

BEFORE THE ILLINOIS POLLUTION CONTROL BOARD

IN THE MATTER OF:)
)
PROPOSED SITE SPECIFIC)
RULE FOR SANITARY DISTRICT) R14-24
OF DECATUR FROM 35 ILL. ADM.) (Site Specific Rule – Water)
CODE SECTION 302.208(e).)

NOTICE OF FILING

TO: Don Brown Tim Fox
Clerk of the Board Hearing Officer
Illinois Pollution Control Board Illinois Pollution Control Board
100 W. Randolph Street, Suite 11-500 100 W. Randolph Street, Suite 11-500
Chicago, Illinois 60601 Chicago, Illinois 60601
(VIA ELECTRONIC MAIL) (VIA ELECTRONIC MAIL)

(SEE PERSONS ON ATTACHED SERVICE LIST)

PLEASE TAKE NOTICE that I have today filed with the Office of the Clerk of the Illinois Pollution Control Board the **SANITARY DISTRICT OF DECATUR'S MOTION TO FILE REVISED EXHIBITS 14 AND 28, NEW EXHIBITS 45 AND 46, REVISED EXHIBIT LIST, AND MINOR REVISION TO PROPOSED SUBSECTION 303.410**, a copy of which is herewith served upon you.

Respectfully submitted,

SANITARY DISTRICT OF DECATUR

Date: April 20, 2018

By: /s/ Katherine D. Hodge
One of Its Attorneys

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CERTIFICATE OF SERVICE

I, Katherine D. Hodge, the undersigned, on oath state the following:

That I have served the attached **SANITARY DISTRICT OF DECATUR'S MOTION TO FILE REVISED EXHIBITS 14 AND 28, NEW EXHIBITS 45 AND 46, REVISED EXHIBIT LIST, AND MINOR REVISION TO PROPOSED SUBSECTION 303.410**, via electronic mail upon:

Don Brown
Clerk of the Board
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That my email address is Katherine.Hodge@heplerbroom.com.

That the number of pages in the email transmission is 574.

That the email transmission took place before 5:00 p.m. on the date of April 20, 2018.

/s/ Katherine D. Hodge

Katherine D. Hodge

Date: April 20, 2018

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PROPOSED SITE SPECIFIC)
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REVISED EXHIBITS 14 AND 28, NEW EXHIBITS 45 AND 46,
REVISED EXHIBIT LIST, AND MINOR
REVISION TO PROPOSED SUBSECTION 303.410**

The Petitioner, SANITARY DISTRICT OF DECATUR (“District”), by and through its attorneys, HEPLERBROOM, LLC, hereby requests the Illinois Pollution Control Board (“Board”) to accept for filing the District’s Revised Exhibits 14 and 28, New Exhibits 45 and 46, Revised Exhibit List, and Minor Revision to Proposed Subsection 303.410. In support of this Motion, the District states as follows:

1. The District filed its original Petition for Site Specific Rule from 35 Ill. Admin. Code Section 302.208(e) (“Original Petition”), with the Board on June 30, 2014.
2. The District filed its Amended Petition for Site Specific Rule from 35 Ill. Admin. Code Section 302.208(e) (“Amended Petition”), with the Board on November 30, 2017.
3. The District’s Amended Petition included: 1) the Proposed Site Specific Rule; 2) the Statement of Facts; 3) a Statement of Purpose and Effect of Proposal; 4) a Motion to Waive Requirement to Submit 200 Signatures; 5) the Proposed Rule Language; 6) an Exhibit List, and 7) forty-four (44) exhibits including Exhibit 14 (Estimate of the BLM Adjustment to the Nickel Criterion for the Sanitary District of Decatur, Illinois, dated January 16, 2014) and Exhibit 28 (Development of a Water Effect Ratio (“WER”) for Nickel in the Sangamon River (Nov. 29,

2017 Draft)), which provide technical support for the District's site-specific water quality standard for nickel for the Sangamon River.

4. Since filing its Amended Petition, the District has continued to work cooperatively with the Illinois Environmental Protection Agency ("Illinois EPA") and the United States Environmental Protection Agency ("USEPA") to address technical issues on the proposed site-specific standard.

5. As a result of continuing discussions and correspondence with Illinois EPA and USEPA, the District has made certain revisions and clarifications to Exhibits 14 and 28.

6. Specifically, the District seeks to file revised Exhibit 14, Estimate of the BLM Adjustment to the Nickel Criterion for the Sanitary District of Decatur, Illinois, dated April 10, 2018, with the Board that, among other topics, more fully describes the overall calibration results to fish and invertebrates and updates the dissolved organic carbon ("DOC") based on a more complete dataset. The revised Exhibit 14, attached to this Motion, is intended to supersede and replace the Exhibit 14 submitted with the Amended Petition on November 30, 2017. In addition, the District is attaching to this Motion a redlined copy of revised Exhibit 14 that clearly shows the revised text for the convenience of the Board and public.¹

7. Further, the District seeks to file revised Exhibit 28, Development of a Water Effect Ratio ("WER") for Nickel in the Sangamon River, dated April 12, 2018, with the Board that references the Biotic Ligand Model ("BLM") result using average chemistry and an average DOC consistent with the value used in the DOC-WER calculation. Revised Exhibit 28 also expands the discussion on why multiple species are relevant and describes a Monte Carlo analysis to quantify confidence intervals around the DOC slope. The revised Exhibit 28, attached to this Motion, is intended to supersede and replace the Exhibit 28 submitted with the

¹ The redlined copy of revised Exhibit 14 is not intended to be filed as an exhibit to the Amended Petition.

Amended Petition on November 30, 2017. As with revised Exhibit 14, the District attaches to this Motion a redlined copy of revised Exhibit 28 that clearly shows the revised text for the convenience of the Board and the public.²

8. The District also seeks to file new exhibits, i.e., Exhibit 45 and Exhibit 46.

9. New Exhibit 45 is a document entitled, “R14-24 Sanitary District of Decatur April 16, 2018 Response to IEPA and USEPA,” and consists of the technical correspondence among the District, Illinois EPA, and USEPA leading to the development and refinement of the District’s site-specific proposal and its justification. The District believes that the back and forth style of comments presented would be informative and helpful to the Board’s evaluation of this site-specific rule petition. The correspondence consists of questions and responses among USEPA, Illinois EPA, and the District’s technical consultant, Mr. Robert Santore, regarding original Exhibits 14 and 28, revisions made thereto, and the resulting change to the WER calculation.

10. New Exhibit 46 is a spreadsheet entitled “Nickel Calculator for Illinois, Indiana, Iowa and USEPA” that illustrates how Illinois’ chronic water quality standard for nickel and the District’s proposed site-specific rule compare with USEPA’s national recommended chronic water quality standard for nickel and the chronic water quality standards for nickel in the neighboring states of Indiana and Iowa. Exhibit 46 also factors in the Sangamon River’s hardness value of 359 mg/L to provide an “apples to apples” comparison of anticipated National Pollutant Discharge Elimination System (“NPDES”) permit limits that would apply to the District were it subject to each of those regulatory programs.

11. As a result of the filing of revised Exhibits 14 and 28 and new Exhibits 45 and 46, the District seeks to file a revised Exhibit List, as follows:³

² The redlined copy of revised Exhibit 28 is not intended to be filed as an exhibit to the Amended Petition.

Electronic Filing: Received, Clerk's Office 4/20/2018

- Exhibit 1. District's NPDES Permit (No. IL0028321)
- Exhibit 2. Illinois EPA Memo Regarding Water Quality Based Effluent Limits at the District (November 9, 2006)
- Exhibit 3. District Interim Report (December 20, 2007)
- Exhibit 4. Illinois EPA Letter to the District (April 24, 2009)
- Exhibit 5. Recommendation of the Illinois EPA (April 7, 2014) in PCB 14-111 (Variance – Water)
- Exhibit 6. District Summary of Sample Data Presented to Illinois EPA on October 30, 2007
- Exhibit 7. Illinois EPA e-mail indicating higher permit limit could be justified based on Interim Report (January 2, 2008)
- Exhibit 8. District Interim Report (December 29, 2008)
- Exhibit 9. District Interim Report (December 30, 2009)
- Exhibit 10. District Interim Report (July 1, 2010)
- Exhibit 11. District Interim Report (December 29, 2010)
- Exhibit 12. District Interim Report (June 29, 2011)
- Exhibit 13. Presentation Slides from June 6, 2011 Telephone Call with Illinois EPA and USEPA
- Exhibit 14. Estimate of the BLM Adjustment to the Nickel Criterion for the Sanitary District of Decatur, Illinois, dated ~~January 16, 2014~~ April 10, 2018
- Exhibit 15. District Interim Report (December 21, 2011)
- Exhibit 16. District Interim Report (June 25, 2012)
- Exhibit 17. District Interim Report (December 19, 2012)
- Exhibit 18. District Interim Report (June 27, 2013)
- Exhibit 19. District Interim Report (December 20, 2013)
- Exhibit 20. Table 1 – Weekly Loads to ADM Decatur Complex WWTP (August – November 2010)
- Exhibit 21. Figure 1 – ADM Flow Data
- Exhibit 22. ADM Operating Permit No. 2015-SC-60414 (Dec. 29, 2015)
- Exhibit 23. District Executive Order to ADM (Feb. 1, 2016)
- Exhibit 24. District's Response to U.S. EPA Toxicity Testing Comments Sanitary District of Decatur, Illinois;
- Exhibit 25. U.S. EPA Follow Up to the District's Response to U.S. EPA Toxicity Testing Comments Sanitary District of Decatur, Illinois;
- Exhibit 26. Review of Water Quality Factors that Affect Nickel Bioavailability to Aquatic Organisms, R. Santore Draft Manuscript (provided on April 12, 2016)
- Exhibit 27. Progress Report – Nickel WER Project (March 2016)

³ Through this Motion, the District also updates the references to Exhibits 14 and 28 on pages 24 and 36, respectively, in the Amended Petition.

- Exhibit 28. Development of a Water Effect Ratio for Nickel in the Sangamon River (~~Nov. 29, 2017 Draft~~) (April 12, 2018)
- Exhibit 29. A Review of Water Quality Factors that Affect nickel Bioavailability to Aquatic Organisms, R. Santore, Current Draft Manuscript (Draft Current as of Nov. 29, 2017)
- Exhibit 30. Table 2 – Monitoring Data (March 2007 – October 2017)
- Exhibit 31. ISWS Map 5 Sangamon Region (April 2002)
- Exhibit 32. Ecological Condition of a Stretch of the Sangamon River Receiving Effluent from the Sanitary District of Decatur, Eastern Illinois University Report (May 2017)
- Exhibit 33. Biotic Assessment of Water Quality in a Stretch of the Sangamon River Receiving Effluent from the Sanitary District of Decatur, Eastern Illinois University Report (May 2015)
- Exhibit 34. Ecological Condition of a Sangamon River Receiving Effluent from the Sanitary District of Decatur, Eastern Illinois University Report (May 2016)
- Exhibit 35. Biotic Assessment of Water Quality in a Stretch of the Sangamon River Receiving Effluent from the Sanitary District of Decatur, Eastern Illinois University Report (May 2014)
- Exhibit 36. Biotic Assessment of Water Quality in a Stretch of the Sangamon River Receiving Effluent from the Sanitary District of Decatur, Eastern Illinois University Report (May 2013)
- Exhibit 37. Biotic Assessment of Water Quality in a Stretch of the Sangamon River Receiving Effluent from the Sanitary District of Decatur, Eastern Illinois University Report (May 2012)
- Exhibit 38. Biotic Assessment of Water Quality in a Reach of the Sangamon River Receiving Effluent from the Sanitary District of Decatur, Eastern Illinois University Report (May 2011)
- Exhibit 39. Biotic Assessment of Water Quality in a Reach of the Sangamon River Receiving Effluent from the Sanitary District of Decatur, Eastern Illinois University Report (August 2010)
- Exhibit 40. Biotic Assessment of Water Quality in a Reach of the Sangamon River Receiving Effluent from the Sanitary District of Decatur, Eastern Illinois University Report (July 2009)
- Exhibit 41. EcoCAT Report (Nov. 29, 2017)
- Exhibit 42. Table 3 – Summary of Technologies Reviewed by ADM Under Variance Granted by Board
- Exhibit 43. Table 4 – Technical Challenges on Scale Up for Nickel Remediation Chemistries
- Exhibit 44. ADM Industrial Discharge Permit

Exhibit 45. Sanitary District of Decatur April 16, 2018 Response to IEPA and USEPA Comments dated January 16 and 19, 2018

Exhibit 46. Nickel Calculator for Illinois, Indiana, Iowa, and USEPA

12. As a result of the revisions to Exhibits 14 and 28, the District seeks to file a minor revision to Proposed Section 303.410 to reflect the updated WER of 2.50, as follows:

Section 303.410 Chronic Nickel Water Quality Standard for Segment of the Sangamon River

The general use chronic water quality standard for dissolved nickel contained in Section 302.208(e) shall not apply to the Sangamon River, which receives discharges from the Sanitary District of Decatur's Main STP, from that facility's Outfall 001 located at 39° 49' 56" North Latitude, 89° 0' 7" West Longitude, to the point of the confluence of the Sangamon River with the South Fork of the Sangamon River near Riverton. Instead, nickel levels in such waters shall meet a chronic water quality standard for dissolved nickel as follows:

$$\text{Chronic Dissolved Nickel Standard} = \exp[A+B\ln(H)] \times 0.997^* \times \text{WER},$$

where A = -2.286, B = 0.846, ln(H) = natural logarithm of Hardness,
* = conversion factor multiplier for dissolved metals, and WER = 2.3350

13. Factoring into the above equation the Illinois EPA-determined critical hardness value of 359 mg/L and nickel translator value of 0.966 results in an anticipated National Pollutant Discharge Elimination System ("NPDES") permit limit of 38.20 µg/L (0.0382 mg/L) total nickel for the District. For comparison purposes, USEPA's national recommended chronic water quality standard for nickel would result in an anticipated NPDES permit limit of approximately 153.81 µg/L (0.154 mg/L) when applying the Sangamon River's hardness value of 359 mg/L.⁴ Iowa's chronic water quality standard for nickel, at a hardness 359 mg/L, would similarly result in an anticipated NPDES permit limit of 153.81 µg/L (0.154 mg/L).⁵ And Indiana's chronic water quality standard for nickel, at a hardness of 359 mg/L, would result in an anticipated

⁴ USEPA National Recommended Water Quality Criteria – Aquatic Life Criteria Table, available at: <https://www.epa.gov/wqc/national-recommended-water-quality-criteria-aquatic-life-criteria-table>.

⁵ 567 Iowa Adm. Code 61.3(3).

NPDES permit limit of 464.89 µg/L (0.465 mg/L).⁶ See Exhibit 46, attached, for the calculations, which will be more fully described in Mr. Santore's pre-filed testimony.

WHEREFORE, for the above and foregoing reasons, the District hereby respectfully requests the Board to accept for filing, the District's Revised Exhibits 14 and 28, New Exhibits 45 and 46, Revised Exhibit List, and Minor Revision to Proposed Subsection 303.410.

Respectfully submitted,

SANITARY DISTRICT OF DECATUR,

By: /s/ Katherine D. Hodge
One of Its Attorneys

Date: April 20, 2018

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⁶ 327 Indiana Adm. Code 2-1-6.

