1-1 as the example). The proposed regression-model approach is sample-specific, meaning a site-specific standard is derived for each sample based on its water chemistry. Operationally, the approach is consistent with the current hardness-based standards approach whereby the copper standard for a single sample is determined based on its hardness concentration. Therefore, Chino envisions that compliance evaluations (i.e., determining whether measured copper concentrations in a sample are acceptable) that use SSC developed with the proposed regression-model approach will be the same as compliance evaluations that use criteria developed with the current hardness-based approach.

Elements of the WER procedure are still applied in this approach to account for copper toxicity differences between site and laboratory waters, but the numerator of the WER (i.e., the Site-water toxicity endpoint) is modeled based on the statistical relationship between measured toxicity and measured water chemistry. By applying the WER procedure framework to this approach, hardness is accounted for by normalizing the site and laboratory toxicity endpoints to the same hardness and by using the WER to adjust the sample's hardness-based standard. Thus, criteria-adjustments made using the proposed model are still hardness-specific, but they also take into account other toxicity-modifying water chemistry parameters.

4.2.1 Model Application to Acute and Chronic Criteria

As described in ARCADIS (2013a), surface-water samples used in the WER toxicity tests were collected from pools that were found in predominately bedrock sections of drainage channels, ranging in size from small and shallow to large and deep pools. Although some of these pools were more perennial in nature (such as some pools in Rustler Canyon), many were temporary pools (i.e., intermittent or ephemeral) that were formed from recent precipitation.

Site-specific copper criteria derived from the proposed approach are applicable to acute or chronic criteria. In accord with USEPA WER guidance (USEPA 1994 and 2001), a WER derived from acute toxicity tests is applied to both acute and chronic criteria. As stated in USEPA (2001), because the involvement of strong binding agents causes the WER to increase as the effect concentration decreases, the WER derived from acute tests is expected to be protective of chronic effects. Thus, the WER derived from the proposed approach can be applied to the existing Criteria Maximum Concentrations (CMC [acute criteria]) or the Criterion Continuous Concentration (CCC [chronic criteria]) to derive a Site-specific acute or chronic criterion.

4.2.2 Margin of Safety Applications

As described in USEPA (1994), ambient water quality criteria are typically overprotective of aquatic life uses because they are derived to be environmentally conservative in most bodies of water. The WER procedure is a USEPA-developed method intended to decrease or eliminate overprotection in waters that contain elevated concentrations of water chemistry parameters that protect against metal toxicity. In the traditional WER procedure (where multiple WERs are determined and the geometric mean WER is typically used to derive site-specific criteria for one or more bodies of water), variation in WERs and water chemistry can be a concern when considering the appropriate level of protection and conservatism. Spatial variation among WERs within a body of water is not a concern in the USEPA (1994) sample-specific approach (described in Section 3.1) because compliance is evaluated based on the chemistry, toxicity, and criteria of a single effluent and its receiving water. The proposed application of the MLR-model described herein is similar to this approach in that criteria and compliance is computed on a sample-by-sample basis.

A margin of safety in the proposed MLR-model approach is important to ensure that a sufficient level of protection to resident aquatic life is afforded by a derived site-specific standard. The proposed model approach has several features that do provide a margin of safety to ensure the approach is applied in an environmentally conservative way.

4.2.2.1 WER Denominator

Based on toxicity results measured in this study, use of the SMAV as the denominator to measured Site toxicity values provides a conservative WER value because of differences in organism sensitivity represented by each toxicity endpoint. The Criteria Adjustment Interim Report (ARCADIS 2013a) and response to comments (ARCADIS 2013b) evaluated possible WER denominators, including (1) matched-laboratory water tests conducted side-by-side with Site water tests; (2) the geometric mean of these laboratory tests; (3) the re-calculated SMAV (recalculated by excluding nominal toxicity endpoints from the USEPA [2001] SMAV value); and (4) the SMAV presented in USEPA (2001), which is the WER denominator proposed in this approach). Of the potential denominators, the USEPA (2001) SMAV is the largest value, which results in the smallest WER when applied to Site toxicity values. As a result, this yields a conservative WER and thus provides a margin of safety when used to derive a Site-specific standard. The basis of this conclusion is described in more detail below (also refer to ARCADIS 2013a for further discussion of laboratory-water toxicity endpoints).

Toxicity endpoints measured in the laboratory water toxicity tests were always less than the *D. magna* SMAV presented in USEPA (2001). All aspects of the laboratory water toxicity tests (test design, water chemistry, and toxicity results) were evaluated to ensure results were appropriate and acceptable according to guidance provided in USEPA (1994). ARCADIS (2013a) showed that the laboratory dilution water chemistry was acceptable and representative of standard reconstituted water used to derived national criteria (i.e., low TOC and TSS, appropriate hardness concentrations, and appropriate alkalinity and pH for the hardness ranges tested). Additionally, copper toxicity endpoints were within the range reported by others (including the copper toxicity values for *D. magna* used to derive the current copper standard and *D. magna* toxicity values used in the USEPA [2001] SMAV calculation).

After validating all aspects of laboratory dilution water tests, the copper toxicity differences measured between Site and laboratory waters can be assumed to represent the mitigating properties of site-specific water chemistry. Applying the SMAV to the WER denominator can therefore provide a margin of safety because the sensitivity of the numerator (i.e., site-water toxicity endpoint) is not adjusted to correspond to the sensitivity of the denominator (i.e., organisms represented by the SMAV). Therefore, this ensures a conservative WER value is derived.

4.2.2.2 *Chemistry Variability and Model Limits*

A major advantage of the WER model approach is that it accounts for water chemistry variability when deriving a site-specific standard because the numeric value of the site-specific standard is a function of the water chemistry for a sample. This approach is consistent with the current hardness-based approach whereby a copper standard is derived based on the hardness concentration of a sample. As with the hardness-based approach, it is important to apply the WER model to water chemistries within the range of those used to develop the model. For example, the current hardness-based approach specifies upper and lower hardness limits to the criteria equation: 25 mg/L and 400 mg/L as $CaCO_3$. These limits approximate the range of hardness concentrations from toxicity studies used to develop the hardness-based criteria; application of the equation to hardness concentrations outside of this range is uncertain because the linear relationship between toxicity and hardness might not apply. Therefore, a hardness of 25 mg/L $CaCO_3$ is used to calculate criteria in samples with hardness less than 25 mg/L and a hardness of 400 mg/L CaCO3 is used to calculate criteria in samples with hardness greater than 400 mg/L. As described below, this framework can also be applied to the WER model approach to ensure criteria adjustments are made in an environmentally conservative way.

Site-specific copper toxicity was measured over a relatively wide range of water chemistries, particularly dissolved organic carbon and alkalinity (the two predictor variables in the proposed WER model). The upper range of DOC and alkalinity concentrations used to develop the WER model will be used as the upper limits when applying the equation to a sample's water chemistry to derive SSC. Based on the Site toxicity data, these ranges are:

- Dissolved Organic Carbon range: 1.2 mg/L - 15.7 mg/L. In samples with DOC concentrations greater than 16 mg/L, a value of 16 will be used in the WER model equation.
- Alkalinity range: 27 mg/L – 250 mg/L. In samples with alkalinity concentrations greater than 250, a value of 250 will be used in the WER model equation.

Applying these limits to samples containing DOC and/or alkalinity concentrations greater than this range provides a margin of safety because more protection against copper toxicity is expected at concentrations greater than those tested and used to develop the model. In this way, the model can be applied in an environmentally conservative way when addressing potential uncertainty associated with applying the model to DOC and/or alkalinity concentrations greater than the model's range.

For samples containing DOC and/or alkalinity concentrations less than the range used to develop the WER model (i.e., DOC = 1.2 mg/L; alkalinity = 27 mg/L), Chino does not propose to apply the lower limits of the model when deriving a SSC. Although a lower limit is applied in the current hardness-based approach, less protection against copper toxicity is expected at lower DOC and alkalinity concentrations. Therefore, in samples in which alkalinity or DOC is less than the model range, it would not be conservative to apply the lower limits of the model range to derive a SSC. Figure 13 graphically depicts example SSC values calculated using the proposed WER model equation across a range of DOC and alkalinity concentrations (including alkalinity concentrations less than 27 mg/L; the minimum of the model range). This clearly shows that, depending on DOC concentrations, SSC values calculated at low alkalinities (i.e., less than 10 mg/L) can be much lower than SSC values calculated at 27 mg/L, thereby providing an environmentally conservative way to handle alkalinity values less than the model range.

An evaluation of STSIU surface-water chemistry variability is provided in **Appendix E**. Samples available for the evaluation include STSIU surface-water samples collected during the monsoon season in three different years (2010, 2011, and 2013). During the 2011 WER sampling, water chemistry was collected at five additional sample locations (in addition to the 18 WER sampling locations) to increase the spatial distribution of chemistry samples in the STSIU study area (toxicity tests were not performed on these five additional locations). Chemistry samples were also collected during the 2010 Wet Season Survey, which was performed during the planning phases of the current study to gain a better understanding of Site-water chemistries. Last, samples were collected during August 2013 to support this evaluation. As described in **Appendix E**, drainage areas sampled in 2013 contained more water than previous years due to strong monsoonal precipitation that occur prior to, and during, the 2013 sampling effort. Previous STSIU surface-water investigations (*i.e., the STSIU Remedial Investigation and Ecological Risk Assessment*) primarily evaluated metal compliance trends, and therefore did not sample all chemical parameters necessary to compare with the model range.

In total, 49 distinct surface-water samples have been collected in the STSIU study area and analyzed for the complete set of water chemistries (including alkalinity and DOC model parameters). This includes the 17 samples used to develop the WER model and 32 additional samples collected to evaluate water chemistry characteristics. Overall, this evaluation indicates that the range of chemistry used to develop the WER model (i.e., the range of DOC and alkalinity measured in the 17 toxicity tests conducted using various STSIU surface waters) is representative of the range of chemistries typically observed in the STSIU surface waters. Additionally, **Appendix E** shows that the range of other parameters determined in this study to be significant predictors of Site-specific toxicity (i.e., TOC, Hardness/Alkalinity and TSS) also compared well with ambient samples collected across STSIU.

The WER model was developed from chemistry and toxicity data collected across eight sub-watershed units during two distinct sampling events in the 2011 monsoon season. As a result, this model is based on a wide spatial range of STSIU surface-water samples. Given the limited persistence of water in the STSIU drainages, and limitations associated with the lack of water in many of these drainages during the dry season (and the lack of water in many portions of these drainages during the wet season), these samples also provide a temporal range representative of local climate and hydrology. Therefore, the current model is calibrated to a sufficient temporal and spatial range for application to STSIU surface waters.

As stated previously, an advantage of the model is that it predicts toxicity well across the wide range of water chemistry values that thus far have been recorded for STSIU waters. That is, model-predicted EC50 values are a function of water chemistry values (analogous to hardness-based criteria or BLM-based predictions, which also are considered to be applicable across the entire range of water chemistry with which they were calibrated). For this reason, water chemistry variability within STSIU is not expected to be a limitation of this model-based approach; instead, site-specific criteria values derived from this model-based approach will be reflective of the water chemistry variability expected at STSIU.

