Heavy Metals at Municipal Plants – Removal and Limit Mitigation

Jurek Patoczka[1, *], Dennis McIntyre[2]

[1] Hatch Mott MacDonald
[2] Great Lakes Environmental Center
* To whom correspondence should be addressed: jurek.patoczka@hatchmott.com

ABSTRACT

Very stringent, Water Quality Based Limits (WQBL) for some heavy metals as well as organic toxic compounds, are now commonly imposed on municipal plants in New Jersey and elsewhere. For facilities discharging to intermittent or small flow streams, a situation common in New Jersey, WQBL on order of 20 ug/L for copper and 150 ug/L for zinc are typical. The paper discusses options available for conventional treatment plants for improved heavy metals removal, once technical and regulatory options available for increase of the limit are exhausted. Full scale data and jar test results on removal of trace concentrations of copper and zinc are presented. Results of several Water Effect Ratio studies for copper are compared with BLM predictions for the same effluent.

KEYWORDS: Copper, zinc, heavy metals, water effect ratio, WER, Biotic Ligand Model, BML

INTRODUCTION

Beginning in early 2000 New Jersey Department of Environmental Protection (NJDEP) started to enforce Surface Water Quality Criteria (SWQC) for heavy metals and other toxic pollutants. Many dischargers, including a number of small and very small plants, have received stringent limits for toxic compounds - copper and zinc in particular, sometimes silver, mercury, arsenic, lead, and cyanide. In some cases, limits for some organic toxic pollutants were also proposed; specifically for Trihalomethanes (THMs) and Bis (2-Ethylhexyl) Phthalate (usually detected in the effluent as a result of sampling/ laboratory contamination).

A review of the various approaches and alternatives used for minimizing exposure of dischargers is presented below.

LIMIT IMPOSITION

WQBLs are based on a numerical value of SWQC for the given pollutant. If any of the toxic pollutants with a SWQC is reported as detected (see insert) in the plant effluent, NJDEP will calculate Waste Load Allocation (WLA) for this parameter based on the dilution available in the receiving stream. If the maximum effluent concentration on record is greater than the applicable WLA, the limit is imposed (i.e. the so-called “Cause Analysis” is positive). Several factors/variables and calculation steps are involved in the derivation of the numerical value of the limit, including:

1. Multiple SWQC (acute, chronic, human health)
2. Multiple stream design flows (dilution)
3. Soluble to total recoverable translators for metals
4. Site-specific hardness for most of the metals
5. Effluent variability as measured by coefficient of variation (CV)
6. Water effect ratio (WER)

It should be noted that the triggering event for calculating and imposition, if warranted, of a limit for a toxic pollutant, is the reported presence of a pollutant in the effluent. The "presence" is defined as a detection of the pollutant at any level, even at concentration lower than the NJDEP-recommended maximum Recommended Quantification Level (RQL). Most laboratories are capable of analyzing effluent samples at detection levels lower than RQL, and the resulting detections could trigger DEP's attention to the parameter. This is somewhat unfair, as use of a better laboratory and more accurate method could penalize the discharger.

LIMIT MODIFICATION OR REMOVAL

Usually, the site-specific values for the above listed variables are not known and in such case default values are used (100 mg/L as $CaCO_3$ for hardness, CV of 0.6, WER of 1.0 and default translator value). Development of appropriate, site-specific values for the above listed variables is the main avenue for a significant increase or removal of the limit on technical grounds. However, any modification of the proposed limit, based on development of site-specific information, will be allowed by the NJDEP only if a study to determine background (upstream of the discharge) concentration of the pollutant is conducted as well (if there is insufficient existing data). This is because in the default limit calculation mode, the background concentration of zero is assumed.

Below is a run-down of the practical results and issues encountered during the process of deriving appropriate limits for a number of New Jersey dischargers based on site-specific information, preserving numbering in the list of variables listed above:

1. In 2006 the SWQC for several parameters of concern were changed. The most important changes were:
    a. SWQC for copper was reduced by approximately 25%, resulting in imposition of commensurably more stringent limits for new dischargers and for others in recalculation of previously imposed limits during the next permit renewal,
    b. SWQC for chloroform, a THM, has increased more than ten-fold, and this should allow all dischargers with a chloroform limit (or detections in the effluent) to escape compliance problems,
    c. SWQC for bromodichloromethane (BDCM), a THM, has almost doubled. This increased the calculated limit for several dischargers, although the enforceable limit may still be the 5 ug/L Recommended Quantification Level (RQL),

   d. SWQC for chlorodibromomethane (CDBM) was cut by more than two orders of magnitude, and this could impact dischargers using chlorination in the near future (if they have any detects for CDBM in their effluent).