Exhibit 14

Prepared for Proposed Site Specific Rule for Sanitary District of Decatur
From 35 Ill. Adm. Code Section 302.208(e)

ESTIMATE OF THE BLM ADJUSTMENT TO THE NICKEL CRITERION FOR THE SANITARY DISTRICT OF DECATUR, ILLINOIS

**Prepared by
Robert Santore**

April 10, 2018

I. INTRODUCTION

This report was prepared in support of the Sanitary District of Decatur's ("District") Petition to the Illinois Pollution Control Board ("Board") seeking a Site Specific Rule to establish an alternative water quality standard ("WQS") for Nickel from the point of its discharge into the Sangamon River from its Main Sewage Treatment Plant ("Main Plant") to the point of the confluence of the Sangamon River with the South Fork of the Sangamon River near Riverton, Illinois. The purpose of this report is to present the calculations, comparisons, and findings acquired from using the federally approved Biotic Ligand Model ("BLM") to adjust the Nickel WQS such that it considers local conditions found in that segment of the Sangamon River.

Adjustment of the WQS for metals in consideration of the local chemical conditions has frequently been shown to be appropriate at sites across the United States, since WQSs are based on water quality criteria ("WQC") that are defined using a traditional methodology that does not consider many of the factors that are known to affect metal toxicity to aquatic organisms. For example, the WQC for several metals (including Silver ("Ag"), Cadmium ("Cd"), Chromium (III) ("Cr(III)"), Lead ("Pb"), Nickel ("Ni"), and Zinc ("Zn"), as well as Copper ("Cu") prior to development of the BLM) are dependent on the hardness of the local water. The term "hardness" refers to the mineral content of the water and is primarily associated with the combined concentration of Calcium ("Ca") and Magnesium ("Mg"). Hardness is one of several key water quality constituents that have been shown to affect metal bioavailability and toxicity. The United States Environmental Protection Agency's ("US EPA") approach for deriving metals WQC as hardness-dependent relationships has considered how variation in toxic response may differ in areas that naturally have either very hard or very soft water.

However, factors other than hardness have been shown to affect metal bioavailability, and in particular variation in pH, Alkalinity ("Alk"), and the presence of natural organic matter ("NOM") have all been shown to be as important, or even more important, than hardness in determining metal toxicity (Erickson, et al., 1996). These factors may increase or decrease the toxicity of metals. The dependence of metal toxicity on local chemical factors is referred to as the "bioavailability" of the metal to aquatic organisms. Since these bioavailability factors are not considered by WQC approaches that only consider hardness, the WQC may be more or less protective than needed for a specific receiving water. This issue has long been recognized by US EPA and, in response, US EPA has developed procedures for derivation of site specific adjustments to WQC (Carlson, et al. 1984; US EPA, 1992, 1994a). In particular, the Water Effect Ratio ("WER") approach is intended to account for local bioavailability factors that can affect metal toxicity (US EPA, 1994b). The site specific adjustment to a WQC provided by a WER is intended to correct for deficiencies in the WQC derivation process and to reduce the degree to which a WQC is over-protective or under-protective for a given location.

II. BACKGROUND ON NICKEL BLM

Although the WER has been in use for decades, it requires toxicity testing with multiple aquatic organisms in multiple samples. Costs and time required to accommodate WER testing can be significant. As an alternative, the BLM is a computational approach that can simulate the effects of water chemistry on metal toxicity, and on the physiological response of aquatic organisms to metals (Di Toro, et al, 2001; Santore, et al, 2001). The BLM provides information that is similar to the WER, but does so with much less cost and time required. The BLM is a mechanistic approach, not an empirical approach like the hardness equation, and it considers effects from numerous chemical factors such as pH, the presence of NOM, Alkalinity, and major ions (including cations that contribute to hardness). The BLM considers how these factors affect either metal chemistry or organism physiology to determine metal bioavailability (Figure 1).

The BLM has been adopted by US EPA as a replacement for the hardness equation in the WQC for copper (US EPA, 2007). The use of the BLM provides similar benefits as the WER, and for criteria based on the BLM, the use of the WER is no longer required. For metals (such as Nickel) where US EPA has not adopted a BLM-based procedure for replacement of the hardness equation, the BLM can be used in a manner similar to the WER to modify the hardness equation based WQC. Use of the BLM to derive a site specific WQC provides the same level of protection as intended by US EPA guidelines (Stephan, et al, 1985). To the extent that a BLM derived site specific WQC is different from the national ambient WQC, those differences reflect how local factors which are not considered by the hardness-equation may change metal bioavailability and toxicity.

The BLM can be used to determine modifications to chemistry of receiving water using a procedure that is analogous to the WER. The WER compares the toxicity of Nickel or other toxicant in receiving water to that in reference water. The reference water is intended to represent the conditions comparable to those used to develop the toxicity database in which the acute and chronic WQC were developed. The WER is then simply the ratio of the measured toxic endpoint in the receiving water to that in the reference water. If multiple receiving water and reference water samples are used to generate the WER, the WER is determined for each pair of samples, and then an overall WER is usually determined as the geometric mean. The reference water chemistry must meet WER guidelines (US EPA, 1994b), and US EPA has provided synthetic recipes suitable for generating reference water samples with various hardness concentrations. These recipes can be incorporated into the BLM application to predict toxicity endpoints for suitable reference water that can be used in a WER-type analysis.

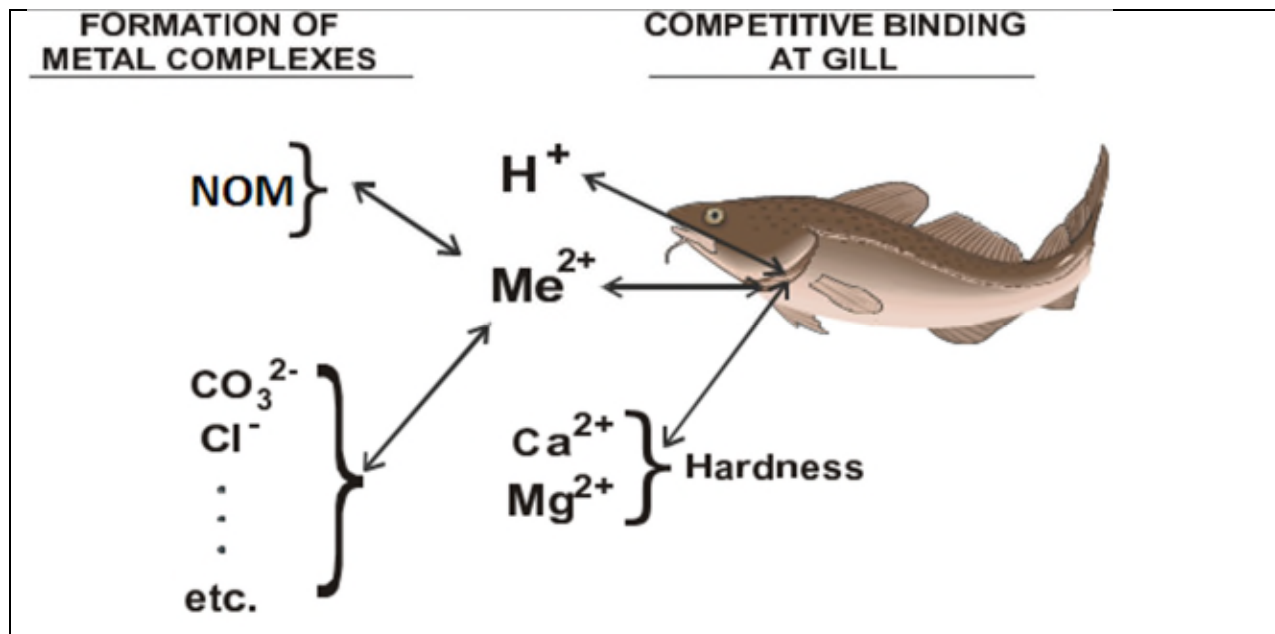


Figure 1. Conceptual model of the chemical and physiological processes represented in the BLM. Water chemistry, including inorganic complexes and binding by NOM, can affect the chemical speciation and reactivity of a metal (i.e., Me^{2+}). The accumulation of metal on biological surfaces, such as gill membranes, is related to the chemical reactivity of the metal as well as other factors such as pH and competitive binding of cations. The BLM is a general framework that has been applied to acute and chronic responses of numerous metals including Aluminum (“Al”), Ag, Cd, Cobalt (“Co”), Cu, Ni, Pb, and Zn.

III. BLM RESULTS WITH MEASURED WATER QUALITY

A. Overall Calibration Results to Fish and Invertebrates

The BLM is a generalized mechanistic approach that has been applied to a number of different metals including Nickel. Development efforts for Nickel focused on explaining available toxicity data for sensitive aquatic invertebrates and fish in a project sponsored by the Water Environment Research Foundation (“WERF”) (WERF, 2003). The project for WERF included a detailed review of the chemical speciation of Nickel in freshwaters, analysis of Nickel accumulation in aquatic organisms, and a summary of important bioavailability factors, including pH, Alkalinity, hardness, and the presence of NOM. The application of the Nickel BLM to aquatic toxicity data was subsequently expanded to provide a comprehensive analysis of all of the acute and chronic toxicity data that have been published to date (see, for example, the many hundreds of individual toxicity tests documented in Table 5 of Santore et al, 2017). This comprehensive review of nickel toxicity literature shows that the major toxicity modifying factors for nickel are NOM (quantified as dissolved organic carbon, or DOC) and hardness. Furthermore, the bioavailability effects that are evident from studies over a range of DOC or hardness values shows a consistent response for diverse organism types over a wide range of conditions (Santore et al, 2017). The consistency of the effects of these important toxicity

modifying factors suggest that a mechanistic framework such as the BLM, should be able to explain and predict the effects of variable water chemistry on nickel toxicity for a variety of aquatic species over a wide range of conditions. The performance of the Nickel BLM was quite good, with excellent agreement between predicted and measured toxicity over a range of several orders of magnitude (Figure 2). Nearly all of the predicted toxicity values are within a factor of two of measured values.

Agreement with a factor of two of a given measured toxicity value has been shown to be about the degree to which replicate measurements agree with a mean value. Replicate toxicity tests used to determine replicate LC50 values for the same organism in the same water frequently does not produce exactly the same result. For example, replicate copper toxicity measurements, expressed as the median lethal concentration to 50% of the population (LC50), made to the same species of fish in water samples from Lake Superior tend to fall in $\pm 2x$ envelope around a central mean (Figure 3; data are from Erickson et al., 1996). If replicate measurements agree with a central mean value no better than $\pm 2x$, then comparison of predicted toxicity values with measured values with a factor of $\pm 2x$ would be the best that could be expected. Hence, predicted values such as those shown in Figure 2 are often shown within a $\pm 2x$ envelope around the line of perfect agreement, and predicted values that fall within this envelope show excellent agreement with measured values.

The strength of the predictive ability of the BLM lies in the mechanistic and generalized nature of the model. Although the model simulates a complex set of chemical reactions and biological accumulation processes, these processes are characterized as generalized reactions based on thermodynamics. The model can therefore predict accumulation in aquatic organisms without recalibration of any of the model parameters that describe chemical speciation, or organism accumulation. Application of the same model and same model parameters are used to predict effects to diverse aquatic organisms including fish and invertebrates. The consistency of this approach is evidence of the mechanistic and generally applicable nature of this analysis. The only parameter that varies from one organism to another is the concentration of accumulated metal associated with toxicity (Santore, et al, 2001). The resulting model is capable of simulating Nickel toxicity to a range of organisms in a wide range of chemical conditions (Figure 2).

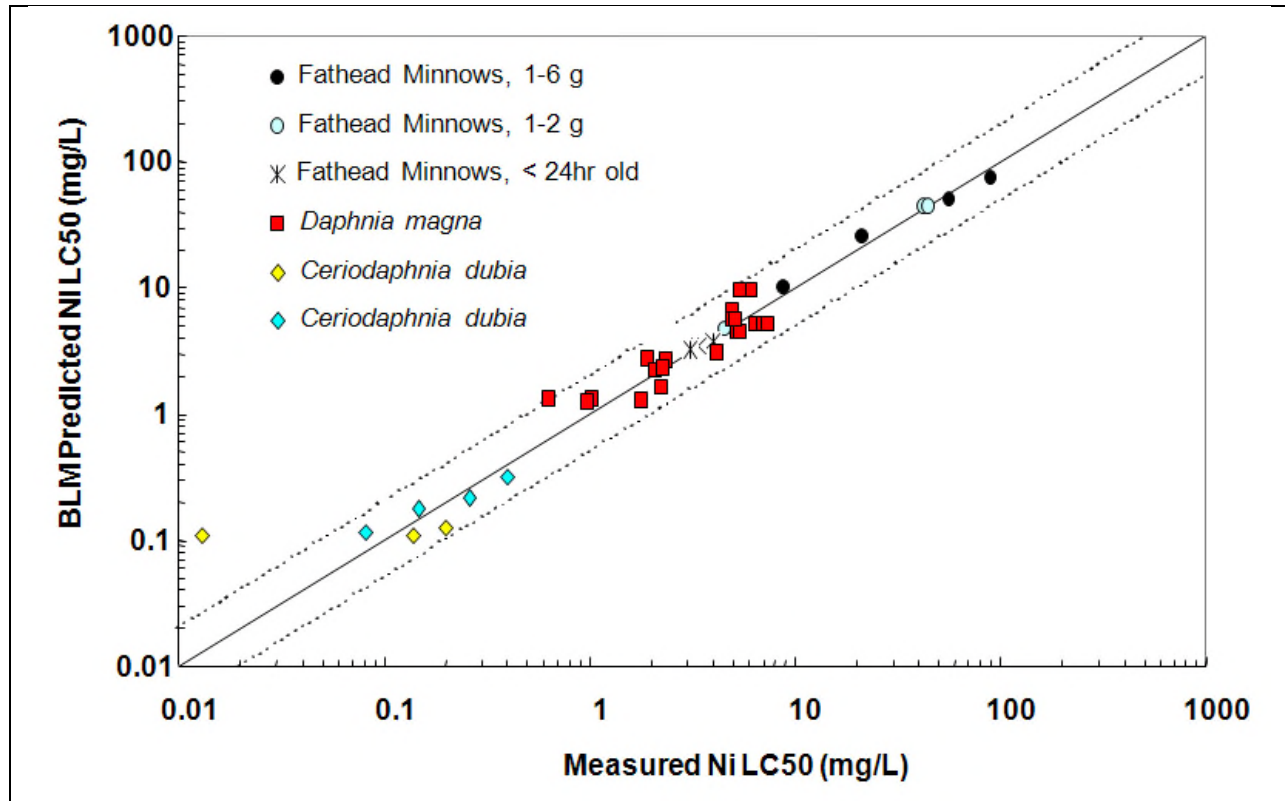


Figure 2. Comparison of the calibrated Nickel BLM to sensitive freshwater aquatic invertebrates and fish. Measured toxicity, as the lethal concentration to 50% of the test organisms, is shown on the horizontal axis. Predicted toxicity is shown on the vertical axis. The diagonal solid black line shows perfect agreement between measured and predicted values, and the dashed black lines show a region of \pm factor of 2x from perfect agreement. The \pm factor of 2x is intended to show agreement between measured and predicted values that comparable to the expected agreement between replicate measurements.