4.2.2.3 Geographic Extent of Model Application

Some additional background information will be useful to this discussion. The STSIU study area was established as part of the AOC to address potential releases of mining-related constituents to the surrounding landscape. The conceptual site model for STSIU identified fugitive dust emissions from the smelter as the primary source of contamination to STSIU soils and drainage areas. The smelter is no longer an active source of contamination because it was dismantled in 2007 (active smelting operations ceased in 2002). Copper is the primary constituent of concern within the STSIU area (SRK 2008).

The STSIU surface-water drainages evaluated in this study and proposed for SSC application were not contaminated by point-sources of contamination such as discharges or tailings. Instead, these drainages were contaminated by a diffuse, non-point source of copper contamination (i.e., historic emissions). Based on previous Site investigations, including a recently completed hydrology-based Use Attainability Analysis (UAA) (ARCADIS 2013c), most surface-water drainages in the STSIU area are characterized as ephemeral, flowing only in direct response to monsoonal precipitation. As a result, surface waters in STSIU have limited temporal and spatial persistence. Besides direct storm flow runoff, STSIU surface-water environments consist of isolated pools, typically located in the higher elevations of STSIU and within predominately bedrock channels. This has been observed consistently throughout various Site investigations, including the surface-water sampling sampling conducted to support this study.

From information collected in this study and previous Site investigations, the surface-water sample locations discussed and graphically depicted in Appendix E largely represent the drainage locations where surface-water pools tend to exist in STSIU, particularly during the wet season (since most of these locations are completely dry outside of the wet season). Because of this, the available surface-water chemistry data, collected across a wide spatial and temporal range, provides a strong representation of the types and chemistry of available surface waters in STSIU.

Appendix E shows that the chemistry range used to develop the model sufficiently represents the range of ambient surface waters in the STSIU study area. Therefore, the recommended geographic range for model application is the STSIU study area (**Figure 1**), excluding any portion of Hanover and Whitewater Creeks. Application of this model to surface waters outside of the STSIU study area is not recommended or proposed because the model is calibrated to the specific chemistry of STSIU surface waters, which is distinct from other surrounding surface waters given the unique geologic, hydrologic and upland characteristics of the STSIU area. For example, Hanover and Whitewater Creeks, the primary adjacent surface waters to STSIU, are characterized by substantially greater water hardness concentrations compared to STSIU surface waters and the range used to develop the WER model.

4.2.2.4 Protectiveness Inherent in Criteria Derivation

The proposed WER-model approach does not decrease any of the protectiveness inherent in the process of derivation of water quality criteria that is prescribed in USEPA (1985), including protecting 95% of the species, dividing the final acute value (FAV) by 2 to derive an acute criterion, and dividing the FAV by the acute-chronic ratio to derive a chronic criterion. Accounting for the toxicity-modifying effects of water chemistry parameters (which is all the proposed WER-model approach does) will not decrease the protectiveness of the criteria-derivation procedure.

5. Conclusions and Recommendations

The conceptual approach of developing a WER model that can be applied to STSIU surface waters was presented in the ARCADIS (2011) work plan. By letter dated September 1, 2011, NMED provided comments to this work plan and expressed agreement with a general WER-model approach, recognizing that the nature of this study differs significantly from the specific scenarios addressed in the USEPA (1994)

WER guidance. Results from the studies described in that work plan were evaluated against USEPA WER acceptability criteria and fully reported in the Interim Report (ARCADIS 2013a).

Using the chemistry and toxicity data reported in ARCADIS (2013a), a draft version of this report was submitted to NMED SWQB in April 2013, prior to the June 10 2013 meeting between Chino and NMED SWQB that was mostly focused on this WER model approach. Based on discussions from that meeting and from NMED SWQB comments to the draft report (dated July 1, 2013), this current revised Copper Toxicity Model report provides the statistical basis and specific guidelines for implementing a WER model to derive copper SSC that can be applied to STSIU surface waters. The sampling and toxicity testing methods, proposed WER model, and recommendations for implementing the proposed WER model are consistent with the general WER-model approach discussed in previous reports.

The proposed WER model was selected based on statistical relations between Site chemistry and measured toxicity and by linking these relations to the dominant mechanisms of copper toxicity that occur within the specific range of STSIU water chemistries. From a statistical standpoint, the proposed model was determined as the best-fit statistical model based on the level of statistical significance associated with MLR analysis, by evaluating the co-linearity of input parameters, and by considering the accuracy of model predictions. Additionally, recommendations for implementing the model are based on an understanding of the hydrology, upland properties, nature and extent of contamination, and surface-water chemistry that is known to occur throughout the study area.

Regarding model-input parameters, NMED's comments to the ARCADIS (2011) work plan suggested that TSS and pH be evaluated in addition to dissolved organic carbon, hardness, and alkalinity. These parameters are discussed in Section 3, and the statistical results are listed in **Table 3** and **Appendices B**, **C**, and **D** (in addition to evaluations of other model input parameters not specifically identified by NMED comments). Based on this evaluation, it is concluded that although these water chemistry parameters (as well as other water chemistry parameters) can affect copper toxicity, they are not significant drivers or reliable predictors of copper toxicity within STSIU surface waters.

Including TSS and pH as model parameters did not provide a better-fit model based on these analyses; neither of these parameters was significantly associated with observed toxicity values (judged by the level of statistical significance of each parameter in the MLR models and based on the Pearson Correlation summary). In fact, pH should have little direct effect on copper toxicity at pH values above approximately 6.5, because hydrogen ions (H^+, of which pH is an index) are not an effective competitor for binding to biotic ligands until the pH is below approximately 6.5 (because H^+ concentration increases as pH decreases). Therefore, at pH values characteristic of most STSIU waters, H^+ ions provide relatively little protection against copper toxicity. In contrast, pH can have an important indirect effect on copper bioavailability by changing the bicarbonate/carbonate (HCO_3^-/CO_3^{2-}) ratio in the exposure water and leading to higher concentrations of carbonate (which has a higher affinity for copper than bicarbonate has) at higher pH values. However, because alkalinity generally increases as pH increases, the two parameters usually are well-correlated. Therefore, inclusion of pH and alkalinity in a statistical-based model would be duplicative and might cause the model to be unstable because of high co-linearity between the two predictor variables.

As proposed in the work plan, BLM evaluations were also performed on water samples used in the toxicity tests; and these results were summarized in this report. These BLM analyses confirmed general correlation and regression trends observed between water chemistry and toxicity values, and provided additional verification of the WER model's performance. On the basis of model accuracy, the MLR model approach was determined to provide better predictions, without systematically over- or under-predicting toxicity values (in contrast to the BLM that systematically under-predicted toxicity [i.e., the BLM predicted higher EC50 values than the measured EC50 values]).

In conclusion, this report proposes a specific WER model that can be applied to STSIU surface waters to derive site-specific copper criteria. The proposed model has high predictability and covers wide temporal and spatial conditions found in STSIU surface waters. As demonstrated in this report, the specific implementation steps and margin of safety recommendations proposed herein for deriving and applying SSC to STSIU surface waters provides a technically-defensible basis to address Site-specific challenges, while also providing for environmentally conservative SSC. Therefore, Chino recommends that NMED adopt this MLR-model approach for deriving SSC in STSIU surface waters.

6. References

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Tables

TABLE 1
SUMMARY OF MEASURED DISSOLVED COPPER CONCENTRATIONS AND COPPER COMPLIANCE EVALUATIONS BASED ON THE HARDNESS CMC AND WER-ADJUSTED CMC

FREEPORT-MCMORAN CHINO MINES COMPANY
VANADIUM, NEW MEXICO
SMELTER/TAILINGS SOILS IU SITE-SPECIFIC COPPER TOXICITY MODEL REPORT

Sample ID	Dissolved Cu (µg/L)	Dissolved Cu WER[1]	Hardness (mg/L as $CaCO_3$)	Dissolved Cu Hardness CMC[2]	Hardness-Based Cu CMC Compliance Ratio[3]	WER-Adjusted Cu CMC Compliance Ratio[4]
1-1	5.9	6.651	90	12.2	0.48	0.07
1-2	6.5	5.334	84	11.4	0.57	0.11
1-D1-2	32.3	13.104	54	7.5	4.30	0.33
1-D2-1	32.8	8.027	42	5.9	5.53	0.69
1-6	57.4	14.407	54	7.5	7.63	0.53
1-7	43.0	4.717	106	14.2	3.03	0.64
1-9	7.1	2.207	88	11.9	0.60	0.27
1-10	5.4	2.804	262	33.3	0.16	0.06
1-11	4.3	5.956	154	20.2	0.21	0.04
1-12	2.1	0.989	76	10.4	0.20	0.20
1-RCS1	5.0	3.273	48	6.7	0.74	0.23
2-1	3.4	4.046	104	13.9	0.24	0.06
2-6	30.2	6.151	50	7.0	4.32	0.70
2-D1-2	17.9	5.724	60	8.3	2.16	0.38
2-9	13.7	11.530	82	11.1	1.23	0.11
2-11	7.9	6.889	102	13.7	0.58	0.08
2-12	3.6	2.251	80	10.9	0.33	0.15

Notes:

[1] WER = Site water EC50 / 19.31 (SMAV reported by USEPA [2001]).

[2] Dissolved Cu CMC = exp(0.9422[ln(hardness)]+-1.7)(0.96)

[3] Hardness-based Cu CMC compliance ratio = Dissolved Cu / Hardness-Based CMC

[4] WER-adjusted Cu CMC compliance ratio = Dissolved Cu / (WER x hardness-based Cu CMC)

CMC = criteria maximum concentration

SMAV = species mean acute value

WER = water effect ratio

TABLE 2
ANALYTICAL CHEMISTRY RESULTS AND TOXICITY ENDPOINTS MEASURED IN WER SAMPLES AND USED TO DEVELOP THE PROPOSED WER MODEL

FREEPORT-MCMORAN CHINO MINES COMPANY
VANADIUM, NEW MEXICO
SMELTER/TAILINGS SOILS IU SITE-SPECIFIC COPPER TOXICITY MODEL REPORT

Parameters / Sample IDs	Round 1 Samples												Round 2 Samples					
	1-1	1-2	1-5	1-6	1-7	1-9	1-10	1-11	1-12	1-RCS1	1-D1-2	1-D2-1	2-1	2-6	2-9	2-11	2-12	2-D1-2
Major Cations (mg/L)																		
Calcium, dissolved	23.7	20	17.2	12.3	28.3	19.1	56.6	34.9	17.4	9.9	13.9	11.6	25.2	10.5	18.9	25.6	15.9	14.9
Calcium, total	24.6	20.7	17.4	12.7	27.1	19.5	57.7	35.9	18.5	10.5	14.2	11.8	28.3	11	19.8	26.7	19.7	15.7
Magnesium, dissolved	7.7	7.5	5.2	5.7	10.3	9.3	28.2	18.6	7.4	4.8	4.2	3.7	8.2	5.1	9.3	13.3	7	4.8
Magnesium, total	8.1	7.9	5.5	5.9	10.7	9.5	28.7	19.2	7.9	5.1	4.2	3.9	8.8	5.4	10	14.1	8.6	5.1
Potassium, dissolved	3	2.6	3.6	3.7	5.2	3.5	4	6.9	3.1	2.3	3.0	3.3	2.6	3.1	8.4	5.2	2.8	2.6
Sodium, dissolved	16.7	17.6	14.5	7.2	8.8	9.4	32.2	10.5	8.3	5.2	17.8	12.1	20.2	6.4	10.5	7.8	7.4	17.1
Metals (µg/L)																		
Aluminum, dissolved	4	6	7	12	7	4	2	21	5	<1	42	16	<1	5	7	10	8	<1
Aluminum, total	32	33	263	87	269	67	32	741	65	14	712	1600	29	282	307	1260	123	1060
Cadmium, dissolved	<0.1	<0.1	0.2	<0.1	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Cadmium, total	<0.1	<0.1	0.3	<0.1	0.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Copper, dissolved	6.9	6.5	32.3	67.4	43	7.1	5.4	4.3	2.1	5	32.3	32.8	3.4	30.2	13.7	7.9	3.6	17.9
Copper, total	7.1	8	63.1	133	66.6	8.8	7.1	5.8	3	6	111.3	102.2	4.2	48.5	20.7	10.7	4.9	43
Iron, dissolved	90	<20	40	80	<20	<20	<20	<20	<20	<20	150	40	<20	40	30	<20	<20	20
Iron, total	230	60	330	410	300	60	<20	460	40	<20	590	1320	130	400	430	890	70	870
Lead, dissolved	<0.1	<0.1	0.3	0.4	0.2	<0.1	<0.1	<0.1	<0.1	<0.1	0.5	0.4	<0.1	<0.1	0.2	0.2	0.2	<0.1
Lead, total	0.1	0.1	0.3	0.3	0.2	<0.1	<0.1	0.3	<0.1	<0.1	0.7	0.9	<0.1	0.3	0.5	0.3	<0.1	0.8
Manganese, dissolved	21.6	46.8	72.7	18.2	52.1	16.3	19.4	186.6	12.2	3	19.3	182.3	3.2	17.6	33.7	30.8	16.1	11
Manganese, total	36.9	71.1	137.2	74.9	171.4	93	28.6	258	14.7	17.7	46.7	198.5	55.4	70.9	261	113.6	24.7	38.1
Zinc, dissolved	3	3	8	4	3	3	3	3	3	<2	3	8	2	3	2	5	4	2
Zinc, total	4	2	10	4	4	<2	2	3	4	4	5	7	4	3	3	4	3	7
Wet Chemistry (ACZ Laboratory)																		
Bicarbonate as CaCO3 (mg/L)	68	56	24	41	63	87	232	163	27	26	74	24	89	36	90	102	31	60
Dissolved organic carbon (DOC) (mg/L)	10.7	7.8	3.5	12.5	7.8	2.5	4.7	16.7	1.2	3.2	10.0	5.8	11	11.4	12.3	12.3	3.1	10.5
Total organic carbon (TOC) (mg/L)	16.2	8	2.7	14.0	6.8	3.2	4.8	14.3	3	4.3	9.0	6.0	11.2	10.2	15.1	13.5	6.5	8.4
Carbonate as CaCO3 (mg/L)	<2	<2	<2	<2	<2	<2	6	3	<2	3	<2	<2	<2	<2	5	<2	<2	<2
Cation-Anion Balance %	3.8	2.1	2.6	3.4	-1.9	2.3	3.1	4	2.7	0	5.6	7.1	0	4	2.2	3.7	-8.1	0
Chloride (mg/L)	7	7	4	4	4	2	15	8	3	<1	3	3	8	2	6	6	3	2
Hardness as CaCO3 (mg/L)	91	81	64	54	108	86	257	164	74	46	52	44	97	47	86	119	69	57
Hydroxide as CaCO3 (mg/L)	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
pH[1]	8.2	7.8	7.5	7.5	8.0	8.2	8.3	8.3	7.2	8.6	7.9	7.0	8.2	7.5	8.5	8.1	7.7	8
Total dissolved solids (TDS) (mg/L)	200	200	180	130	210	180	390	240	150	90	150	160	210	130	200	190	170	170
Total suspended solids (TSS) (mg/L)	<5	<5	5	<5	9	<5	6	10	<5	<5	<5	5	<5	<5	10	6	12	8
Sulfate (mg/L)	48	48	65	23	64	17	53	16	58	25	9	37	40.7	23.3	8.7	22.6	64.4	31.8
Sum of Anions (meq/L)	2.5	2.3	1.9	1.4	2.7	2.1	6.2	3.6	1.8	1.1	1.7	1.3	2.8	1.2	2.2	2.6	2	1.9
Sum of Cations (meq/L)	2.7	2.4	2.0	1.5	2.6	2.2	6.6	3.9	1.9	1.1	1.9	1.5	2.8	1.3	2.3	2.8	1.7	1.9
Total Alkalinity (mg/L)	68	56	24	41	63	87	238	166	27	30	74	24	89	36	95	102	31	60
Wet Chemistry (GEI Laboratory)																		
Analysis Temperature °C	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20
Total Hardness (mg $CaCO_3$/L)	90	84	62	54	108	88	262	164	76	48	54	42	104	50	82	102	80	60
pH	8	7.47	7.54	7.57	7.93	8.04	8.31	8.22	9.35	8.67	8.06	8.16	8.19	7.14	8.44	7.99	7.4	7.82
Alkalinity (mg $CaCO_3$/L)	74	60	26	42	66	90	250	170	104[2]	32	76	28	96	40	102	106	34	64
Conductivity (mS/cm)	0.274	0.265	0.222	0.159	0.277	0.224	0.590	0.376	0.224	0.134	0.190	0.166	0.294	0.145	0.242	0.287	0.234	0.21
Total Dissolved Solids (mg/L)	134	130	109	78	136	110	289	184	110	66	93	82	144	71	119	141	115	103
Dissolved Oxygen (mg/L)	8.3	7.5	7.2	7	7.2	7.2	7.8	7.3	7.6	8.5	6.9	5.8	8.1	7.4	7.2	7.2	7.2	7.4
Site Water EC50																		
Dissolved copper EC50 (µg/L)	116.3	87.4	<32.5[3]	155.7	96.2	37.8	134.2	172.8	14.7	31.7	141.6	68.4	81.06	61.82	>164.7[4]	135.5	36.23	68.31

Notes:

[1] Analysis exceeded method hold time. pH is a field test with no hold time.

[2] Based on the hardness values measured upon sample collection and test initiation this measured alkalinity value is considered inaccurate (ACZ-measured alkalinity of 27 mg/L used for regressions).

[3] No exposure treatment adversely affected less than 50% of test organisms: therefore the EC50 concentration is less than the lowest Cu concentration

[4] No exposure treatment adversely affected more than 50% of test organisms: therefore the EC50 concentration is greater than the highest Cu concentration

Bolded values- analyte concentration detected at a value between a MDL and PQL. The associated value is an estimated quantity.

< values - the material was analyzed for, but was not detected above the level of the associated value. The associated value is either the sample quantification limit or the sample detection limit.

mg/L = milligrams per liter.

µg/L = micrograms per liter.

meq/L = milliequivalents per liter.

°C = degrees celsius.

mg $CaCO_3$/L = milligrams calcium carbonate per liter.

mS/cm = millisiemens per centimeter.

mg NH3/L = milligrams ammonia per liter.

TABLE 3
Statistical Summaries of Step-Wise Multiple Linear Regression Analysis

FREEPORT-MCMORAN CHINO MINES COMPANY
VANADIUM, NEW MEXICO
SMELTER/TAILINGS SOILS IU SITE-SPECIFIC COPPER TOXICITY MODEL REPORT

Summary of additional multiple regression analyses performed for WER model evaluation.

1. Input Parameters: TOC, Hardness/Alkalinity, TDS

R^2 = 0.869
Adj R^2 = 0.838
Regression p-value = < 0.001
Log LC50 = -0.128 + (0.703 * log TOC) - (0.787 * log (H/A)) + (0.653 * log TDS)

	Coefficient	Std. Error	t	p-value	VIF
Constant	-0.128	0.536	-0.238	0.815	
log TOC	0.703	0.149	4.718	<0.001	1.302
log (H/A)	-0.787	0.226	-3.485	0.004	1.336
log TDS	0.653	0.233	2.8	0.015	1.073

2. Input Parameters: DOC, Hardness/Alkalinity, TDS

R^2 = 0.868
Adj R^2 = 0.838
Regression p-value = < 0.001
Log LC50 = -0.0439 + (0.633 * log DOC) - (0.438 * log (H/A)) + (0.645 * log TDS)

	Coefficient	Std. Error	t	P	VIF
Constant	-0.0439	0.534	-0.0822	0.936	
log DOC	0.633	0.135	4.701	<0.001	1.865
log (H/A)	-0.438	0.268	-1.631	0.127	1.878
log TDS	0.645	0.234	2.759	0.016	1.075

3. Input Parameters: TOC, Hardness/Alkalinity, TDS, pH

R^2 = 0.871
Adj R^2 = 0.828
Regression p-value = < 0.001
Log LC50 = 0.122 + (0.674 * log TOC) - (0.790 * log (H/A)) + (0.663 * log TDS) - (0.0308 * pH)

	Coefficient	Std. Error	t	P	VIF
Constant	0.122	0.778	0.157	0.878	
log TOC	0.674	0.166	4.051	0.002	1.524
log (H/A)	-0.79	0.233	-3.39	0.005	1.338
log TDS	0.663	0.242	2.746	0.018	1.083
pH	-0.0308	0.0674	-0.458	0.655	1.202

4. Input Parameters: DOC, Hardness/Alkalinity, TDS, pH

R^2 = 0.869
Adj R^2 = 0.826
Regression p-value = < 0.001
Log LC50 = -0.254 + (0.664 * log DOC) - (0.411 * log (H/A)) + (0.634 * log TDS) + (0.0256 * pH)

	Coefficient	Std. Error	t	P	VIF
Constant	-0.254	0.824	-0.309	0.763	
log DOC	0.664	0.166	4.009	0.002	2.628
log (H/A)	-0.411	0.288	-1.426	0.179	2.021
log TDS	0.634	0.244	2.598	0.023	1.092
pH	0.0256	0.0744	0.344	0.736	1.447

TABLE 3
Statistical Summaries of Step-Wise Multiple Linear Regression Analysis

FREEPORT-MCMORAN CHINO MINES COMPANY
VANADIUM, NEW MEXICO
SMELTER/TAILINGS SOILS IU SITE-SPECIFIC COPPER TOXICITY MODEL REPORT

5. Input Parameters: TOC, Hardness/Alkalinity, (TDS + TSS)

R^2 = 0.869

Adj R^2 = 0.838

Regression p-value = < 0.001

Log LC50 = -0.126 + (0.700 * log TOC) - (0.794 * log (H/A)) + (0.650 * Log TDS+TSS)

	Coefficient	Std. Error	t	P	VIF
Constant	-0.126	0.536	-0.235	0.818	
log TOC	0.7	0.149	4.692	<0.001	1.304
log (H/A)	-0.794	0.226	-3.517	0.004	1.332
Log TDS+TSS	0.65	0.232	2.796	0.015	1.071

6. Input Parameters: DOC, Hardness/Alkalinity, (TDS + TSS)

R^2 = 0.867

Adj R^2 = 0.837

Regression p-value = < 0.001

Log LC50 = -0.0365 + (0.630 * log DOC) - (0.447 * log (H/A)) + (0.640 * Log TDS+TSS)

	Coefficient	Std. Error	t	P	VIF
Constant	-0.0365	0.536	-0.0682	0.947	
log DOC	0.63	0.135	4.658	<0.001	1.868
log (H/A)	-0.447	0.269	-1.662	0.12	1.872
Log TDS+TSS	0.64	0.234	2.737	0.017	1.073