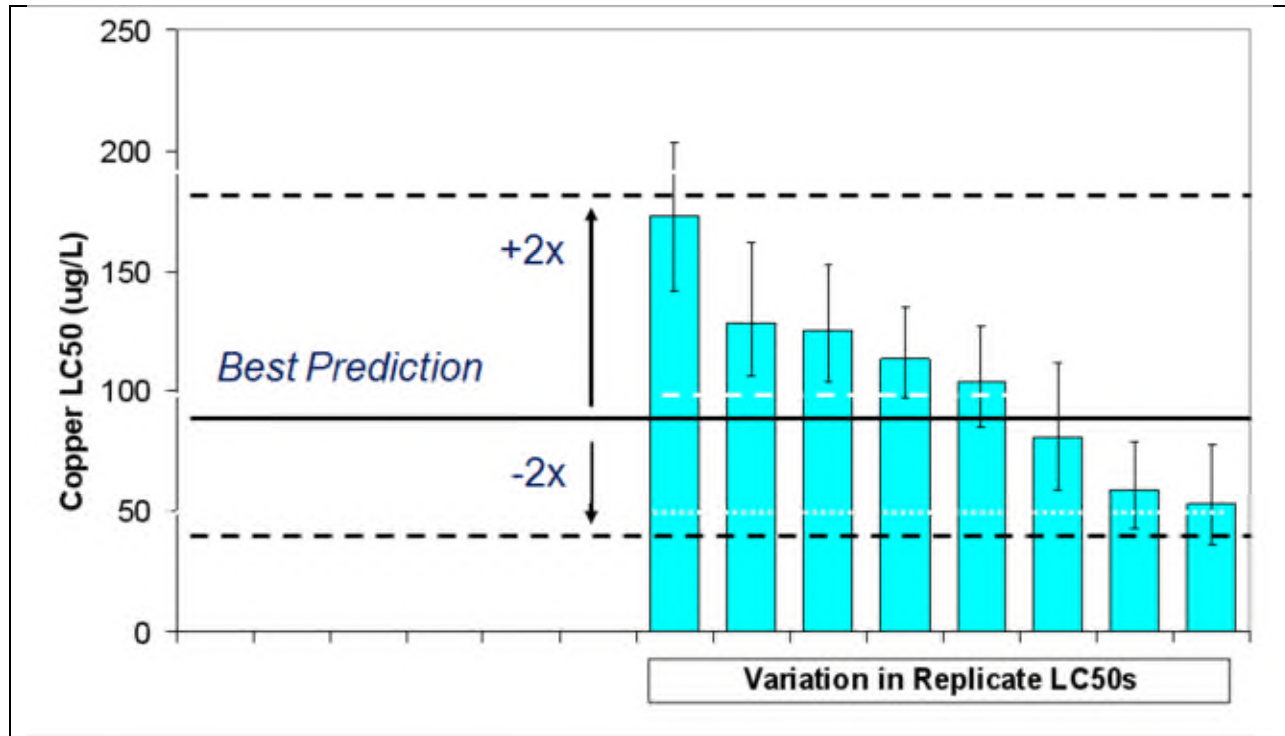


Figure 3. Variation in replicate measurements of LC50 of copper to fathead minnow in Lake Superior water tends to fall in an envelope of plus or minus 2 times the geometric mean value (date from Erickson et al., 1996). The dark solid line labeled “Best Prediction” is shown at the geometric mean of the measured values. The dashed lines correspond to an envelope showing plus or minus a factor of two. Since all of these measured values are from water samples with the same chemistry, the BLM would predict the same LC50 in every case.

IV. CALCULATED WER WITH PREDICTED TOXICITY TO *DAPHNIA MAGNA*

As discussed in Section II of this report, the BLM for Nickel can be used to calculate a site specific WQC by using the model to calculate a WER for the receiving water downstream of the Main Plant. Samples were collected at two locations downstream of the Main Plant discharge, and chemical analyses for BLM input parameters were measured on these samples. Similar analyses were made on samples taken from the Main Plant effluent, although these were not used in the WER analysis. Measured chemical parameters used as input parameters to the Nickel BLM are shown in Table 1. In addition to the measured parameters in the special study samples listed in Table 1, the BLM was also used to estimate a WER based on average chemistry. An average value was calculated for all parameters measured in the RD at Rock Springs, and RD at Lincoln samples except for DOC. The average DOC was based on an expanded list of monitoring stations that included the RD at Rock Springs, and RD at Lincoln samples, but also included samples from other downstream locations. These same DOC samples were used in a separate analysis that focuses only on the influence of DOC on Nickel toxicity. The average value was used in the BLM analysis to provide a consistent set of conditions to compare the results of these two methods.

The BLM for Nickel was run with these input data to determine Nickel toxicity to *D. magna*, which is a sensitive invertebrate recommended for use in WER testing for Nickel (USEPA, 1994b, Appendix I). For calculation of WER values, the predicted toxicity in these site waters was compared with toxicity in a reference water sample. According to the WER guidance document, suitable reference water must have a hardness concentration close to, but not in excess of, the measured hardness in the site water (US EPA, 1994b). The US EPA's recipe for "very hard" water with a hardness of 317 mg/L as Calcium Carbonate ("CaCO₃"), compared with hardness in the site water of 347, would be a suitable choice for use as a reference water for WER testing at the site. Calculated LC50 values for site and reference water are shown in Table 2.

Table 1. Input chemistry used for BLM analyses. For site waters, Sangamon River samples collected at the Rock Springs Trail bridge approximately one-half mile downstream (RD at Rock Springs) and at the South Lincoln Memorial Parkway bridge approximately six miles downstream (RD at Lincoln) were used to characterize the chemistry of the receiving water downstream of the plant. The presence of NOM was characterized by the dissolved organic carbon (“DOC”) concentration. For calculation of WER, the US EPA’s ”very hard” water recipe was used as a reference sample. Variation of an assumed DOC in the reference water sample from 0.5 to 2.0 mg C/L was included in the BLM analysis.

Sample Description		Temp °C	pH	DOC mg C/L	Ca	Mg	Na	K	SO4 mg / L	Cl	Alk
RD at Rock Springs	8/26/2010	23	8.00	12	56	53	396	86	298	446	365
RD at Rock Springs	9/9/2010	21	8.09	10	64	48	286	53	214	304	341
RD at Lincoln	8/26/2010	25	8.00	10	58	46	296	60	225	450	321
RD at Lincoln	9/9/2010	21	8.10	7.9	65	43	192	35	146	202	315
Final Effluent	8/26/2010	30	8.09	13	56	62	504	112	374	558	400
Final Effluent	9/9/2010	28	7.90	14	62	62	474	91	328	477	399
Average chemistry		24.25	8.05	8.33	61	48	293	58	221	351	336
US EPA Very Hard	DOC=0.5	20	8.20	0.5	47	48	105	8	304	8	229
US EPA Very Hard	DOC=1.0	20	8.20	1	47	48	105	8	304	8	229
US EPA Very Hard	DOC=2.0	20	8.20	2	47	48	105	8	304	8	229

Table 2. Predicted toxicity to *D. magna* by the Nickel BLM in site and reference water samples used in WER analysis. For calculation of WER values, the average LC50 determined in site water was divided by the average LC50 in the reference water. The US EPA's "very hard" recipe for synthetic water was chosen as the reference water due to the good correspondence between the hardness in this recipe and at the site.

Sample Description		Ni LC50 mg/L	Average Ni LC50 mg/L	Average WER
RD at Rock Springs	8/26/2010	32.38	28.89	2.92
RD at Rock Springs	9/9/2010	25.61		
RD at Lincoln	8/26/2010	25.55	22.84	2.31
RD at Lincoln	9/9/2010	20.13		
Final Effluent	8/26/2010	44.52	43.78	4.42
Final Effluent	9/9/2010	43.04		
Average chemistry		26.01	26.01	2.63
US EPA Very Hard	DOC=0.5	9.82	9.90	
US EPA Very Hard	DOC=1.0	9.88		
US EPA Very Hard	DOC=2.0	10.00		

Site water was characterized by performing two separate sampling events at both Rock Springs B and Lincoln Homestead. The BLM calculated LC50 values to *D. magna* in site-waters downstream of the Main Plant ranged from 22.84 mg/L to 28.89 mg/L (Table 2). For comparison, the calculated LC50 for reference water based on the US EPA's "very hard" water recipe was 9.9 mg/L. The WER values for each sampling location, calculated by dividing site water LC50 by the reference water LC50, correspond to 2.31 and 2.92 for Rock Springs B and Lincoln Homestead. Since these values are similar, an overall WER for the site can be determined by averaging to obtain an overall WER for the site of 2.62.

Another way to derive an average WER for the site is by applying the BLM to the average chemistry shown in Table 1. The DOC value for this average chemistry considers many more samples, and is therefore a better overall estimate of the average DOC in downstream receiving waters. The WER that results from using the BLM with average chemistry is 2.63, which is nearly identical to the result obtained from the special study samples. Since this value incorporates more of the downstream monitoring data, it will be used as the overall result from the BLM WER analysis. However, there is very good consistency between this value and the other methods that were evaluated to derive an average WER.

Predicted toxicity in the Final Effluent and the resulting WER value is also shown for comparison in Table 2, but these values were not averaged into the overall WER for the site. The predicted average LC50 in effluent samples was 43.78 mg/L, which is considerably higher

than in downstream receiving water samples. The chemistry for the effluent shown in Table 1 indicates that effluent samples had higher concentrations of cations, such as Ca, Mg, and Sodium (“Na”), as well as a higher concentration of NOM (measured as DOC). All of these factors would tend to further mitigate against Nickel toxicity to aquatic organisms, which is why the predicted LC50 in effluent samples is higher. As a result, Nickel toxicity would be lower in any areas that are poorly mixed downstream of the discharge, and the resulting WER would be protective for these areas as well.

V. SENSITIVITY TO VARIATION IN WATER CHEMISTRY

Since relatively few samples were used in the BLM analysis summarized in Tables 1 and 2, an additional analysis was conducted to see what effect natural variation in downstream water chemistry would have on the predicted toxicity. Additional monitoring data were used to characterize variation in measured chemistry corresponding to BLM input parameters. Monitoring data describing the variability in downstream chemistry was collected by the District, and combined with monitoring data for the Sangamon River collected by Eastern Illinois University. Samples collected for these monitoring studies were obtained at a number of different stations downstream of the Main Plant, including Lincoln, Rock Springs, and Wyckles Bridge, as well as unnamed stations 100 yards and 600 yards downstream. Variability in measured chemistry in the pooled data from these sampling stations includes both spatial and temporal variation. From these available data, the 10th, 25th, 75th, and 90th percentiles were estimated for key water quality parameters that are known to affect Nickel bioavailability, including pH, DOC, Ca, Mg, Na, and Alkalinity (Table 3). A set of base case conditions was established as the median value for all parameters. Variation in Potassium (“K”), Sulfate (“SO₄”), and Chlorine (“Cl”) was not considered since these parameters are not important in determining the bioavailability of nickel.

Table 3. Variation in water quality parameters that affect Nickel bioavailability was characterized as the 10th, 25th, 75th, and 90th percentile estimated from a dataset of pooled measurements are stations downstream of the Decatur Plant. The values for the base case were based on median values from the same dataset.

Test	Temp. C	pH SU	DOC mg/L	Ca mg/L	Mg mg/L	Na mg/L	K mg/L	SO ₄ mg/L	Cl mg/L	Alk mg/L
<i>base</i>	17.78	8.14	9.99	37.1	44.7	244.00	47.4	185.5	326.0	279.00
<i>10th</i>		7.96	3.7	25.4	15.8	202.4				151.2
<i>25th</i>		8.03	6.4	30.5	20.1	218.0				223.0
<i>75th</i>		8.29	14.8	73.6	64.9	270.0				321.0
<i>90th</i>		8.47	28.2	84.3	74.3	285.6				451.2

These data correspond to pre-existing monitoring studies and were not specifically collected for BLM analyses. Consequently, not all BLM parameters were measured in every sample. For the purposes of conducting a sensitivity analyses, these data are suitable for showing the expected downstream variation in individual parameters. Available data are plotted in Figure 4 for river samples and Figure 5 for effluent samples.

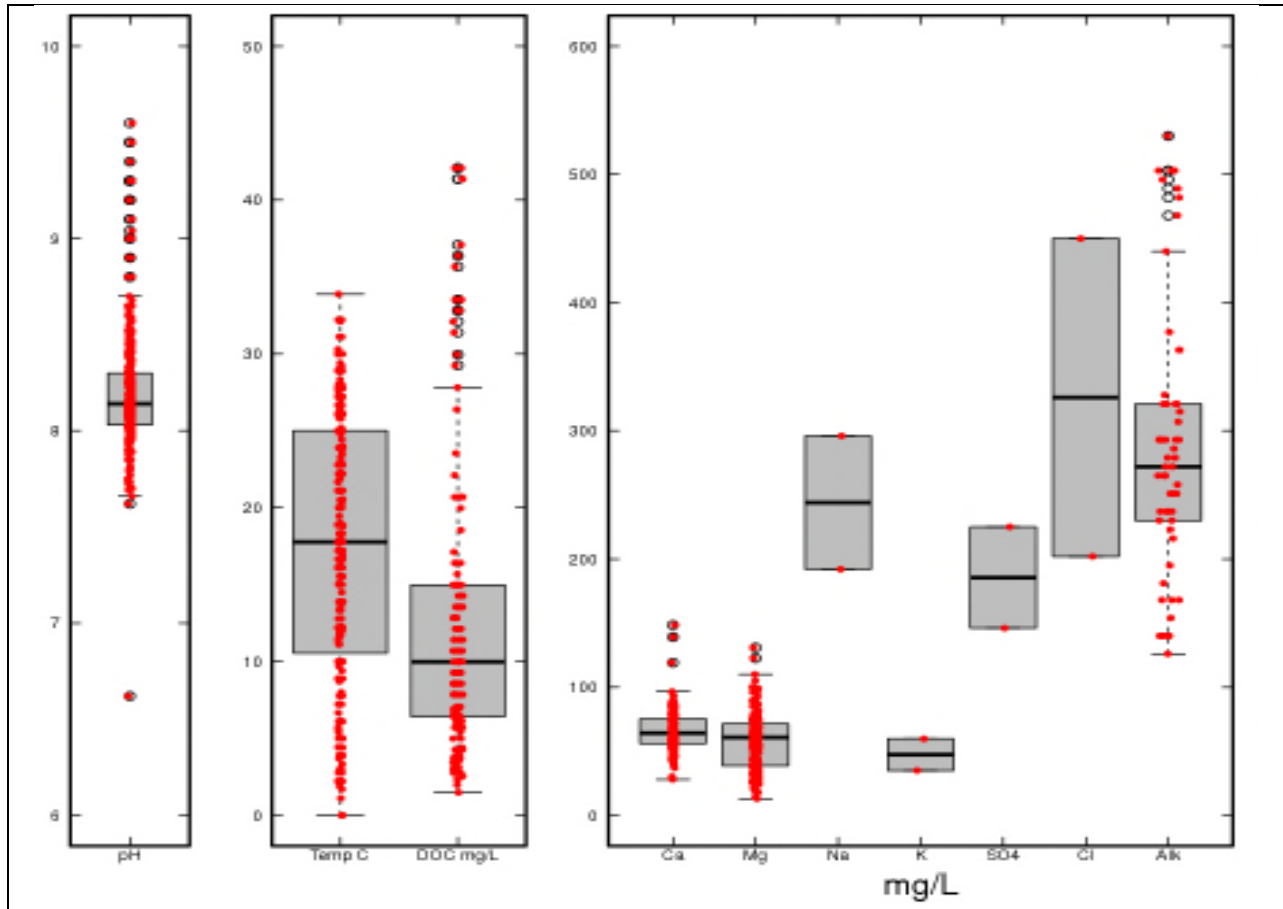


Figure 4. Box and whisker plots showing distributions of measured values for BLM input parameters in river samples. Average values are shown by a black line in the middle of each box and represent mean (pH, Temp, DOC) or geometric mean (Ca, Mg, Na, K, SO₄, Cl, Alk) depending on whether parameters are expected to be normally or log-normally distributed. For each box, the lower edge of the box represents the 25th percentile, the upper edge of the box represents the 75th percentile, and whiskers extend to minimum and maximum values exclusive of extreme values. Individual observations are shown as small red circles.