7. Input Parameters: TOC, Hardness/Alkalinity, TSS, pH

R^2 = 0.815

Adj R^2 = 0.753

Regression p-value = < 0.001

Log LC50 = 1.330 + (0.697 * log TOC) - (0.907 * log (H/A)) + (0.176 * Log TSS) - (0.0110 * pH)

	Coefficient	Std. Error	t	P	VIF
Constant	1.33	0.741	1.794	0.098	
log TOC	0.697	0.199	3.5	0.004	1.524
log (H/A)	-0.907	0.275	-3.299	0.006	1.295
Log TSS	0.176	0.139	1.267	0.229	1.022
pH	-0.011	0.0804	-0.137	0.893	1.191

8. Input Parameters: DOC, Hardness/Alkalinity, TSS, pH

R^2 = 0.811

Adj R^2 = 0.748

Regression p-value = < 0.001

Log LC50 = 0.906 + (0.689 * log DOC) - (0.509 * log (H/A)) + (0.137 * Log TSS) + (0.0460 * pH)

	Coefficient	Std. Error	t	P	VIF
Constant	0.906	0.828	1.094	0.296	
log DOC	0.689	0.201	3.427	0.005	2.672
log (H/A)	-0.509	0.348	-1.465	0.169	2.027
Log TSS	0.137	0.142	0.97	0.351	1.047
pH	0.046	0.0889	0.518	0.614	1.427

TABLE 3
Statistical Summaries of Step-Wise Multiple Linear Regression Analysis

FREEPORT-MCMORAN CHINO MINES COMPANY
VANADIUM, NEW MEXICO
SMELTER/TAILINGS SOILS IU SITE-SPECIFIC COPPER TOXICITY MODEL REPORT

9. Input Parameters: TOC, Hardness/Alkalinity, TSS

$R^2 = 0.814$
Adj $R^2 = 0.772$
Regression p-value = < 0.001
Log LC50 = 1.232 + (0.707 * log TOC) - (0.905 * log (H/A)) + (0.176 * Log TSS)

	Coefficient	Std. Error	t	P	VIF
Constant	1.232	0.186	6.631	<0.001	
log TOC	0.707	0.178	3.975	0.002	1.315
log (H/A)	-0.905	0.264	-3.428	0.004	1.293
Log TSS	0.176	0.133	1.321	0.209	1.021

10. Input Parameters: DOC, Hardness/Alkalinity, TSS

$R^2 = 0.807$
Adj $R^2 = 0.762$
Regression p-value = < 0.001
Log LC50 = 1.325 + (0.634 * log DOC) - (0.560 * log (H/A)) + (0.141 * Log TSS)

	Coefficient	Std. Error	t	P	VIF
Constant	1.325	0.172	7.715	<0.001	
log DOC	0.634	0.166	3.825	0.002	1.925
log (H/A)	-0.56	0.324	-1.73	0.107	1.864
Log TSS	0.141	0.138	1.025	0.324	1.045

11. Input Parameters: TOC, Hardness, Alkalinity, TSS

$R^2 = 0.844$
Adj $R^2 = 0.792$
Regression p-value = < 0.001
Log LC50 = 0.705 + (0.730 * log TOC) - (0.549 * log Hardness) + (0.837 * log Alkalinity) + (0.102 * Log TSS)

	Coefficient	Std. Error	t	P	VIF
Constant	0.705	0.39	1.807	0.096	
log TOC	0.73	0.17	4.286	0.001	1.325
log Hardness	-0.549	0.344	-1.596	0.136	3.899
log Alkalinity	0.837	0.256	3.271	0.007	4.052
Log TSS	0.102	0.136	0.752	0.467	1.171

12. Input Parameters: DOC, Hardness, Alkalinity, TSS

$R^2 = 0.855$
Adj $R^2 = 0.807$
Regression p-value = < 0.001
Log LC50 = 0.621 + (0.690 * log DOC) - (0.0456 * log Hardness) + (0.417 * log Alkalinity) + (0.0393 * Log TSS)

	Coefficient	Std. Error	t	P	VIF
Constant	0.621	0.383	1.621	0.131	
log DOC	0.69	0.152	4.545	<0.001	1.992
log Hardness	-0.0456	0.388	-0.117	0.908	5.334
log Alkalinity	0.417	0.3	1.39	0.19	5.998
log TSS	0.0393	0.134	0.294	0.774	1.22

TABLE 3
Statistical Summaries of Step-Wise Multiple Linear Regression Analysis

FREEPORT-MCMORAN CHINO MINES COMPANY
VANADIUM, NEW MEXICO
SMELTER/TAILINGS SOILS IU SITE-SPECIFIC COPPER TOXICITY MODEL REPORT

13. Input Parameters: TOC, Hardness, Alkalinity, TSS, pH

R^2 = 0.847
Adj R^2 = 0.778
Regression p-value = < 0.001

Log LC50 = 0.993 + (0.698 * log TOC) - (0.530 * log Hardness) + (0.838 * log Alkalinity) + (0.0960 * Log TSS) - (0.0365 * pH)

	Coefficient	Std. Error	t	P	VIF
Constant	0.993	0.736	1.348	0.205	
log TOC	0.698	0.189	3.695	0.004	1.524
log Hardness	-0.53	0.358	-1.481	0.167	3.949
log Alkalinity	0.838	0.265	3.167	0.009	4.053
log TSS	0.096	0.141	0.68	0.511	1.181
pH	-0.0365	0.078	-0.468	0.649	1.247

14. Input Parameters: DOC, Hardness, Alkalinity, TSS, pH

R^2 = 0.856
Adj R^2 = 0.791
Regression p-value = < 0.001

Log LC50 = 0.437 + (0.715 * log DOC) - (0.0328 * log Hardness) + (0.396 * log Alkalinity) + (0.0399 * Log TSS) + (0.0219 * pH)

	Coefficient	Std. Error	t	P	VIF
Constant	0.437	0.795	0.55	0.593	
log DOC	0.715	0.184	3.894	0.003	2.687
log Hardness	-0.0328	0.407	-0.0806	0.937	5.41
log Alkalinity	0.396	0.322	1.229	0.245	6.381
log TSS	0.0399	0.139	0.286	0.78	1.22
pH	0.0219	0.082	0.267	0.795	1.463

15. Input Parameters: TOC, Alkalinity, TDS

R^2 = 0.810
Adj R^2 = 0.766
Regression p-value = < 0.001

Log LC50 = 0.0802 + (0.846 * log TOC) + (0.471 * log Alkalinity) + (0.0904 * log TDS)

	Coefficient	Std. Error	t	P	VIF
Constant	0.0802	0.724	0.111	0.914	
log TOC	0.846	0.166	5.107	<0.001	1.114
log Alkalinity	0.471	0.225	2.096	0.056	2.775
log TDS	0.0904	0.437	0.207	0.839	2.605

16. Input Parameters: DOC, Alkalinity, TDS

R^2 = 0.861
Adj R^2 = 0.829
Regression p-value = <0.001

Log LC50 = 0.134 + (0.718 * log DOC) + (0.273 * log Alkalinity) + (0.296 * log TDS)

	Coefficient	Std. Error	t	P	VIF
Constant	0.134	0.618	0.217	0.832	
log DOC	0.718	0.113	6.347	<0.001	1.246
log Alkalinity	0.273	0.202	1.353	0.199	3.046
log TDS	0.296	0.378	0.783	0.448	2.659

TABLE 3
Statistical Summaries of Step-Wise Multiple Linear Regression Analysis

FREEPORT-MCMORAN CHINO MINES COMPANY
VANADIUM, NEW MEXICO
SMELTER/TAILINGS SOILS IU SITE-SPECIFIC COPPER TOXICITY MODEL REPORT

17. Input Parameters: TOC, Alkalinity

R^2 = 0.810
Adj R^2 = 0.782
Regression p-value = < 0.001
Log LC50 = 0.220 + (0.843 * logTOC) + (0.507 * log Alkalinity)

	Coefficient	Std. Error	t	P	VIF
Constant	0.22	0.248	0.888	0.389	
logTOC	0.843	0.159	5.292	<0.001	1.105
log Alkalinity	0.507	0.137	3.704	0.002	1.105

18. Input Parameters: DOC, Alkalinity

R^2 = 0.854
Adj R^2 = 0.833
Regression p-value = < 0.001
Log LC50 = 0.588 + (0.703 * log DOC) + (0.395 * log Alkalinity)

	Coefficient	Std. Error	t	P	VIF
Constant	0.588	0.209	2.811	0.014	
log DOC	0.703	0.11	6.393	<0.001	1.212
log Alkalinity	0.395	0.125	3.152	0.007	1.212

19. Input Parameters: TOC, Alkalinity, pH

R^2 = 0.816
Adj R^2 = 0.773
Regression p-value = < 0.001
Log LC50 = 0.646 + (0.793 * log TOC) + (0.523 * log Alkalinity) - (0.0511 * pH)

	Coefficient	Std. Error	t	P	VIF
Constant	0.646	0.7	0.924	0.373	
log TOC	0.793	0.18	4.403	<0.001	1.354
log Alkalinity	0.523	0.142	3.685	0.003	1.141
pH	-0.0511	0.0782	-0.653	0.525	1.226

20. Input Parameters: DOC, Alkalinity, pH

R^2 = 0.855
Adj R^2 = 0.822
Regression p-value = < 0.001
Log LC50 = 0.418 + (0.725 * log DOC) + (0.384 * log Alkalinity) + (0.0214 * pH)

	Coefficient	Std. Error	t	P	VIF
Constant	0.418	0.632	0.662	0.52	
log DOC	0.725	0.136	5.312	<0.001	1.742
log Alkalinity	0.384	0.136	2.824	0.014	1.329
pH	0.0214	0.0751	0.285	0.78	1.439

TABLE 4
INSTRUCTIONS AND A STEP-BY-STEP EXAMPLE FOR USING THE PROPOSED WER MODEL TO DERIVE AND APPLY SSC TO STSIU SURFACE WATERS

FREEPORT-MCMORAN CHINO MINES COMPANY
VANADIUM, NEW MEXICO
SMELTER/TAILINGS SOILS IU SITE-SPECIFIC COPPER TOXICITY MODEL REPORT

The following provides step-by-step directions for applying the MLR-model to derive site-specific copper criteria. Water chemistry from sample WER-1-1 is provided below and used throughout the calculation as an example.

$$Proposed\ MLR\ Model\colon\ Log\ EC50 = 0.588 + (0.703 * \log DOC) + (0.395 * \log Alkalinity)$$

Sample WER-1-1 water chemistry (select parameters required for MLR-model application):
DOC = 10.7
Alkalinity = 74
Hardness = 90