The distribution of values for each parameter are shown as box and whisker diagrams constructed so that the lower edge of the box represents the 25th percentile, the upper edge of the box represents the 75th percentile, and whiskers extend to minimum and maximum values exclusive of extreme values. Median values are shown as the solid black horizontal line in the middle of each box. Individual observations are shown as small red circles. For river samples,

there was a large amount of data characterizing pH, Alkalinity, DOC, and hardness cations (Ca and Mg), which are the bioavailability factors that are the most important for determining Nickel toxicity (Figure 4). There were relatively few samples characterizing K, and SO₄, but these parameters have little to no effect on Nickel toxicity and do not need to be considered in the uncertainty analysis. There were also relatively few observations for Na, but the estimated variation in Na concentrations is similar to that seen for Ca and Mg and is, therefore, likely to be a reasonable characterization of variation in downstream chemistry. For effluent samples there were many more measurements of anion concentrations (Figure 5), and in comparison with river samples the effluents tended to have lower pH values and higher DOC and ion concentrations. The variation in pH, DOC, and ion concentrations show in these two datasets are consistent with the values seen in detailed sample analyses reported in Table 1.

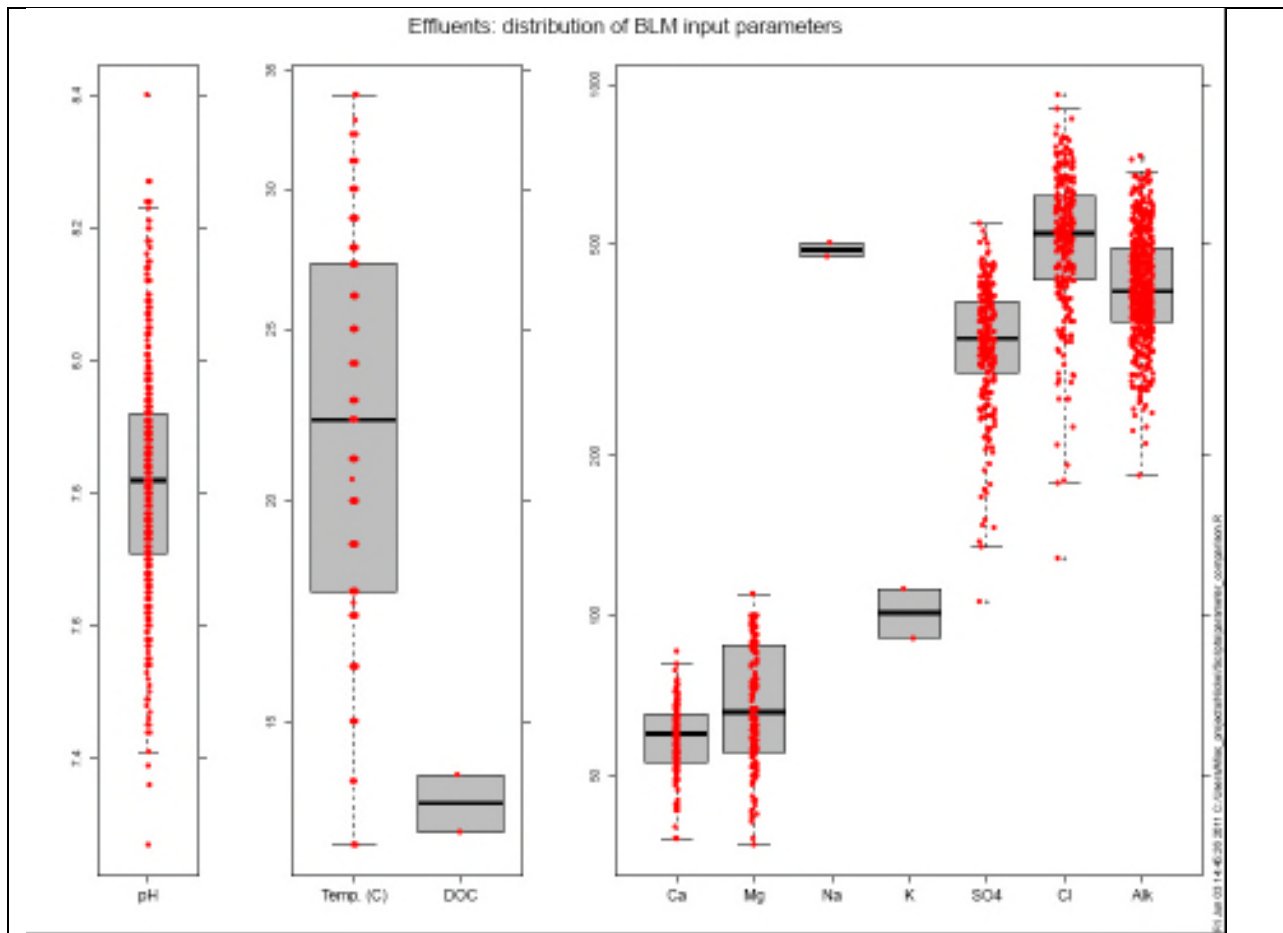


Figure 5. Box and whisker plots showing distributions of measured values for BLM input parameters in effluent samples. Average values are shown by a black line in the middle of each box and represent mean (pH, Temp, DOC) or geometric mean (Ca, Mg, Na, K, SO₄, Cl, Alk) depending on whether parameters are expected to be normally or log-normally distributed. For each box, the lower edge of the box represents the 25th percentile, the upper edge of the box represents the 75th percentile, and whiskers extend to minimum and maximum values exclusive of extreme values. Individual observations are shown as small red circles.

Variability in BLM input parameters was used in a sensitivity analysis to determine the degree to which predicted toxicity may be expected to change over time. The model was first run for a base case that used median values for all parameters shown in Figure 4 and Table 3.

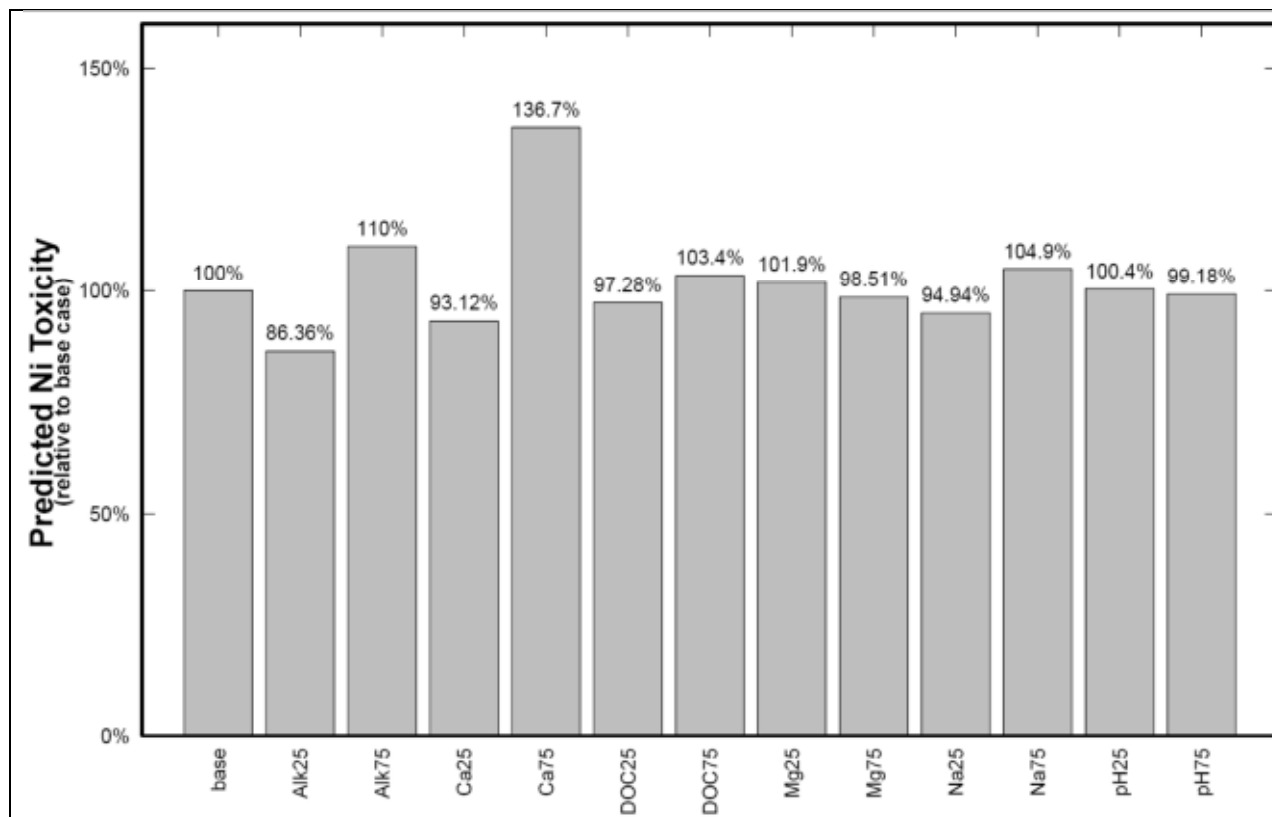


Figure 6. Sensitivity analysis of varying input parameters to the BLM on predicted Nickel toxicity in river samples. For the base case, average values for all parameters shown in Figure 4 were used. A series of additional simulations were then run to see the effect of variation in individual parameter values on the base case. For each additional simulation, the base case was modified with either the 25th or the 75th percentile value of an input variable, while all other parameters were held at the values used for the base case. For example, the result labeled “Alk25” uses the 25th percentile for Alkalinity (shown in Figure 4), and the result “Alk75” uses the 75th percentile for Alkalinity. Sensitivity results for other parameters are labeled with a similar labeling scheme.

For each BLM parameter, two additional runs were then performed by substituting either the 25% or 75% value from the box and whisker plots in Figure 4 for the average value, while keeping all other parameters constant, at their respective average. The resulting sensitivity analyses are shown in Figure 6 for river samples considering variation at the 25th and 75th percentile, and Figure 7 considering variation at the 10th and 90th percentiles.

Variation in input values at the 25th and 75th percentiles for river water samples had relatively little effect on the predicted Nickel toxicity, with the largest effects resulting from changes in Alkalinity and Calcium concentrations. A similar pattern was observed when variation at the 10th and 90th percentiles were considered (Figure 7). Even at these extreme values, the expected variation in predicted Nickel toxicity ranges from about 70 to 150 percent of the base case value. Guidance for derivation of site-specific adjustments to WQC based on the WER procedure allow simple geometric means of individual WER values when the range in values is within a factor of 5. Since the effects of the variation in river water chemistry on Nickel toxicity will be well within those limits, this uncertainty analysis supports the conclusion that average conditions from a relatively small number of samples should provide an acceptable characterization for deriving a site-specific Nickel criterion. As a result of these sensitivity analyses, the calculated WER for the site is not expected to significantly change as a result of variability in water quality within ranges comparable to these existing monitoring datasets.

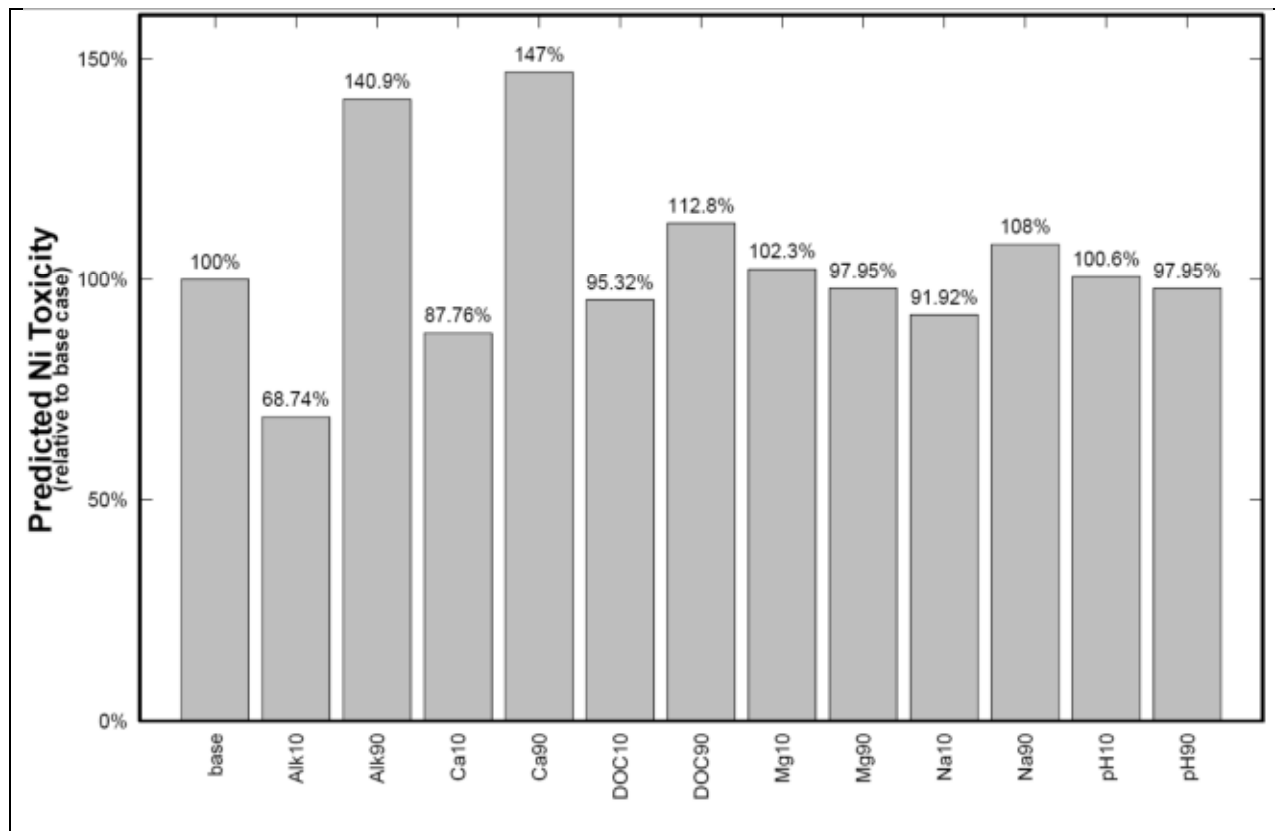


Figure 7. Sensitivity analysis of varying input parameters to the BLM on predicted Nickel toxicity in river samples. For the base case, average values for all parameters shown in Figure 4 were used. A series of additional simulations were then run to see the effect of variation in individual parameter values on the base case. For each additional simulation, the base case was modified with either the 10th or the 90th percentile value of an input variable, while all other parameters were held at the values used for the base case. For example, the result labeled “Alk10” uses the 10th percentile for Alkalinity (shown in Figure 4), and the result “Alk90” uses the 90th percentile for Alkalinity. Sensitivity results for other parameters are labeled with a similar labeling scheme.