Step 1. Input a sample's measured water chemistry values into the MLR-model equation to calculate a predicted Site water copper EC50 value:

$$Log\ EC50 = 0.588 + (0.703 * \log DOC) + (0.395 * \log Alkalinity)$$

$$Predicted\ EC50 = 10^{(0.588+(0.703 \times \log 10.7)+(0.395 \times \log 74)}$$

$$Predicted\ EC50 = 112.203$$

Step 2. Normalize the predicted Site water EC50 to a standard hardness using the copper-criteria hardness slope:

$$EC50_{hardness\ normalized} = EC50_{at\ sample\ hardness} \times \left(\frac{Standard\ Hardness}{Sample\ Hardness}\right)^{0.9422}$$

$$EC50_{hardness\ normalized} = 112.203 \times \left(\frac{100}{90}\right)^{0.9422}$$

$$EC50_{hardness\ normalized} = 123.91$$

Step 3. Divide the normalized predicted Site EC50 by the hardness-normalized *D. magna* SMAV for copper to calculate a sample WER:

$$Sample\ WER = \frac{Site\ Water\ EC50_{hardness\ normalized}}{D.magna\ SMAVhardness_{normalized}}$$

$$Sample\ WER = \frac{123.91}{19.31}$$

$$Sample\ WER = 6.417$$

Step 4. Multiply the sample WER by the hardness-based standard to derive a site-specific standard:

$$Sample\ site\ specfic\ Cu\ CMC = WER \times Hardness\ \text{Based Standard}$$

$$Sample\ site\ specfic\ Cu\ CMC = 6.417 \times 12.169$$

$$Sample\ site\ specfic\ Cu\ CMC = 78.088 \frac{\mu g}{L}\ dissolved\ Cu$$

Figures

CITY: Lakewood DIV/GROUP: IM DB: MLM LD: PIC: PM: TM: TR:
Project #63424.001
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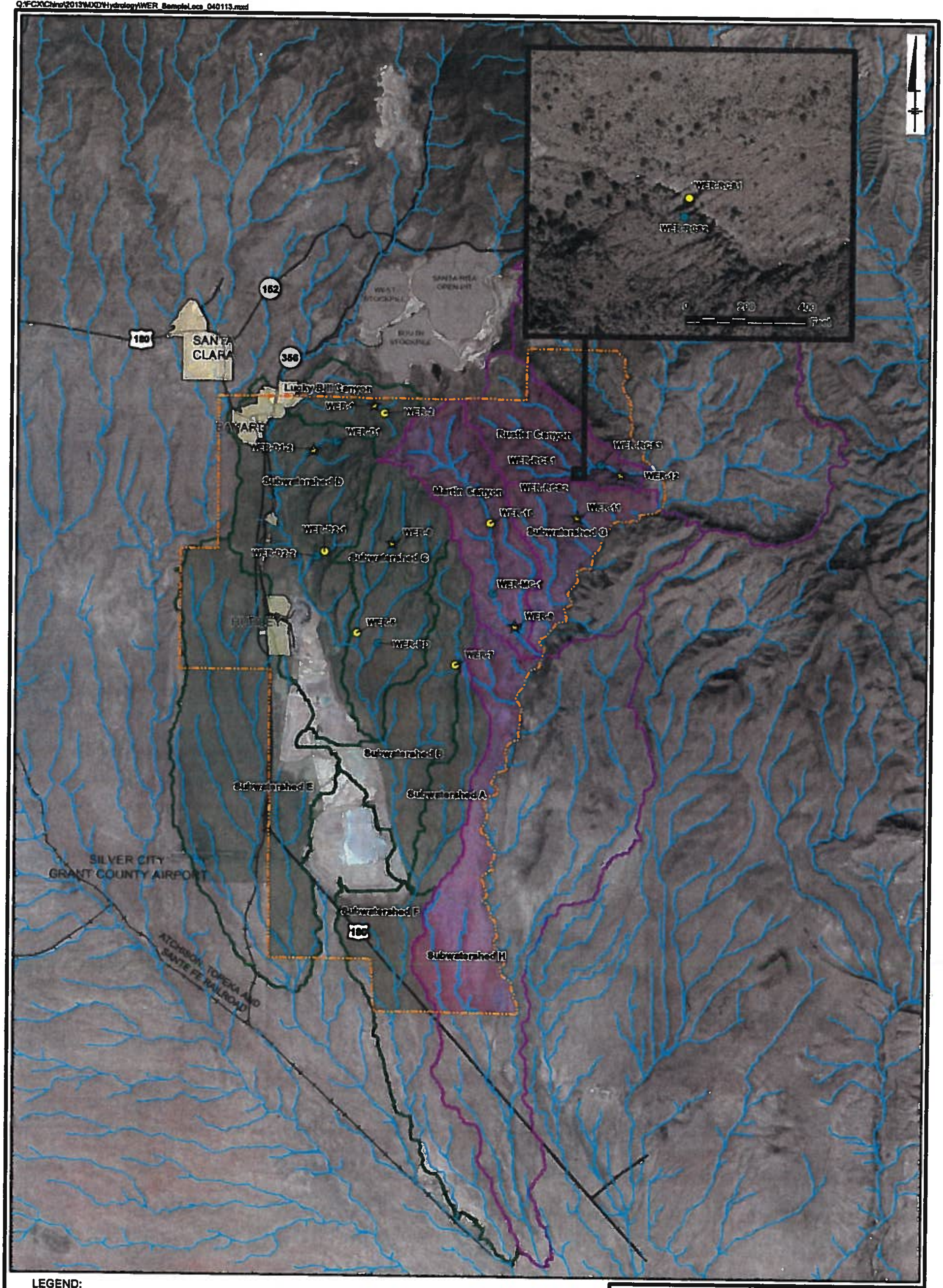


LEGEND:

- ● Analytical Sample Only
- ○ Tox and Analytical Sample
- ☆ Tox and Analytical Sample (Sampled Twice)
- ▭ STSIU Study Boundary
- ▭ City Areas
- — Drainages
- ▭ Lampbright Subwatershed Boundaries
- ▨ Lampbright Subwatersheds within AOC
- ▭ Hanover-Whitewater Subwatershed Boundaries
- ▨ Hanover-Whitwater Subwatersheds within AOC
- ▨ Stockpiles
- — Highway
- —+— Railroad
- — Town Roads

0 1.8 3.6 Miles
GRAPHIC SCALE

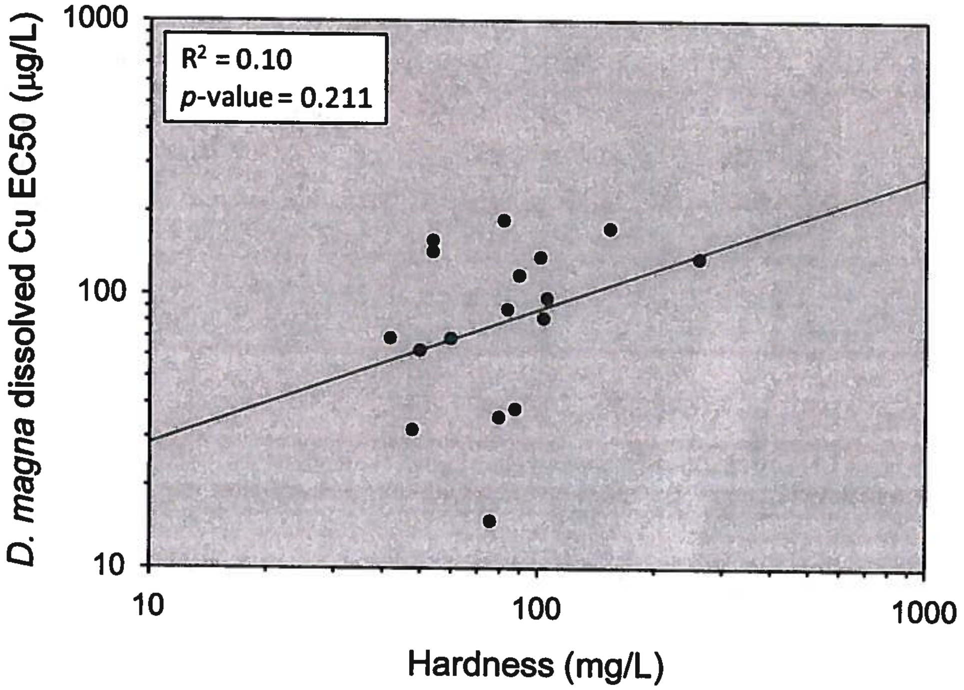
FREEPORT-MCMORAN CHINO MINES COMPANY
VANADIUM, NEW MEXICO

SITE-SPECIFIC COPPER TOXICITY MODEL REPORT

WER SAMPLE LOCATIONS

ARCADIS

FIGURE
1



Notes:

R^2 = Coefficient of determination
p-value = Statistical level of significance
Toxicity and chemistry data were log-transformed
for regression analysis

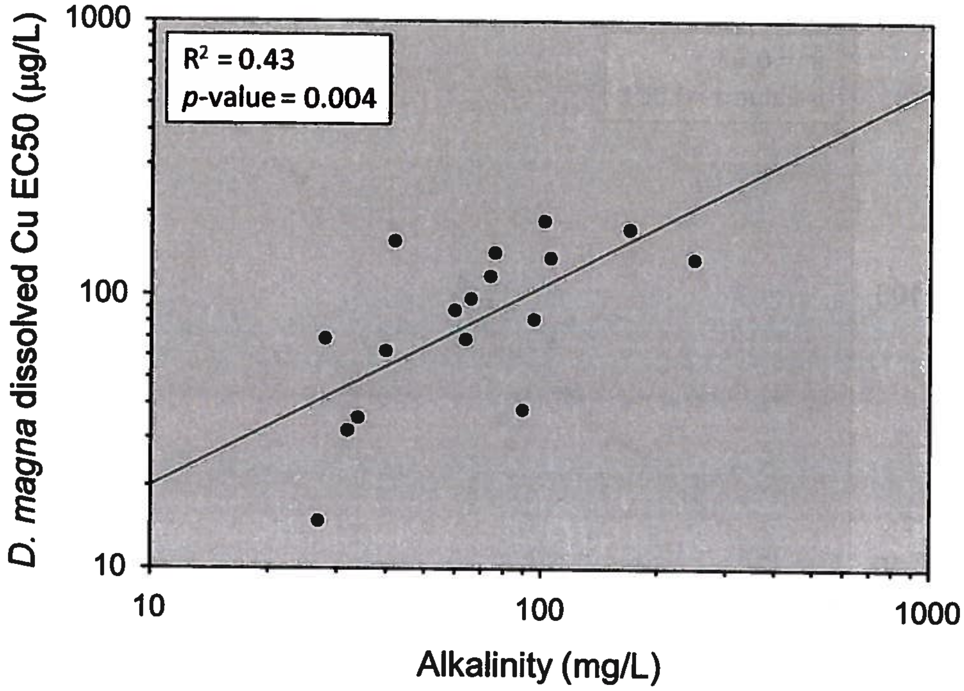
FREEPORT-MCMORAN CHINO MINES COMPANY
VANADIUM, NEW MEXICO

SITE-SPECIFIC COPPER TOXICITY MODEL REPORT

REGRESSION OF HARDNESS COMPARED TO MEASURED DISSOLVED COPPER EC50 VALUES

ARCADIS

FIGURE
2



Notes:

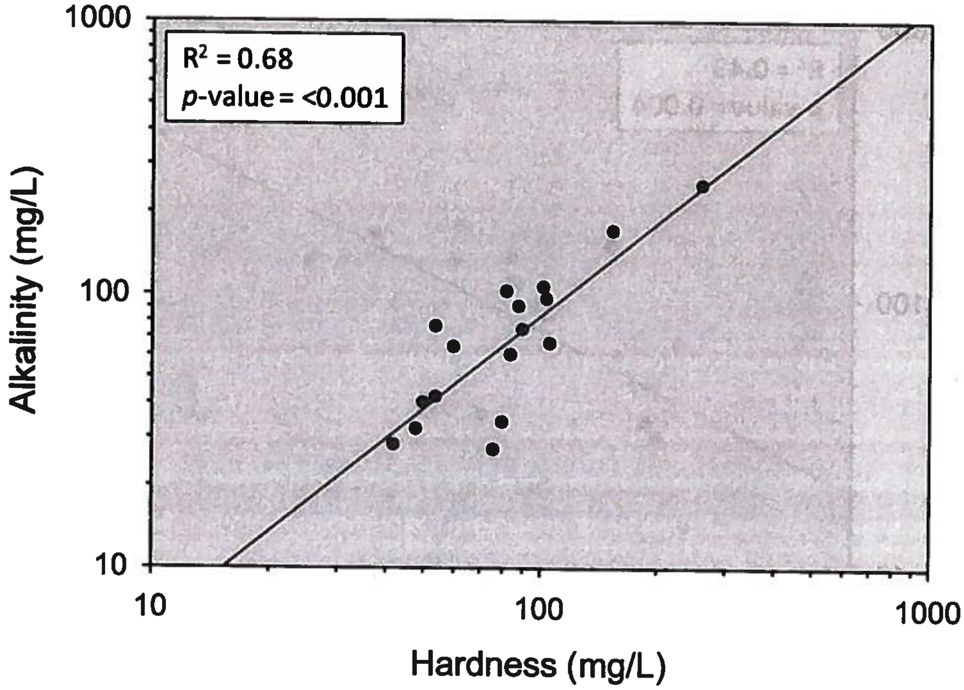
R^2 = Coefficient of determination
p-value = Statistical level of significance
Toxicity and chemistry data were log-transformed for regression analysis

FREEPORT-MCMORAN CHINO MINES COMPANY
VANADIUM, NEW MEXICO
SITE-SPECIFIC COPPER TOXICITY MODEL REPORT

REGRESSION OF ALKALINITY COMPARED TO MEASURED DISSOLVED COPPER EC50 VALUES

ARCADIS

FIGURE
3



Notes:

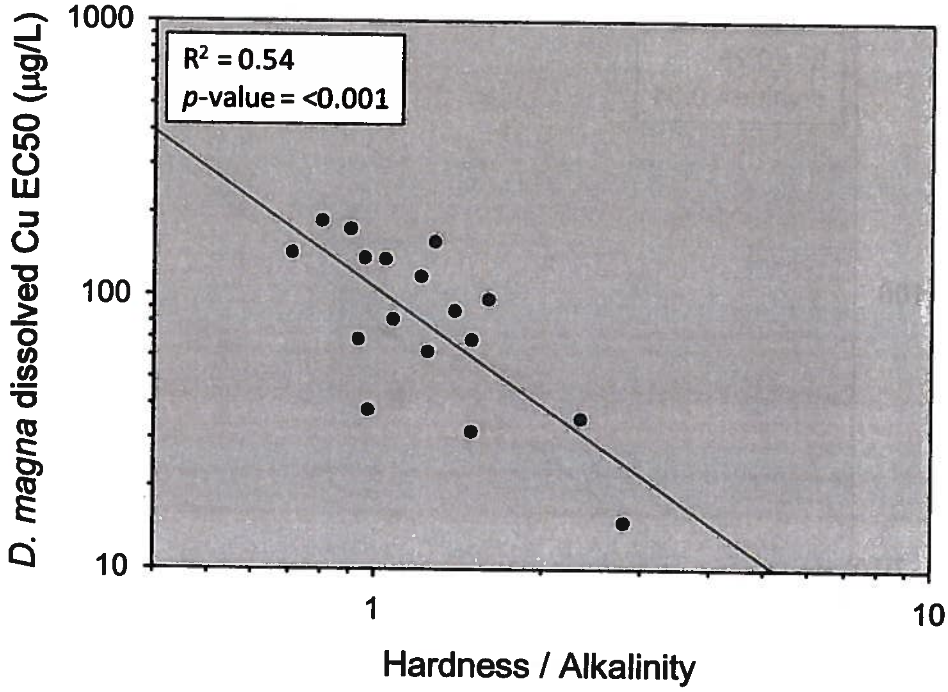
R^2 = Coefficient of determination
p-value = Statistical level of significance
Chemistry data were log-transformed
for regression analysis

FREEPORT-MCMORAN CHINO MINES COMPANY
VANADIUM, NEW MEXICO
SITE-SPECIFIC COPPER TOXICITY MODEL REPORT

REGRESSION OF ALKALINITY COMPARED TO HARDNESS

ARCADIS

FIGURE
4



Notes:

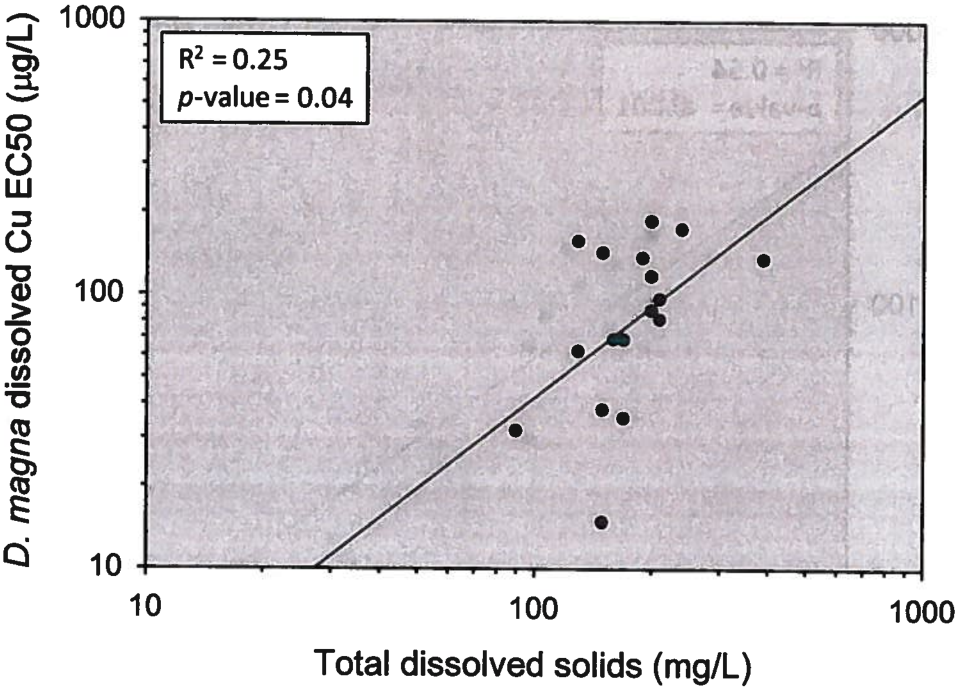
R^2 = Coefficient of determination
p-value = Statistical level of significance
Toxicity and chemistry data were log-transformed for regression analysis

FREEPORT-MCMORAN CHINO MINES COMPANY
VANADIUM, NEW MEXICO
SITE-SPECIFIC COPPER TOXICITY MODEL REPORT

REGRESSION OF HARDNESS/ALKALINITY COMPARED TO MEASURED DISSOLVED COPPER EC50 VALUES

ARCADIS

FIGURE
5



Notes:

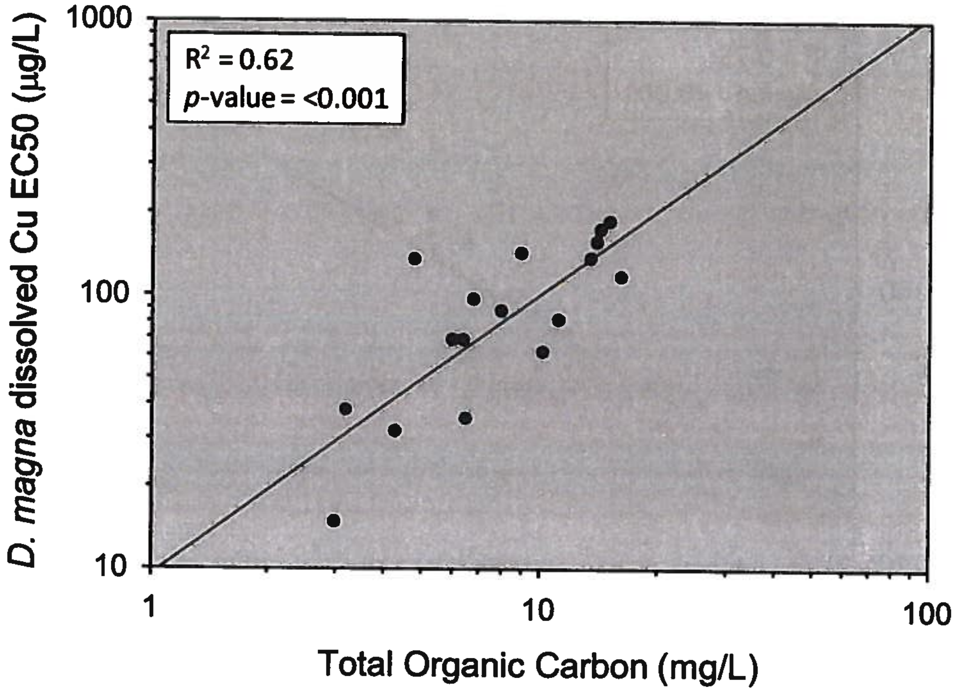
R^2 = Coefficient of determination
p-value = Statistical level of significance
Toxicity and chemistry data were log-transformed
for regression analysis

FREEPORT-MCMORAN CHINO MINES COMPANY
VANADIUM, NEW MEXICO
SITE-SPECIFIC COPPER TOXICITY MODEL REPORT

REGRESSION OF TDS COMPARED TO MEASURED DISSOLVED COPPER EC50 VALUES

ARCADIS

FIGURE
6



Notes:

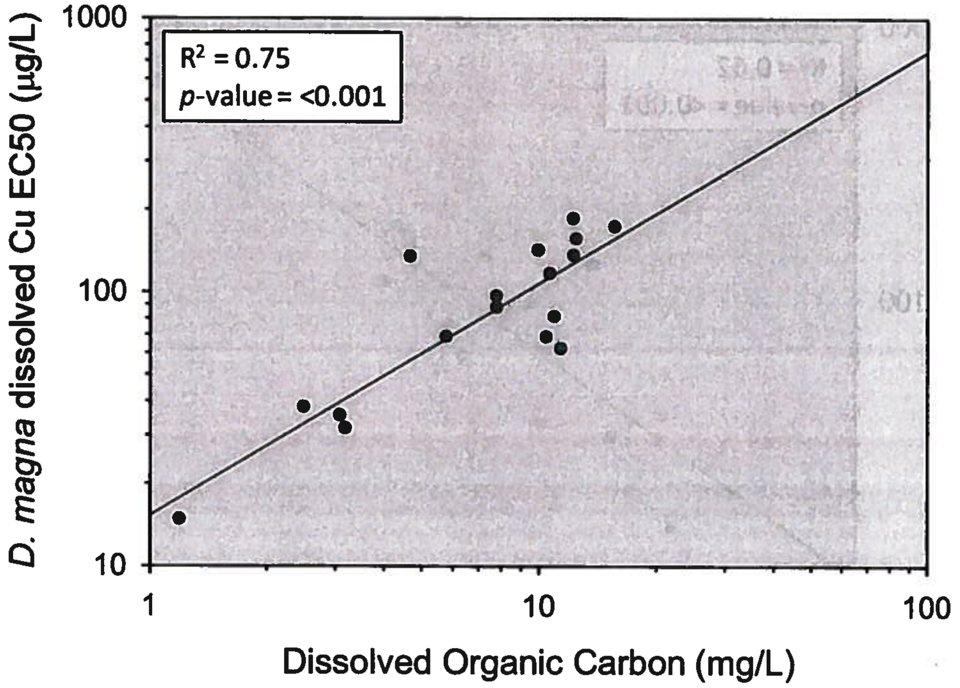
R^2 = Coefficient of determination
p-value = Statistical level of significance
Toxicity and chemistry data were log-transformed for regression analysis