For effluent samples (Figure 8), variation in Alkalinity had the largest effect on predicted Nickel toxicity. However, the resulting variation in predicted LC50 values was small, corresponding to a little more than 10% change relative to the base case. Variation in effluent characteristics is only presented for comparison to that seen for river water, since it is only the downstream river water that will be used to estimate the site-specific Nickel adjustment.

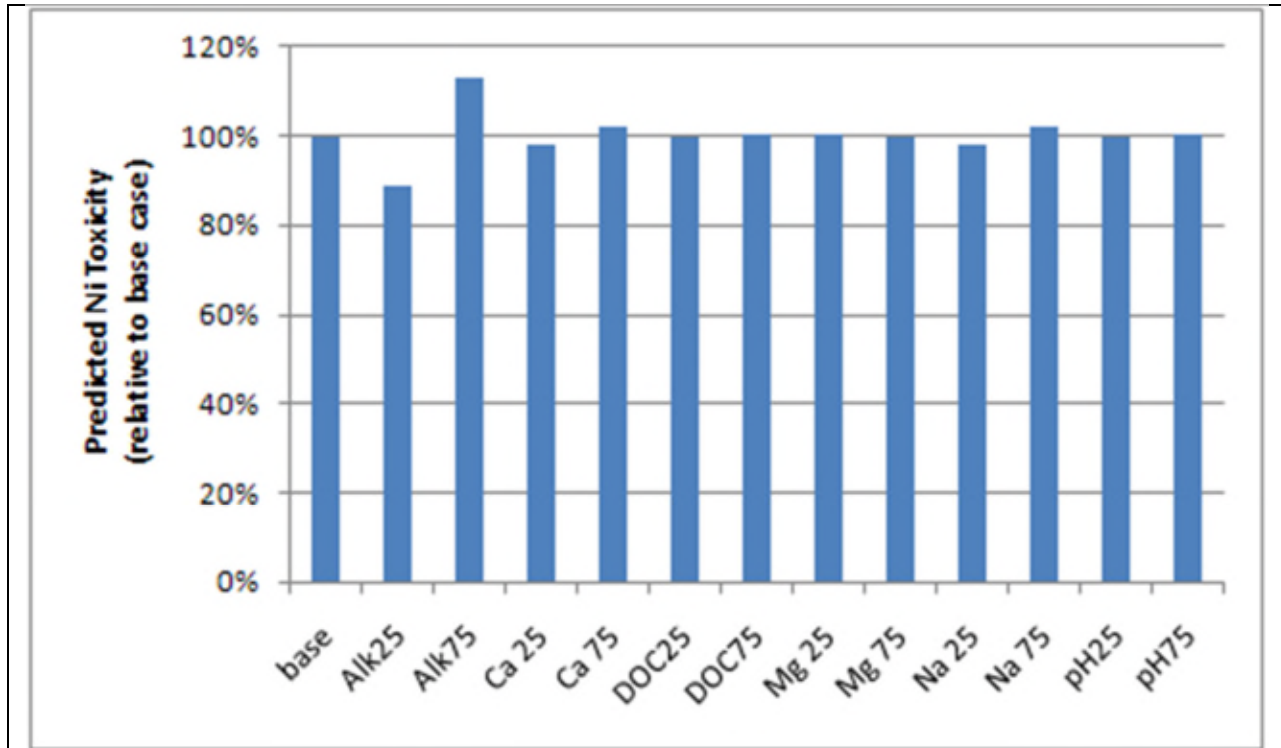


Figure 8. Sensitivity analysis of varying input parameters to the BLM on predicted Nickel toxicity in effluent samples. For the base case, average values for all parameters shown in Figure 5 were used. A series of additional simulations were then run to see the effect of variation in individual parameter values on the base case. For each additional simulation, the base case was modified with either the 25th or the 75th percentile value of an input variable, while all other parameters were held at the values used for the base case. For example, the result labeled “Alk25” uses the 25th percentile for Alkalinity (shown in Figure 5), and the result “Alk75” uses the 75th percentile for Alkalinity. Sensitivity results for other parameters are labeled with a similar labeling scheme.

VI. PREDICTED ESTIMATE OF WQC

With the WER calculated in Section IV, site specific acute and chronic WQC can be calculated for the site. The site specific criteria are calculated as the state standards times the WER. For the receiving water downstream of the site, the average WER is 2.63, resulting in a site specific acute WQC of 638.8 µg/L and a site specific chronic WQC of 38.7 µg/L when applied to IL state standards using the critical hardness value for the Sangamon that was assigned by Illinois EPA (Table 4).

Table 4. Summary of values for corresponding acute^a and chronic^b standards, WER, and resulting site specific standards in receiving water samples downstream of the plant. The Illinois acute and chronic standards for Nickel are based on hardness dependent equations. The average for samples collected in this study are based on the average measured hardness in samples collected for the BLM analysis. Also shown are the site-specific values based on a hardness of 359, which was assigned by the State of Illinois for this site.

Sample Date	Sample Location	Hardness	Nickel Acute ^a Standard	Nickel Chronic ^b Standard	Water Effect Ratio	Site Specific Acute Standard	Site Specific Chronic Standard
		mg/L as CaCO ₃	µg/L	µg/L		µg/L	µg/L
8/26	RD at Rock Springs	357	241.7	14.7	2.63	635.7	38.7
9/9	RD at Rock Springs	360	243.5	14.8		640.4	38.9
8/26	RD at Lincoln	332	227.3	13.8	2.63	597.8	36.3
9/9	RD at Lincoln	341	232.5	14.1		611.5	37.1
Average (this study)		347.5	236.2	14.3	2.63	621.3	37.7
Site specific values using Illinois EPA-assigned critical hardness		359	242.9	14.7	2.63	638.8	38.7

Notes:

^a: Nickel Acute Standard = $\exp[A+B*\ln(H)] * 0.998$ (where A=0.5173; B=0.846)

^b: Nickel Chronic Standard = $\exp[A+B*\ln(H)] * 0.997$ (where A= -2.286; B=0.846)

VII. CONCLUSIONS

Water quality factors such as pH, Alkalinity, ion content, and the presence NOM have been shown to affect metal toxicity. However, the WQC for many metals consider only hardness, making them potentially over-protective or under-protective for many site waters. The BLM is a mechanistic framework suitable for a number of metals, including Nickel, which allows for the consideration of many additional water quality factors. The BLM was adopted by US EPA for the WQC for copper (US EPA, 2007). For metals that do not yet have an approved WQC approach, the BLM can be used to calculate a WER adjustment to derive site specific acute and chronic criteria. Application of the Nickel BLM to calculate Nickel toxicity in samples taken from the Sangamon River downstream of the District's Main Plant compared to a reference water results in a calculated average WER of 2.63. This WER results in a site specific acute criterion of 621.3 $\mu\text{g/L}$ and a site specific chronic criterion of 37.7 $\mu\text{g/L}$ at a hardness equal to 347.5 mg/L. Utilizing the Illinois EPA-assigned hardness of 359 mg/L, the WER results in a corresponding acute criterion of 638.8 $\mu\text{g/L}$ and a site specific chronic criterion of 38.7 $\mu\text{g/L}$.

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Exhibit 14

(Redlined Version)

Prepared for Proposed Site Specific Rule for Sanitary District of Decatur
From 35 Ill. Adm. Code Section 302.208(e)

ESTIMATE OF THE BLM ADJUSTMENT TO THE NICKEL CRITERION FOR THE SANITARY DISTRICT OF DECATUR, ILLINOIS

Prepared by
Robert Santore

HDR | HydroQual

[January 16, 2014](#)

[April 10, 2018](#)

I. INTRODUCTION

This report was prepared in support of the Sanitary District of Decatur's ("District") Petition to the Illinois Pollution Control Board ("Board") seeking a Site Specific Rule to establish an alternative water quality standard ("WQS") for Nickel from the point of its discharge into the Sangamon River from its Main Sewage Treatment Plant ("Main Plant") to the point of the confluence of the Sangamon River with the South Fork of the Sangamon River near Riverton, Illinois. The purpose of this report is to present the calculations, comparisons, and findings acquired from using the federally approved Biotic Ligand Model ("BLM") to adjust the Nickel WQS such that it considers local conditions found in that segment of the Sangamon River.

Adjustment of the WQS for metals in consideration of the local chemical conditions has frequently been shown to be appropriate at sites across the United States, since WQSs are based on water quality criteria ("WQC") that are defined using a traditional methodology that does not consider many of the factors that are known to affect metal toxicity to aquatic organisms. For example, the WQC for several metals (including Silver ("Ag"), Cadmium ("Cd"), Chromium (III) ("Cr(III)"), Lead ("Pb"), Nickel ("Ni"), and Zinc ("Zn"), as well as Copper ("Cu") prior to development of the BLM) are dependent on the hardness of the local water. The term "hardness" refers to the mineral content of the water and is primarily associated with the combined concentration of Calcium ("Ca") and Magnesium ("Mg"). Hardness is one of several key water quality constituents that have been shown to affect metal bioavailability and toxicity. The United States Environmental Protection Agency's ("US EPA") approach for deriving metals WQC as hardness-dependent relationships has considered how variation in toxic response may differ in areas that naturally have either very hard or very soft water.

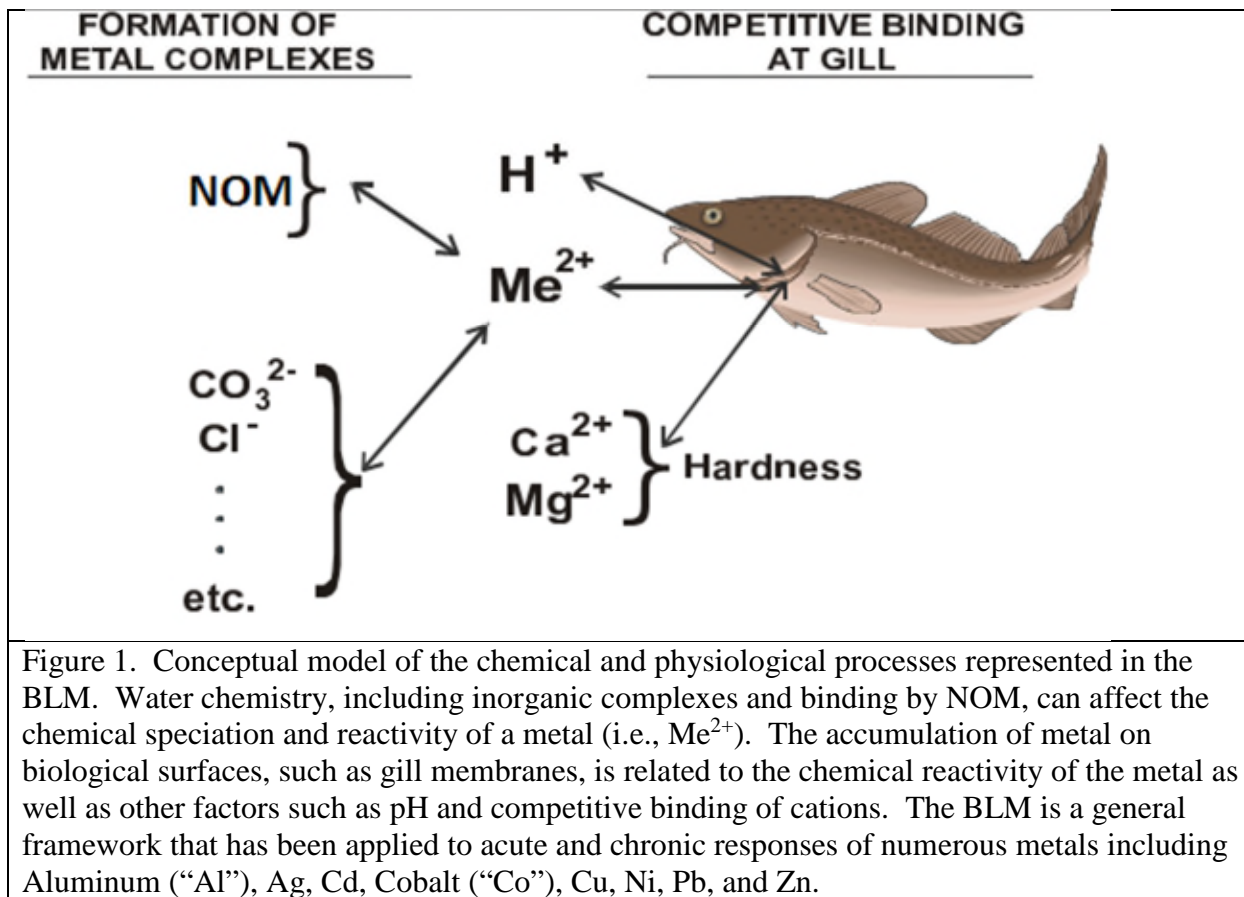
However, factors other than hardness have been shown to affect metal bioavailability, and in particular variation in pH, Alkalinity ("Alk"), and the presence of natural organic matter ("NOM") have all been shown to be as important, or even more important, than hardness in determining metal toxicity (Erickson, et al., 1996). These factors may increase or decrease the toxicity of metals. The dependence of metal toxicity on local chemical factors is referred to as the "bioavailability" of the metal to aquatic organisms. Since these bioavailability factors are not considered by WQC approaches that only consider hardness, the WQC may be more or less protective than needed for a specific receiving water. This issue has long been recognized by US EPA and, in response, US EPA has developed procedures for derivation of site specific adjustments to WQC (Carlson, et al. 1984; US EPA, 1992, 1994a). In particular, the Water Effect Ratio ("WER") approach is intended to account for local bioavailability factors that can affect metal toxicity (US EPA, 1994b). The site specific adjustment to a WQC provided by a WER is intended to correct for deficiencies in the WQC derivation process and to reduce the degree to which a WQC is over-protective or under-protective for a given location.

II. BACKGROUND ON NICKEL BLM

Although the WER has been in use for decades, it requires toxicity testing with multiple aquatic organisms in multiple samples. Costs and time required to accommodate WER testing can be significant. As an alternative, the BLM is a computational approach that can simulate the effects of water chemistry on metal toxicity, and on the physiological response of aquatic organisms to metals (Di Toro, et al, 2001; Santore, et al, 2001). The BLM provides information that is similar to the WER, but does so with much less cost and time required. The BLM is a mechanistic approach, not an empirical approach like the hardness equation, and it considers effects from numerous chemical factors such as pH, the presence of NOM, Alkalinity, and major ions (including cations that contribute to hardness). The BLM considers how these factors affect either metal chemistry or organism physiology to determine metal bioavailability (Figure 1).

The BLM has been adopted by US EPA as a replacement for the hardness equation in the ~~most recently updated metals criteria~~ [WQC for copper](#) (US EPA, 2007). The use of the BLM provides similar benefits as the WER, and for criteria based on the BLM, the use of the WER is no longer required. For metals (such as Nickel) where US EPA has not adopted a BLM-based procedure for replacement of the hardness equation, the BLM can be used in a manner similar to the WER to modify the hardness equation based WQC. Use of the BLM to derive a site specific WQC provides the same level of protection as intended by US EPA guidelines (Stephan, et al, 1985). To the extent that a BLM derived site specific WQC is different from the national ambient WQC, those differences reflect how local factors which are not considered by the hardness-equation may change metal bioavailability and toxicity.