FREEPORT-MCMORAN CHINO MINES COMPANY
VANADIUM, NEW MEXICO
SITE-SPECIFIC COPPER TOXICITY MODEL REPORT

REGRESSION OF TOC COMPARED TO MEASURED DISSOLVED COPPER EC50 VALUES

ARCADIS

FIGURE
7



Notes:

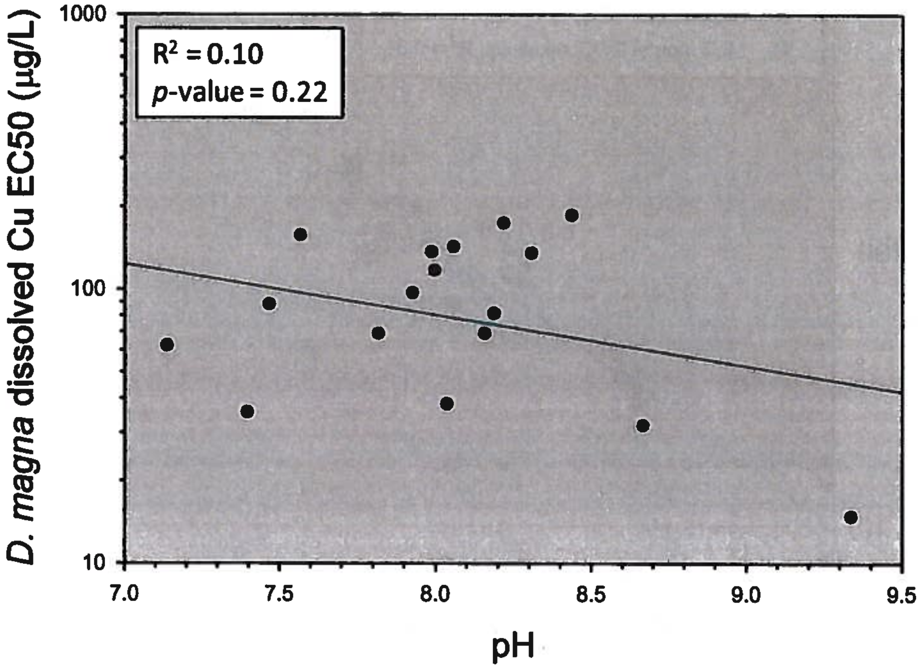
R^2 = Coefficient of determination
p-value = Statistical level of significance
Toxicity and chemistry data were log-transformed for regression analysis

FREEPORT-MCMORAN CHINO MINES COMPANY
VANADIUM, NEW MEXICO
SITE-SPECIFIC COPPER TOXICITY MODEL REPORT

REGRESSION OF DOC COMPARED TO MEASURED DISSOLVED COPPER EC50 VALUES

ARCADIS

FIGURE
8



Notes:

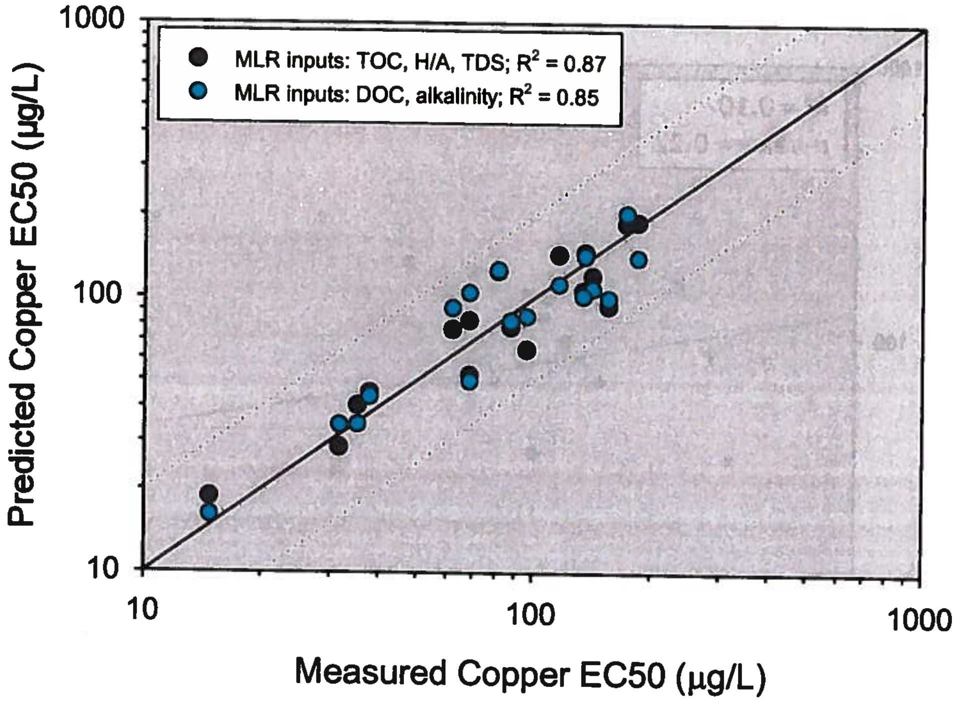
R^2 = Coefficient of determination
p-value = Statistical level of significance
Toxicity data were log-transformed
for regression analysis

FREEPORT-MCMORAN CHINO MINES COMPANY
VANADIUM, NEW MEXICO
SITE-SPECIFIC COPPER TOXICITY MODEL REPORT

REGRESSION OF pH COMPARED TO MEASURED DISSOLVED COPPER EC50 VALUES

ARCADIS

FIGURE
9



Notes:

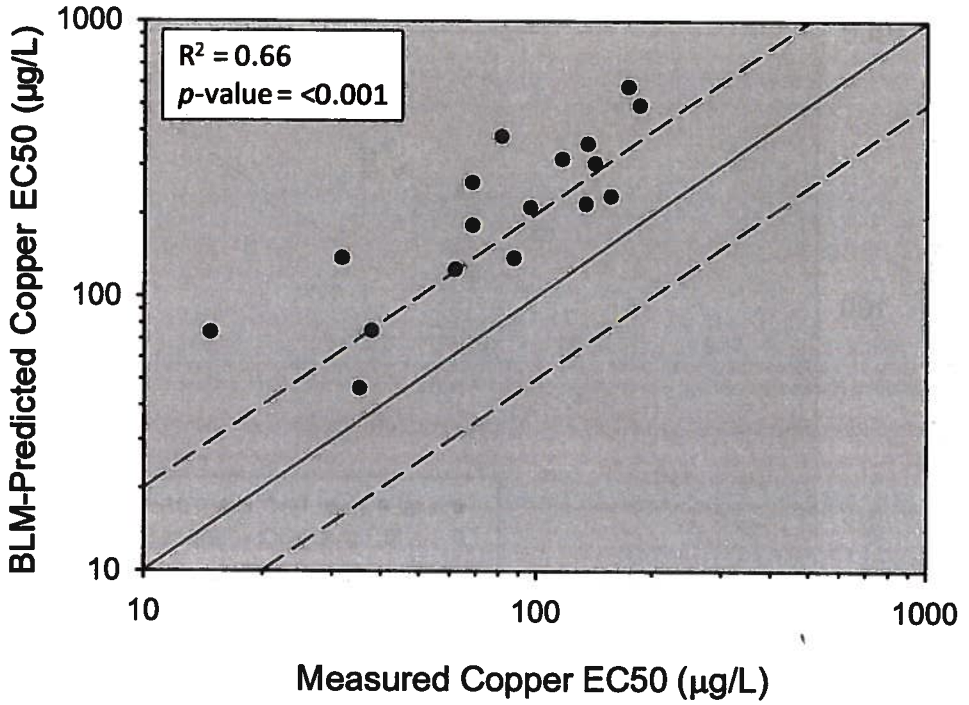
R^2 = Coefficient of determination (for predicted vs. measured EC50 comparison)
p-value = Statistical level of significance
Predicted and measured EC50 values were log-transformed for regression analysis
Solid diagonal line = predicted EC50 equals measured EC50
Dashed diagonal lines= ± 2-fold measured versus predicted

FREEPORT-MCMORAN CHINO MINES COMPANY
VANADIUM, NEW MEXICO
SITE-SPECIFIC COPPER TOXICITY MODEL REPORT

MLR MODEL-PREDICTED DISSOLVED COPPER EC50 VALUES COMPARED TO MEASURED DISSOLVED COPPER EC50 VALUES

ARCADIS

FIGURE
10



Notes:

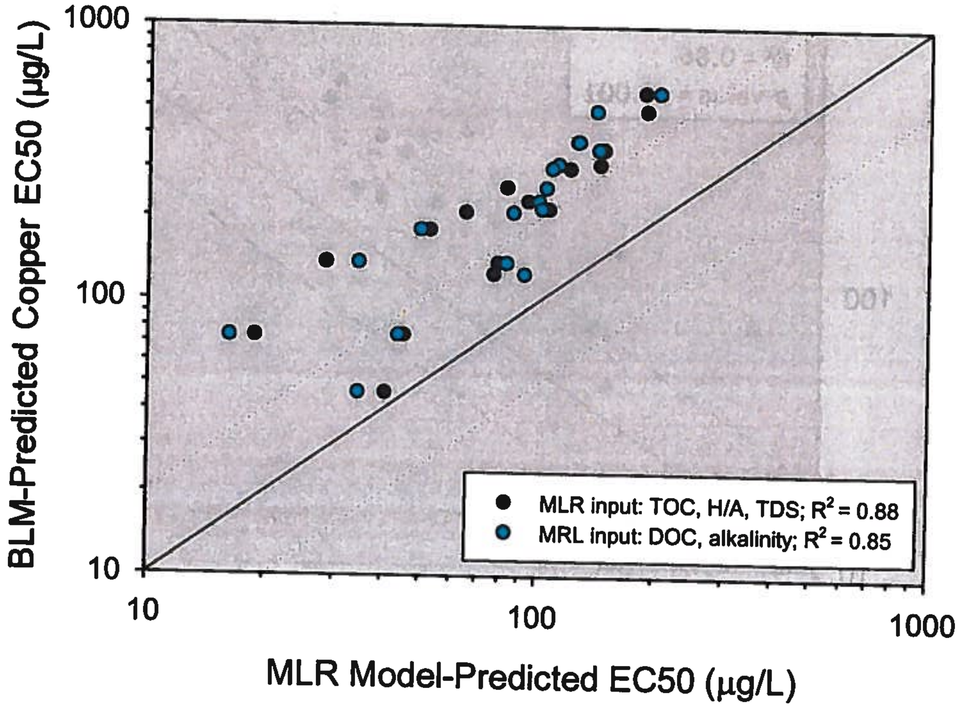
R^2 = Coefficient of determination
p-value = Statistical level of significance
Predicted and measured EC50 values were log-transformed for regression analysis
Solid diagonal line = predicted EC50 equals measured EC50
Dashed diagonal lines= ± 2-fold measured versus predicted