The BLM can be used to determine modifications to chemistry of receiving water using a procedure that is analogous to the WER. The WER compares the toxicity of Nickel or other toxicant in receiving water to that in reference water. The reference water is intended to represent the conditions comparable to those used to develop the toxicity database in which the acute and chronic WQC were developed. The WER is then simply the ratio of the measured toxic endpoint in the receiving water to that in the reference water. If multiple receiving water and reference water samples are used to generate the WER, the WER is determined for each pair of samples, and then an overall WER is usually determined as the geometric mean. The reference water chemistry must meet WER guidelines (US EPA, 1994b), and US EPA has provided synthetic recipes suitable for generating reference water samples with various hardness concentrations. These recipes can be incorporated into the BLM application to predict toxicity endpoints for suitable reference water that can be used in a WER-type analysis.



III. BLM RESULTS WITH MEASURED WATER QUALITY

A. Overall Calibration Results to Fish and Invertebrates

The BLM is a generalized mechanistic approach that has been applied to a number of different metals including Nickel. Development efforts for Nickel focused on explaining available toxicity data for sensitive aquatic invertebrates and fish in a project sponsored by the Water Environment Research Foundation (“WERF”) (WERF, 2003). The project for WERF included a detailed review of the chemical speciation of Nickel in freshwaters, analysis of Nickel accumulation in aquatic organisms, and a summary of important bioavailability factors, including pH, Alkalinity, hardness, and the presence of NOM. [The application of the Nickel BLM to aquatic toxicity data was subsequently expanded to provide a comprehensive analysis of all of the acute and chronic toxicity data that have been published to date \(see, for example, the many hundreds of individual toxicity tests documented in Table 5 of Santore et al, 2017\). This comprehensive review of nickel toxicity literature shows that the major toxicity modifying factors for nickel are NOM \(quantified as dissolved organic carbon, or DOC\) and hardness. Furthermore, the bioavailability effects that are evident from studies over a range of DOC or hardness values shows a consistent response for diverse organism types over a wide range of conditions \(Santore et al, 2017\). The consistency of the effects of these important toxicity](#)

[modifying factors suggest that a mechanistic framework such as the BLM, should be able to explain and predict the effects of variable water chemistry on nickel toxicity for a variety of aquatic species over a wide range of conditions.](#) The performance of the Nickel BLM was quite good, with excellent agreement between predicted and measured toxicity over a range of several orders of magnitude (Figure 2). Nearly all of the predicted toxicity values are within a factor of two of measured values.

Agreement with a factor of two of a given measured toxicity value has been shown to be about the degree to which replicate measurements agree with a mean value. Replicate toxicity tests used to determine replicate LC50 values for the same organism in the same water frequently does not produce exactly the same result. For example, replicate copper toxicity measurements, expressed as the median lethal concentration to 50% of the population (LC50), made to the same species of fish in water samples from Lake Superior tend to fall in $\pm 2x$ envelope around a central mean (Figure 3; data are from Erickson et al., 1996). If replicate measurements agree with a central mean value no better than $\pm 2x$, then comparison of predicted toxicity values with measured values with a factor of $\pm 2x$ would be the best that could be expected. Hence, predicted values such as those shown in Figure 2 are often shown within a $\pm 2x$ envelope around the line of perfect agreement, and predicted values that fall within this envelope show excellent agreement with measured values.

The strength of the predictive ability of the BLM lies in the mechanistic and generalized nature of the model. Although the model simulates a complex set of chemical reactions and biological accumulation processes, these processes are characterized as generalized reactions based on thermodynamics. The model can therefore predict accumulation in aquatic organisms without recalibration of any of the model parameters that describe chemical speciation, or organism accumulation. Application of the same model and same model parameters are used to predict effects to diverse aquatic organisms including fish and invertebrates. The consistency of this approach is evidence of the mechanistic and generally applicable nature of this analysis. The only parameter that varies from one organism to another is the concentration of accumulated metal associated with toxicity (Santore, et al, 2001). The resulting model is capable of simulating Nickel toxicity to a range of organisms in a wide range of chemical conditions (Figure 2).

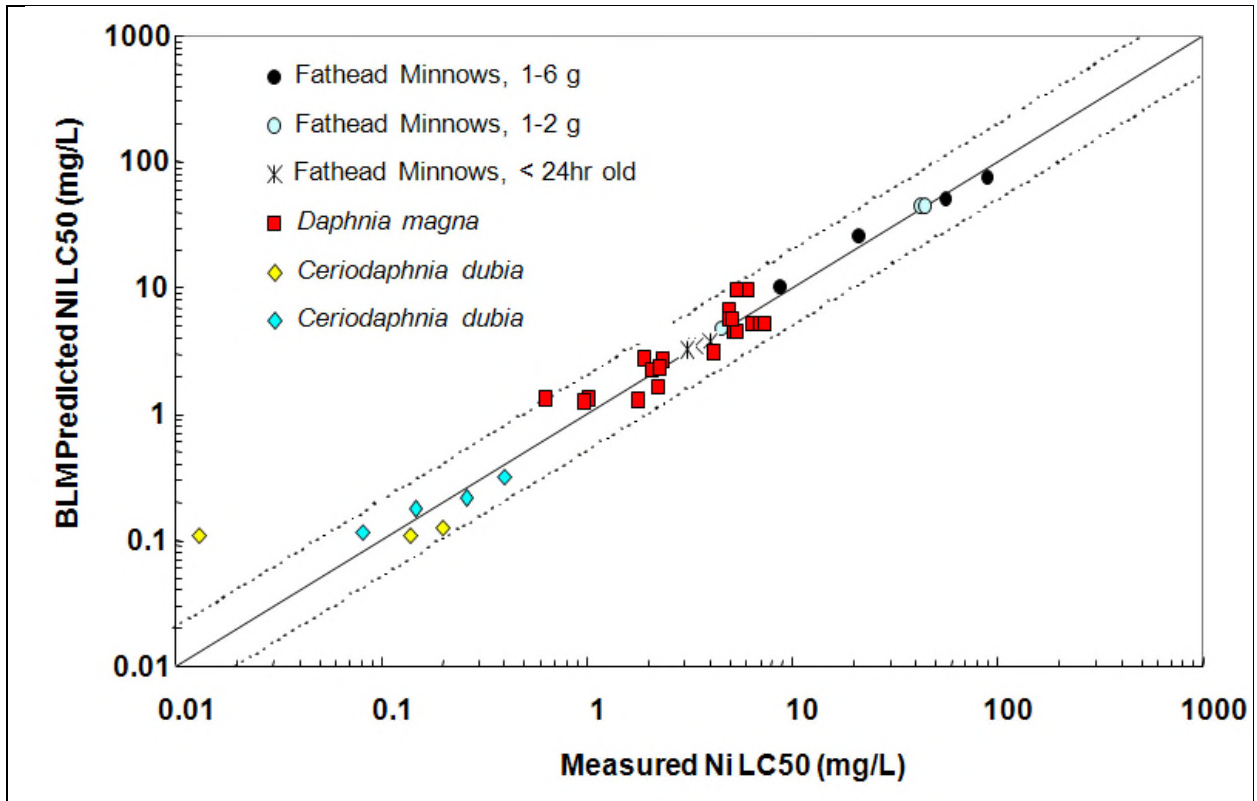


Figure 2. Comparison of the calibrated Nickel BLM to sensitive freshwater aquatic invertebrates and fish. Measured toxicity, as the lethal concentration to 50% of the test organisms, is shown on the horizontal axis. Predicted toxicity is shown on the vertical axis. The diagonal solid black line shows perfect agreement between measured and predicted values, and the dashed black lines show a region of \pm factor of 2x from perfect agreement. The \pm factor of 2x is intended to show agreement between measured and predicted values that comparable to the expected agreement between replicate measurements.

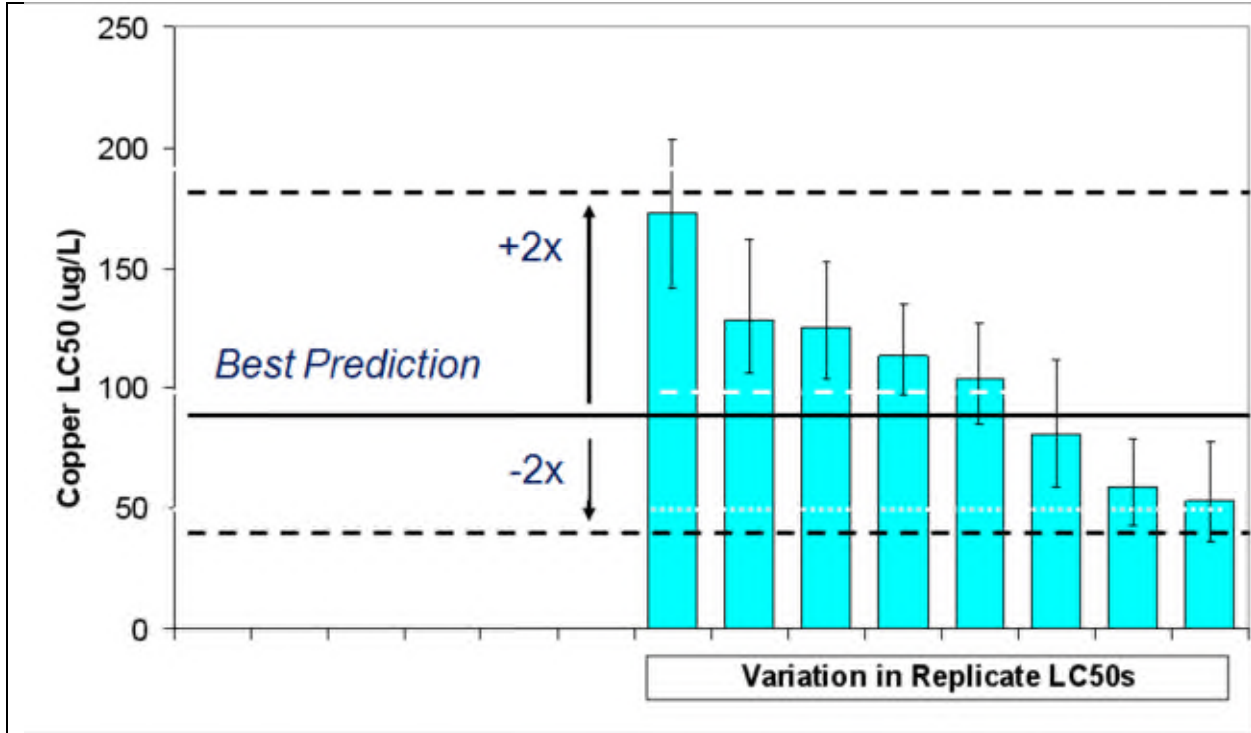


Figure 3. Variation in replicate measurements of LC50 of copper to fathead minnow in Lake Superior water tends to fall in an envelope of plus or minus 2 times the geometric mean value (date from Erickson et al., 1996). The dark solid line labeled “Best Prediction” is shown at the geometric mean of the measured values. The dashed lines correspond to an envelope showing plus or minus a factor of two. Since all of these measured values are from water samples with the same chemistry, the BLM would predict the same LC50 in every case.

IV. CALCULATED WER WITH PREDICTED TOXICITY TO *DAPHNIA MAGNA*

As discussed in Section II of this report, the BLM for Nickel can be used to calculate a site specific WQC by using the model to calculate a WER for the receiving water downstream of the Main Plant. Samples were collected at two locations downstream of the Main Plant discharge, and chemical analyses for BLM input parameters were measured on these samples. Similar analyses were made on samples taken from the Main Plant effluent, although these were not used in the WER analysis. Measured chemical parameters used as input parameters to the Nickel BLM are shown in Table 1. [In addition to the measured parameters in the special study samples listed in Table 1, the BLM was also used to estimate a WER based on average chemistry. An average value was calculated for all parameters measured in the RD at Rock Springs, and RD at Lincoln samples except for DOC. The average DOC was based on an expanded list of monitoring stations that included the RD at Rock Springs, and RD at Lincoln samples, but also included samples from other downstream locations. These same DOC samples were used in a separate analysis that focuses only on the influence of DOC on Nickel toxicity. The average value was used in the BLM analysis to provide a consistent set of conditions to compare the results of these two methods.](#)

The BLM for Nickel was run with these input data to determine Nickel toxicity to *D. magna*, which is a sensitive invertebrate recommended for use in WER testing for Nickel (USEPA, 1994b, Appendix I). For calculation of WER values, the predicted toxicity in these site waters was compared with toxicity in a reference water sample. According to the WER guidance document, suitable reference water must have a hardness concentration close to, but not in excess of, the measured hardness in the site water (US EPA, 1994b). The US EPA's recipe for "very hard" water with a hardness of 317 mg/L as Calcium Carbonate ("CaCO₃"), compared with hardness in the site water of 347, would be a suitable choice for use as a reference water for WER testing at the site. Calculated LC50 values for site and reference water are shown in Table 2.

Table 1. Input chemistry used for BLM analyses. For site waters, Sangamon River samples collected at the Rock Springs Trail bridge approximately one-half mile downstream (RD at Rock Springs) and at the South Lincoln Memorial Parkway bridge approximately six miles downstream (RD at Lincoln) were used to characterize the chemistry of the receiving water downstream of the plant. The presence of NOM was characterized by the dissolved organic carbon (“DOC”) concentration. For calculation of WER, the US EPA’s ”very hard” water recipe was used as a reference sample. Variation of an assumed DOC in the reference water sample from 0.5 to 2.0 mg C/L was included in the BLM analysis.

Sample Description		Temp °C	pH	DOC mg C/L	Ca	Mg	Na	K	SO4 mg / L	Cl	Alk
RD at Rock Springs	8/26/2010	23	8.00	12	56	53	396	86	298	446	365
RD at Rock Springs	9/9/2010	21	8.09	10	64	48	286	53	214	304	341
RD at Lincoln	8/26/2010	25	8.00	10	58	46	296	60	225	450	321
RD at Lincoln	9/9/2010	21	8.10	7.9	65	43	192	35	146	202	315
Final Effluent	8/26/2010	30	8.09	13	56	62	504	112	374	558	400
Final Effluent	9/9/2010	28	7.90	14	62	62	474	91	328	477	399
<u>Average chemistry</u>		<u>24.25</u>	<u>8.05</u>	<u>8.33</u>	<u>61</u>	<u>48</u>	<u>293</u>	<u>58</u>	<u>221</u>	<u>351</u>	<u>336</u>
US EPA Very Hard	DOC=0.5	20	8.20	0.5	47	48	105	8	304	8	229
US EPA Very Hard	DOC=1.0	20	8.20	1	47	48	105	8	304	8	229
US EPA Very Hard	DOC=2.0	20	8.20	2	47	48	105	8	304	8	229

Table 2. Predicted toxicity to *D. magna* by the Nickel BLM in site and reference water samples used in WER analysis. For calculation of WER values, the average LC50 determined in site water was divided by the average LC50 in the reference water. The US EPA's "very hard" recipe for synthetic water was chosen as the reference water due to the good correspondence between the hardness in this recipe and at the site.

Sample Description		Ni LC50 mg/L	Average Ni LC50 mg/L	Average WER
RD at Rock Springs	8/26/2010	32.38	28.89	2.92
RD at Rock Springs	9/9/2010	25.61		
RD at Lincoln	8/26/2010	25.55	22.84	2.31
RD at Lincoln	9/9/2010	20.13		
Final Effluent	8/26/2010	44.52	43.78	4.42
Final Effluent	9/9/2010	43.04		
<u>Average chemistry</u>		<u>26.01</u>	<u>26.01</u>	<u>2.63</u>
US EPA Very Hard	DOC=0.5	9.82	9.90	
US EPA Very Hard	DOC=1.0	9.88		
US EPA Very Hard	DOC=2.0	10.00		

Site water was characterized by performing two separate sampling events at both Rock Springs B and Lincoln Homestead. The BLM calculated LC50 values to *D. magna* in site-waters downstream of the Main Plant ranged from 22.84 mg/L to 28.89 mg/L (Table 2). For comparison, the calculated LC50 for reference water based on the US EPA's "very hard" water recipe was 9.9 mg/L. The WER values for each sampling location, calculated by dividing site water LC50 by the reference water LC50, correspond to 2.31 and 2.92 for Rock Springs B and Lincoln Homestead. Since these values are similar, an overall WER for the site can be determined by averaging to obtain an overall WER for the site of 2.62.

Another way to derive an average WER for the site is by applying the BLM to the average chemistry shown in Table 1. The DOC value for this average chemistry considers many more samples, and is therefore a better overall estimate of the average DOC in downstream receiving waters. The WER that results from using the BLM with average chemistry is 2.63, which is nearly identical to the result obtained from the special study samples. Since this value incorporates more of the downstream monitoring data, it will be used as the overall result from the BLM WER analysis. However, there is very good consistency between this value and the other methods that were evaluated to derive an average WER.

Predicted toxicity in the Final Effluent and the resulting WER value is also shown for comparison in Table 2, but these values were not averaged into the overall WER for the site. The predicted average LC50 in effluent samples was 43.78 mg/L, which is considerably higher

than in downstream receiving water samples. The chemistry for the effluent shown in Table 1 indicates that effluent samples had higher concentrations of cations, such as Ca, Mg, and Sodium (“Na”), as well as a higher concentration of NOM (measured as DOC). All of these factors would tend to further mitigate against Nickel toxicity to aquatic organisms, which is why the predicted LC50 in effluent samples is higher. As a result, Nickel toxicity would be lower in any areas that are poorly mixed downstream of the discharge, and the resulting WER would be protective for these areas as well.

V. SENSITIVITY TO VARIATION IN WATER CHEMISTRY

Since relatively few samples were used in the BLM analysis summarized in Tables 1 and 2, an additional analysis was conducted to see what effect natural variation in downstream water chemistry would have on the predicted toxicity. Additional monitoring data were used to characterize variation in measured chemistry corresponding to BLM input parameters. Monitoring data describing the variability in downstream chemistry was collected by the District, and combined with monitoring data for the Sangamon River collected by Eastern Illinois University. Samples collected for these monitoring studies were obtained at a number of different stations downstream of the Main Plant, including Lincoln, Rock Springs, and Wyckles Bridge, as well as unnamed stations 100 yards and 600 yards downstream. Variability in measured chemistry in the pooled data from these sampling stations includes both spatial and temporal variation. From these available data, the 10th, 25th, 75th, and 90th percentiles were estimated for key water quality parameters that are known to affect Nickel bioavailability, including pH, DOC, Ca, Mg, Na, and Alkalinity (Table 3). A set of base case conditions was established as the median value for all parameters. Variation in Potassium (“K”), Sulfate (“SO4”), and Chlorine (“Cl”) was not considered since these parameters are not important in determining the bioavailability of nickel.

Table 3. Variation in water quality parameters that affect Nickel bioavailability was characterized as the 10th, 25th, 75th, and 90th percentile estimated from a dataset of pooled measurements are stations downstream of the Decatur Plant. The values for the base case were based on median values from the same dataset.

Test	Temp. C	pH SU	DOC mg/L	Ca mg/L	Mg mg/L	Na mg/L	K mg/L	SO4 mg/L	Cl mg/L	Alk mg/L
<i>base</i>	17.78	8.14	9.99	37.1	44.7	244.00	47.4	185.5	326.0	279.00
<i>10th</i>		7.96	3.7	25.4	15.8	202.4				151.2
<i>25th</i>		8.03	6.4	30.5	20.1	218.0				223.0
<i>75th</i>		8.29	14.8	73.6	64.9	270.0				321.0
<i>90th</i>		8.47	28.2	84.3	74.3	285.6				451.2

These data correspond to pre-existing monitoring studies and were not specifically collected for BLM analyses. Consequently, not all BLM parameters were measured in every sample. For the purposes of conducting a sensitivity analyses, these data are suitable for showing the expected downstream variation in individual parameters. Available data are plotted in Figure 4 for river samples and Figure 5 for effluent samples.

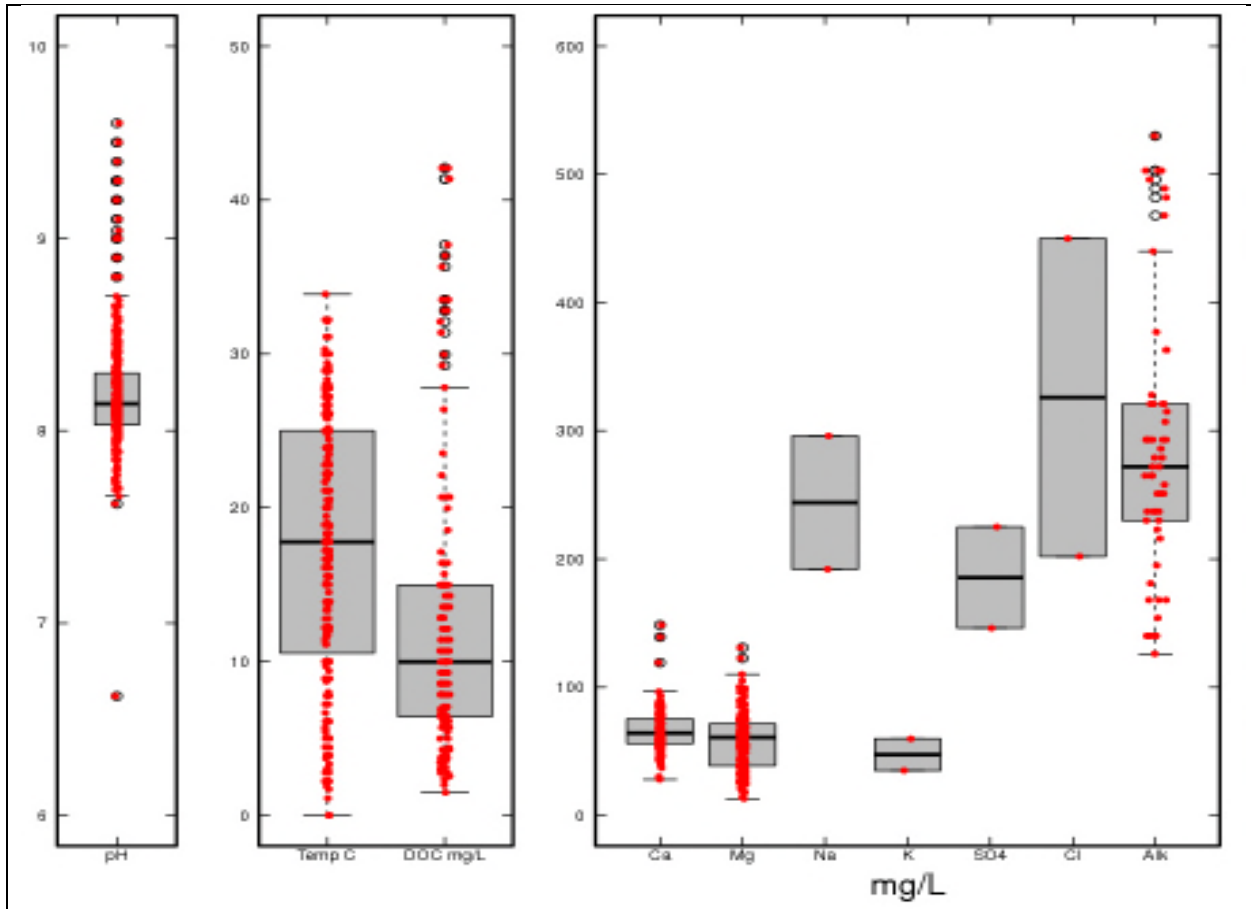


Figure 4. Box and whisker plots showing distributions of measured values for BLM input parameters in river samples. Average values are shown by a black line in the middle of each box and represent mean (pH, Temp, DOC) or geometric mean (Ca, Mg, Na, K, SO₄, Cl, Alk) depending on whether parameters are expected to be normally or log-normally distributed. For each box, the lower edge of the box represents the 25th percentile, the upper edge of the box represents the 75th percentile, and whiskers extend to minimum and maximum values exclusive of extreme values. Individual observations are shown as small red circles.

The distribution of values for each parameter are shown as box and whisker diagrams constructed so that the lower edge of the box represents the 25th percentile, the upper edge of the box represents the 75th percentile, and whiskers extend to minimum and maximum values exclusive of extreme values. Median values are shown as the solid black horizontal line in the middle of each box. Individual observations are shown as small red circles. For river samples,

there was a large amount of data characterizing pH, Alkalinity, DOC, and hardness cations (Ca and Mg), which are the bioavailability factors that are the most important for determining Nickel toxicity (Figure 4). There were relatively few samples characterizing K, and SO₄, but these parameters have little to no effect on Nickel toxicity and do not need to be considered in the uncertainty analysis. There were also relatively few observations for Na, but the estimated variation in Na concentrations is similar to that seen for Ca and Mg and is, therefore, likely to be a reasonable characterization of variation in downstream chemistry. For effluent samples there were many more measurements of anion concentrations (Figure 5), and in comparison with river samples the effluents tended to have lower pH values and higher DOC and ion concentrations. The variation in pH, DOC, and ion concentrations show in these two datasets are consistent with the values seen in detailed sample analyses reported in Table 1.

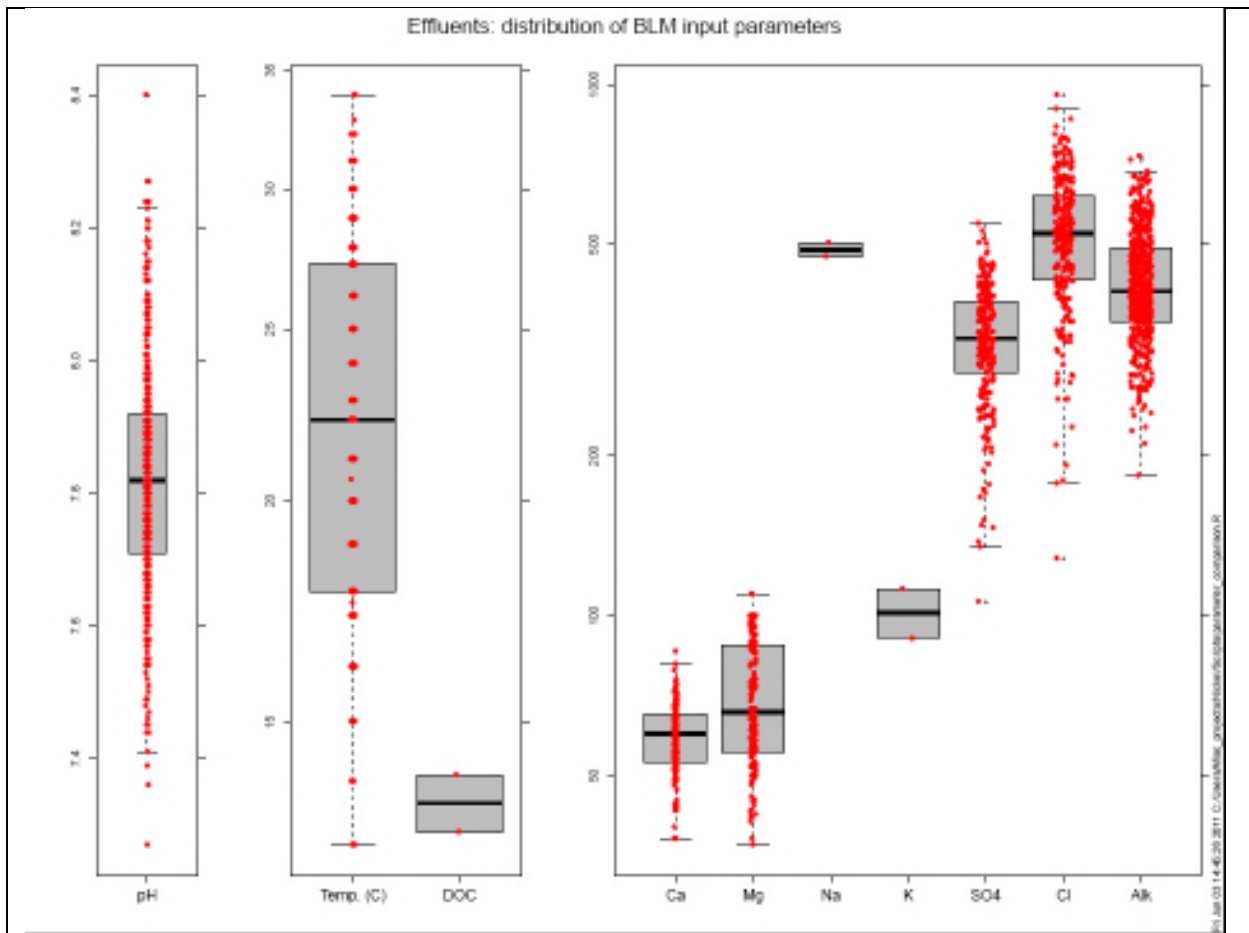


Figure 5. Box and whisker plots showing distributions of measured values for BLM input parameters in effluent samples. Average values are shown by a black line in the middle of each box and represent mean (pH, Temp, DOC) or geometric mean (Ca, Mg, Na, K, SO₄, Cl, Alk) depending on whether parameters are expected to be normally or log-normally distributed. For each box, the lower edge of the box represents the 25th percentile, the upper edge of the box represents the 75th percentile, and whiskers extend to minimum and maximum values exclusive of extreme values. Individual observations are shown as small red circles.

Variability in BLM input parameters was used in a sensitivity analysis to determine the degree to which predicted toxicity may be expected to change over time. The model was first run for a base case that used median values for all parameters shown in Figure 4 and Table 3.