FREEPORT-MCMORAN CHINO MINES COMPANY
VANADIUM, NEW MEXICO
SITE-SPECIFIC COPPER TOXICITY MODEL REPORT

BLM-PREDICTED DISSOLVED COPPER EC50 VALUES COMPARED TO MEASURED DISSOLVED COPPER EC50 VALUES

ARCADIS

FIGURE
11



Notes:

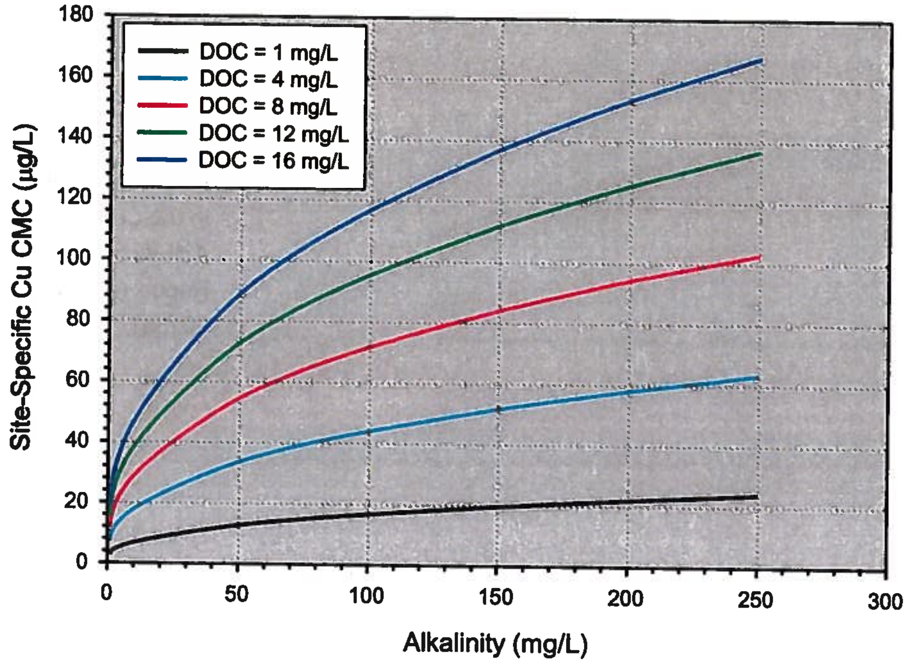
R^2 = Coefficient of determination
p-value = Statistical level of significance
Predicted EC50 values were log-transformed
for regression analysis
Solid diagonal line = BLM predicted EC50 equals MLR-model-predicted EC50
Dashed diagonal lines= ± 2-fold BLM -predicted versus MLR mode predicted

FREEPORT-MCMORAN CHINO MINES COMPANY
VANADIUM, NEW MEXICO
SITE-SPECIFIC COPPER TOXICITY MODEL REPORT

BLM-PREDICTED DISSOLVED COPPER EC50 VALUES COMPARED TO MLR MODEL-PREDICTED DISSOLVED COPPER EC50 VALUES

ARCADIS

FIGURE
12



Notes:

CMC = Criteria Maximum Concentrations
Example Site-specific CMC values calculated at a hardness of 100 mg/L.

FREEPORT-MCMORAN CHINO MINES COMPANY
VANADIUM, NEW MEXICO
SITE-SPECIFIC COPPER TOXICITY MODEL REPORT

EXAMPLE OF SITE-SPECIFIC COPPER CMC CALCULATED USING THE PROPOSED WER MODEL APPROACH OVER AN ALKALINITY AND DOC RANGE

ARCADIS

FIGURE
13

Appendix A

Data Tables Presented
in the Criteria
Adjustment Interim
Report (ARCADIS
2013a)

APPENDIX A: TABLE 1
SUMMARY OF ALL SURFACE WATER SAMPLING LOCATIONS

FREEPORT-MCMORAN CHINO MINES COMPANY
VANADIUM, NEW MEXICO
SMELTER/TAILINGS SOILS IU SITE-SPECIFIC COPPER TOXICITY MODEL REPORT

Sample ID[1]	Drainage Description	Longitude	Latitude	Maximum Length (m)	Maximum Width (m)	Maximum Depth (m)	Temperature (°C)	Conductivity (mS/cm)	Dissolved Oxygen[2] (mg/L)	pH
Round 1 WER Toxicity Samples										
WER-1-1	Lucky Bill	-108.09669	32.76198	15	10	0.61	29.47	0.261	–	7.08
WER-1-2	Lucky Bill	-108.093141	32.759732	20	10	0.23	22.38	0.258	–	6.33
WER-1-5	C-Drainage	-108.101616	32.696746	50	4	0.24	31.67	0.205	–	6.88
WER-1-6	C-Drainage	-108.0899	32.7227	8.5	1.5	0.24	23.13	0.158	–	6.42
WER-1-7	B-Drainage	-108.06822	32.6879	2.5	1.6	0.55	20.94	0.256	–	7.18
WER-1-9	Lower Martin	-108.0479	32.6992	65	7	0.52	21.29	0.197	–	7.5
WER-1-10	Mid Martin	-108.056804	32.728667	15	3.9	0.18	21.84	0.552	–	7.38
WER-1-11	G-Drainage	-108.026981	32.730613	9.4	4.4	0.61	25.47	0.337	–	6.37
WER-1-12	Rustler	-108.012367	32.742963	32.8	5	0.82	22.17	0.215	–	6.09
WER-1-RCS-1	Rustler, south fork	-108.026718	32.74311	10	10	4.5	22.85	0.127	–	8.67
WER-1-D1-2	D1-Drainage	-108.116935	32.748954	5.5	2.5	0.49	17.92	0.182	–	7.41
WER-1-D2-1	D2-Drainage	-108.112792	32.719935	3	3	0.73	22.1	0.164	–	6.62
Round 1 Additional Analytical Samples										
WER-1-D1	D1-Drainage	-108.10912	32.7514	8.7	4.6	0.09	17.04	0.129	–	7.7
WER-D2-2	D2- Drainage	-108.11544	32.7185	2	1	0.15	19.89	0.206	–	7.01
WER-1-BD	C-Drainage	-108.09444	32.6939	2	0.5	0.40	29.72	0.174	–	7.42
WER-MC-1	Martin Canyon	-108.05569	32.7085	30	3	0.15	28.69	0.247	–	7.47
WER-1-RCS2	Rustler Canyon	-108.02677	32.7429	7.5	2.5	0.30	21.52	0.117	–	7.34
WER-1-RCS-3	Rustler Canyon	-108.01934	32.7456	10	2.5	0.46	21.22	0.194	–	6.15
Round 2 WER Toxicity Samples										
WER-2-1	Lucky Bill	-108.09669	32.76198	10	8.5	0.61	20.48	0.291	8.75	7.54
WER-2-6	C-Drainage	-108.0899	32.7227	8	1.5	0.25	16.76	0.144	5	6.94
WER-2-9	Lower Martin	-108.0479	32.6992	21.88	4.75	0.67	20.58	0.232	7.61	8.45
WER-2-11	G-Drainage	-108.026981	32.730613	7.5	3.5	0.76	20.49	0.282	7.48	7.61
WER-2-12	Rustler	-108.012367	32.742963	6.37	1.82	0.30	13.98	0.226	8.03	7.29
WER-2-D1-2	D1-Drainage	-108.116935	32.748954	3	4.4	0.43	13.81	0.205	7.63	7.47

Notes:

1. Sample ID nomenclature: Sample type - Sample round - Sample #.

2. Post-calibration of DO for first round of sampling did not meet calibration performance criteria.

m = meters.

°C = degrees celsius.

mS/cm = millisiemens per cm.

mg/L = milligrams per liter.

APPENDIX A: TABLE 2
SUMMARY OF ANALYTICAL CHEMISTRY METHODS

FREEPORT-MCMORAN CHINO MINES COMPANY
VANADIUM, NEW MEXICO
SMELTER/TAILINGS SOILS IU SITE-SPECIFIC COPPER TOXICITY MODEL REPORT

Constituent	Method	MDL (mg/L)	Sample Holding Time	Preservation
Metals, dissolved				
Aluminum, dissolved	M 200.8 ICP-MS	0.001	180-d	HNO_3 to pH <2
Cadmium, dissolved	M 200.8 ICP-MS	0.0001	180-d	HNO_3 to pH <2
Calcium, dissolved	M 200.7 ICP	0.2	180-d	HNO_3 to pH <2
Copper, dissolved	M 200.8 ICP-MS	0.0005	180-d	HNO_3 to pH <2
Iron, dissolved	M 200.7 ICP	0.02	180-d	HNO_3 to pH <2
Lead, dissolved	M 200.8 ICP-MS	0.0001	180-d	HNO_3 to pH <2
Magnesium, dissolved	M 200.7 ICP	0.2	180-d	HNO_3 to pH <2
Manganese, dissolved	M 200.7 ICP-MS	0.0005	180-d	HNO_3 to pH <2
Potassium, dissolved	M 200.7 ICP	0.3	180-d	HNO_3 to pH <2
Sodium, dissolved	M 200.7 ICP	0.3	180-d	HNO_3 to pH <2
Zinc, dissolved	M 200.8 ICP-MS	0.002	180-d	HNO_3 to pH <2
Metals, total recoverable				
Aluminum, total	M 200.8 ICP-MS	0.001	180-d	HNO_3 to pH <2
Cadmium, total	M 200.8 ICP-MS	0.0001	180-d	HNO_3 to pH <2
Calcium, total	M 200.7 ICP	0.2	180-d	HNO_3 to pH <2
Copper, total	M 200.8 ICP-MS	0.0005	180-d	HNO_3 to pH <2
Iron, total	M 200.7 ICP	0.02	180-d	HNO_3 to pH <3
Lead, total	M 200.8 ICP-MS	0.0001	180-d	HNO_3 to pH <2
Magnesium, total	M 200.7 ICP	0.2	180-d	HNO_3 to pH <2
Manganese, total	M 200.8 ICP-MS	0.0005	180-d	HNO_3 to pH <3
Zinc, total	M 200.8 ICP-MS	0.002	180-d	HNO_3 to pH <2
Water Quality parameters				
Alkalinity as CaCO3	SM2320B -Titration	2	14-d	≤ 6 degree C
Carbon, dissolved organic (DOC)	SM5310B	1	28-d	Sulfuric acid, cool (4 degree C)
Carbon, total organic (TOC)	SM5310B	1	28-d	Sulfuric acid, cool (4 degree C)
Cation-Anion balance	Calculation	Calculation	--	--
Chloride	SM4500CL-E	1	28-d	≤ 6 degree C
Hardness as CaCO3	SM2340B-Calculation	Calculation	--	--
Residue, Filterable (TDS) @ 180 C	SM2540C	10	--	≤ 6 degree C
Sulfate	D516-02 - Turbidimetric	5	28-d	≤ 6 degree C
TDS (calculated)	Calculation	Calculation	--	--
TDS (ratio-measured/calculated)	Calculation	Calculation	--	--
pH	YSI data sonde	--	--	--
Temperature	YSI data sonde	--	--	--
Dissolved Oxygen	YSI data sonde	--	--	--
Conductivity	YSI data sonde	--	--	--

Notes:

*Extended sample hold time may be required for some WER samples.

TDS = Total dissolved solids.

-- Not pertinent to this field.

mg/L = milligrams per liter.