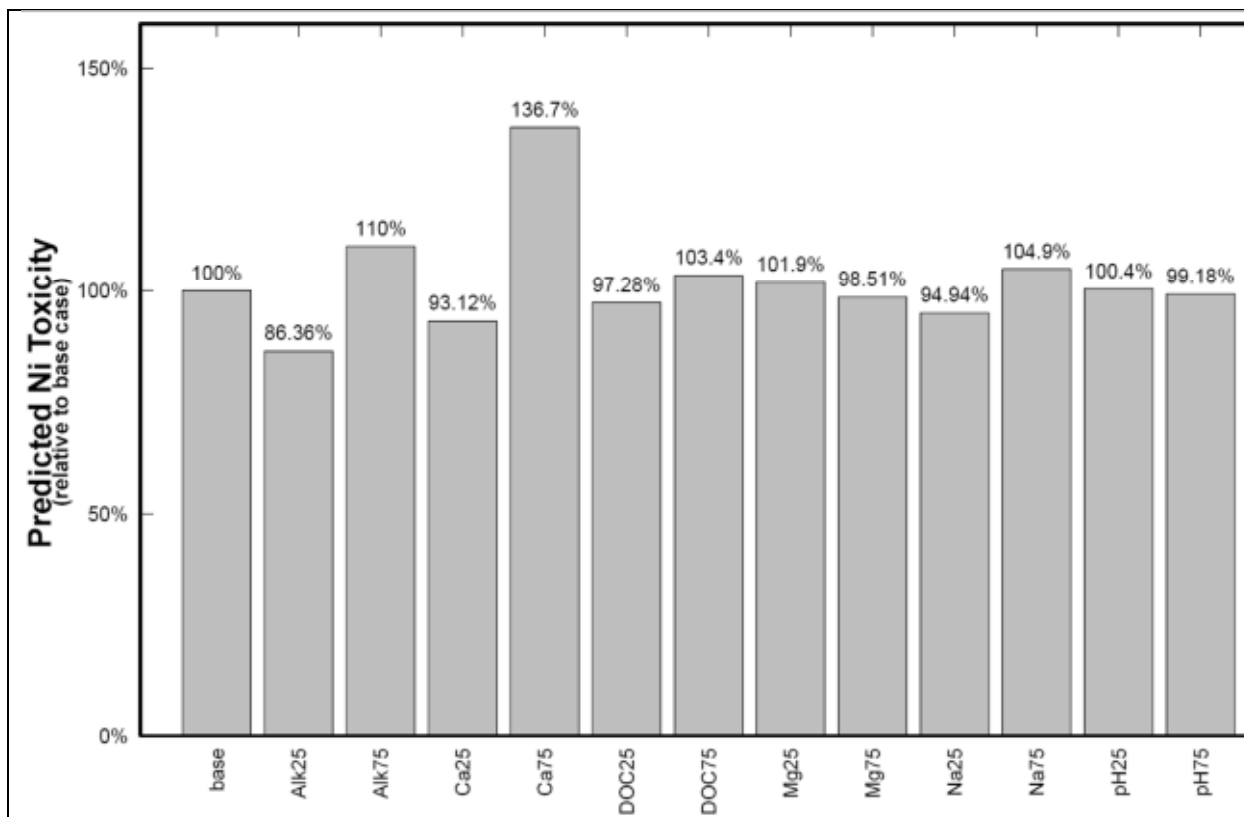


Figure 6. Sensitivity analysis of varying input parameters to the BLM on predicted Nickel toxicity in river samples. For the base case, average values for all parameters shown in Figure 4 were used. A series of additional simulations were then run to see the effect of variation in individual parameter values on the base case. For each additional simulation, the base case was modified with either the 25th or the 75th percentile value of an input variable, while all other parameters were held at the values used for the base case. For example, the result labeled “Alk25” uses the 25th percentile for Alkalinity (shown in Figure 4), and the result “Alk75” uses the 75th percentile for Alkalinity. Sensitivity results for other parameters are labeled with a similar labeling scheme.

For each BLM parameter, two additional runs were then performed by substituting either the 25% or 75% value from the box and whisker plots in Figure 4 for the average value, while keeping all other parameters constant, at their respective average. The resulting sensitivity analyses are shown in Figure 6 for river samples considering variation at the 25th and 75th percentile, and Figure 7 considering variation at the 10th and 90th percentiles.

Variation in input values at the 25th and 75th percentiles for river water samples had relatively little effect on the predicted Nickel toxicity, with the largest effects resulting from changes in Alkalinity and Calcium concentrations. A similar pattern was observed when variation at the 10th and 90th percentiles were considered (Figure 7). Even at these extreme values, the expected variation in predicted Nickel toxicity ranges from about 70 to 150 percent of the base case value. Guidance for derivation of site-specific adjustments to WQC based on the WER procedure allow simple geometric means of individual WER values when the range in values is within a factor of 5. Since the effects of the variation in river water chemistry on Nickel toxicity will be well within those limits, this uncertainty analysis supports the conclusion that average conditions from a relatively small number of samples should provide an acceptable characterization for deriving a site-specific Nickel criterion. As a result of these sensitivity analyses, the calculated WER for the site is not expected to significantly change as a result of variability in water quality within ranges comparable to these existing monitoring datasets.

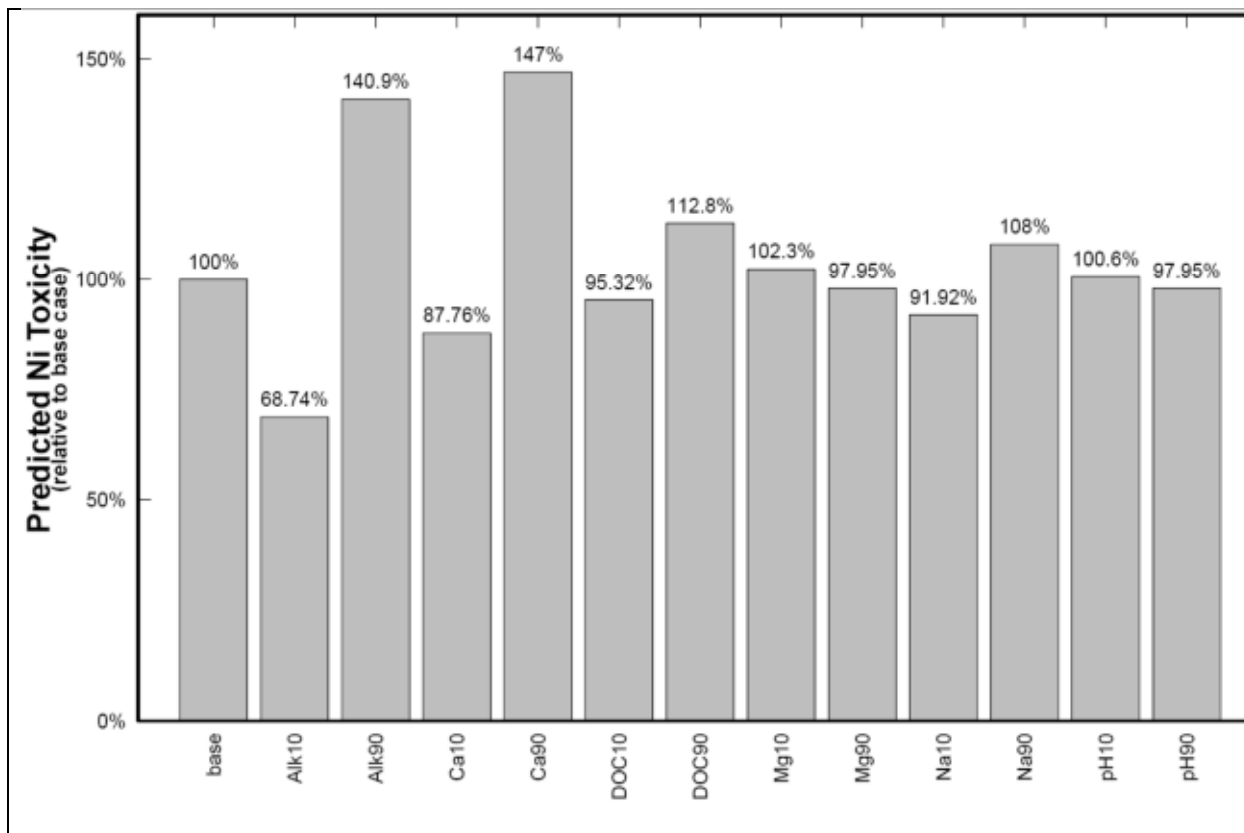


Figure 7. Sensitivity analysis of varying input parameters to the BLM on predicted Nickel toxicity in river samples. For the base case, average values for all parameters shown in Figure 4 were used. A series of additional simulations were then run to see the effect of variation in individual parameter values on the base case. For each additional simulation, the base case was modified with either the 10th or the 90th percentile value of an input variable, while all other parameters were held at the values used for the base case. For example, the result labeled “Alk10” uses the 10th percentile for Alkalinity (shown in Figure 4), and the result “Alk90” uses the 90th percentile for Alkalinity. Sensitivity results for other parameters are labeled with a similar labeling scheme.

For effluent samples (Figure 8), variation in Alkalinity had the largest effect on predicted Nickel toxicity. However, the resulting variation in predicted LC50 values was small, corresponding to a little more than 10% change relative to the base case. Variation in effluent characteristics is only presented for comparison to that seen for river water, since it is only the downstream river water that will be used to estimate the site-specific Nickel adjustment.

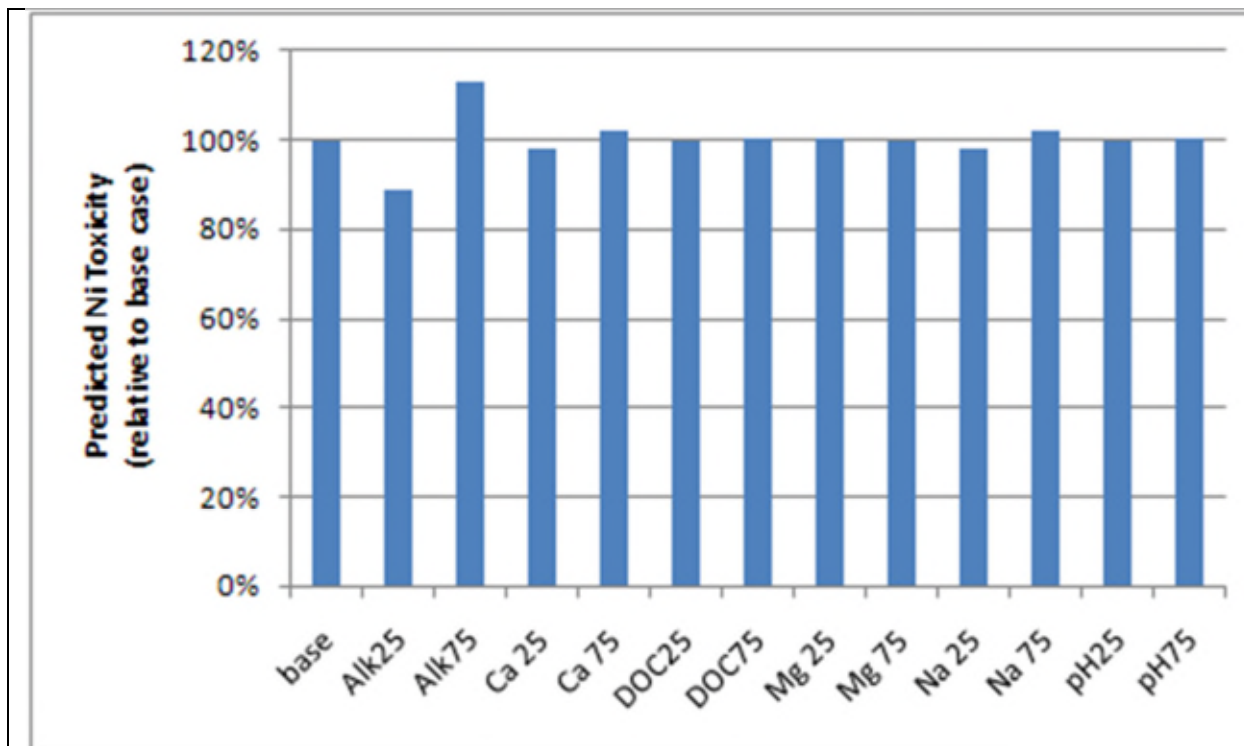


Figure 8. Sensitivity analysis of varying input parameters to the BLM on predicted Nickel toxicity in effluent samples. For the base case, average values for all parameters shown in Figure 5 were used. A series of additional simulations were then run to see the effect of variation in individual parameter values on the base case. For each additional simulation, the base case was modified with either the 25th or the 75th percentile value of an input variable, while all other parameters were held at the values used for the base case. For example, the result labeled “Alk25” uses the 25th percentile for Alkalinity (shown in Figure 5), and the result “Alk75” uses the 75th percentile for Alkalinity. Sensitivity results for other parameters are labeled with a similar labeling scheme.

VI. PREDICTED ESTIMATE OF WQC

With the WER calculated in Section IV, site specific acute and chronic WQC can be calculated for the site. The site specific criteria are calculated as the state standards times the WER. For the receiving water downstream of the site, the average WER is 2.663, resulting in a site specific acute WQC of 614.1638.8 µg/L and a site specific chronic WQC of 37.238.7 µg/L when applied to IL state standards using the critical hardness value for the Sangamon that was assigned by Illinois EPA (Table 4).

Table 4. Summary of values for corresponding acute^a and chronic^b standards, WER, and resulting site specific standards in receiving water samples downstream of the plant. The Illinois acute and chronic standards for Nickel are based on hardness dependent equations. The average for samples collected in this study are based on the average measured hardness in samples collected for the BLM analysis. Also shown are the site-specific values based on a hardness of 359, which was assigned by the State of Illinois for this site.

Sample Date	Sample Location	Hardness	Nickel Acute ^a Standard	Nickel Chronic ^b Standard	Water Effect Ratio	Site Specific Acute Standard	Site Specific Chronic Standard
		mg/L as CaCO ₃	µg/L	µg/L		µg/L	µg/L
8/26	RD at Rock Springs	357	241.7	14.7	<u>2.663</u>	628.5 <u>635.7</u>	38.17
9/9	RD at Rock Springs	360	243.5	14.8		633.0 <u>640.4</u>	38.49
8/26	RD at Lincoln	332	227.3	13.8	<u>2.663</u>	591.1 <u>597.8</u>	35.8 <u>36.3</u>
9/9	RD at Lincoln	341	232.5	14.1		604.6 <u>611.5</u>	36.6 <u>37.1</u>
Average (this study)		347.5	236.2	14.3	<u>2.663</u>	614.1<u>621.3</u>	37.2<u>37.1</u>
Site specific values using Illinois EPA-assigned critical hardness		359	242.9	14.7	<u>2.663</u>	631.5<u>638.8</u>	38.2<u>37.1</u>

Notes:

^a: Nickel Acute Standard = exp[A+B*ln(H)] * 0.998 (where A=0.5173; B=0.846)

^b: Nickel Chronic Standard = exp[A+B*ln(H)] * 0.997 (where A= -2.286; B=0.846)

VII. CONCLUSIONS

Water quality factors such as pH, Alkalinity, ion content, and the presence NOM have been shown to affect metal toxicity. However, the ~~WQC~~WQC for many metals consider only hardness, making them potentially over-protective or under-protective for many site waters. The BLM is a mechanistic framework suitable for a number of metals, including Nickel, which allows for the consideration of many additional water quality factors. The BLM ~~has been~~was adopted by US EPA ~~in~~for the ~~most recently updated metals criteria~~WQC for copper (US EPA, 2007). For metals that do not yet have an approved WQC approach, the BLM can be used to calculate a WER adjustment to derive site specific acute and chronic criteria. Application of the Nickel BLM to calculate Nickel toxicity in samples taken from the Sangamon River downstream of the District's Main Plant compared to a reference water results in a calculated average WER of ~~2.663~~. This WER results in a site specific acute criterion of ~~614.1621.3~~ µg/L and a site specific chronic criterion of ~~37.27~~ µg/L at a hardness equal to 347.5 mg/L. Utilizing the Illinois EPA-assigned hardness of 359 mg/L, the WER results in a corresponding acute criterion of ~~631.5638.8~~ µg/L and a site specific chronic criterion of ~~38.27~~ µg/L.

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