2. During verification of appropriate stream design flows (MA7CD10 and MA1CD10) for upper Passaic River dischargers, a densely populated area, it was noted that the stream design flows used by the Department were lower than the sum of minimum flows of the wastewater treatment plants discharging upstream of the plants in question. Since any determination of a background concentration that goes into calculating the limit includes what is discharged upstream, this is not fair. There are on-going discussions with NJDEP about an appropriate way of addressing this problem.
3. Translators (ratio between dissolved and total recoverable metal in the receiving stream) could give some additional mileage, but usually not much, perhaps 10-15%, if any. In several cases, translator studies or preliminary, informal tests showed no improvement over the default values. In a few cases involving copper, the dissolved values were frequently equal to or greater than total recoverable values, despite careful laboratory practices and controls and some dischargers decided not to pursue formal translator studies for copper.
4. A number of hardness studies were conducted, which involve sampling of the plant effluent and the receiving stream upstream of the outfall at low flow conditions. For each set of such obtained data a lower, 95 % confidence interval around the mean is calculated. The “design” hardness for downstream of the outfall is then calculated from the mass balance, using the critical low flow stream values (MA7CD10 or MA1CD10) and the design flow of the facility. In many cases the appropriate hardness resulting from the study was significantly greater than the default value originally used by the NJDEP. As the SWQC for some metals (such as copper and zinc) is a strong function of the hardness, this resulted in similar increase in the permit limit. See Table 1 for details.
5. The variability (CV) of the effluent results for the given parameter of concern enter the picture when the Long Term Average and Maximum Daily or Monthly Average Limits are calculated from the Waste Load Allocation, which in turn is calculated from the SWQC and the available dilution at critical conditions. In most practical cases concerning metals such as copper and zinc, the value of the CV does not impact the permit limits, but it could for some other toxic compounds.
6. WER Study. This is a study demonstrating that a particular pollutant is less toxic in the site water (includes plant effluent) as compared to the clean, laboratory water in which SWQC were originally developed. WER studies proved to be particularly effective in substantially increasing/removing the copper limits. Discussion about the results of WER studies conducted recently in New Jersey is provided below.

The compliance schedule (effective date of the limit) for limits for toxic pollutants is usually 59 months from the date of the issuance of the permit with new limits. However, the process of preparing the required Work Plan(s) for NJDEP’s approval, execution of the sampling programs and studies, preparation of the resulting reports for submittal to NJDEP for review and execution of the permit modifications could be lengthy and subject to unexpected weather and review-related delays. It is imperative that the process of modification/removal of the permit limits is completed in advance of the original limit becoming effective, as a delay could invoke significant complications related to antidegradation and antibacksliding regulations.

In addition to modifying/removing the limit on technical grounds (as discussed above), another avenues of mitigating permittee's exposure to limits for toxic pollutants are source control and improved treatment. Significant findings and recommendations in that area are provided below.

SOURCE CONTROL AND REMOVAL OF COPPER AND ZINC

Source Control

A major source in raw wastewater of metals of particular concern for most municipal dischargers, i.e. copper and zinc, is the potable water supply. Copper (as well as lead and to some extent zinc) originates mostly from residential plumbing corrosion. A major source of zinc could be zinc orthophosphate-based corrosion inhibitors, which are used by some water purveyors at a dose of up to 0.3 mg/L (300 µg/L) as zinc. In many cases the potable water could easily account for the majority of the copper and zinc found in raw wastewater. Use of alternative corrosion inhibition chemicals (i.e. without zinc component), if practical, is an obvious source control measure. Should raw wastewater data indicate presence of heavy metals at concentrations higher than typical domestic background level (or at highly variable concentrations) a potential industrial or commercial source is indicated and should be investigated.

Copper Removal

Median copper removal across a typical municipal treatment plant is reported at 94% (Sedlak *et al.*, 2000). Results from a series of jar tests conducted at several facilities indicate that some degree of additional removal of copper will be achieved by alum and ferric salts addition to the mixed liquor or secondary effluent at doses typically used for phosphorus control. Figure 1 presents typical results from jar tests indicating that ferric was more effective than alum in copper reduction at an equivalent metal ion dose, although these effects were not consistent. Further increase of alum or ferric dose did not result in significant additional decrease of the residual copper, which was somewhat surprising. Ferric salts, in particular, would be expected to coprecipitate/adsorb available free copper (and zinc) in accordance with well-known scavenging properties of precipitated ferric hydroxide (Farley *et al.*, 1985; Patoczka *et al.*, 1998). However, as demonstrated by Sedlak *et al.* (2004), most copper and zinc in municipal effluents is present in form of EDTA complexes. They found ferric chloride addition to primary clarifier resulted in only 20% removal of copper and zinc. Data from this study (Figure 1) indicate that removal efficiency was highly variable and could be as high as 70%. Higher efficiency likely corresponds to a higher ratio of residual metal to EDTA. Split point chemical addition demonstrated potential benefit, particularly when ferric was used. Adjustments of pH during alum and ferric treatment within the neutral range (Figure 1) had no significant impact on the residual dissolved copper concentration.

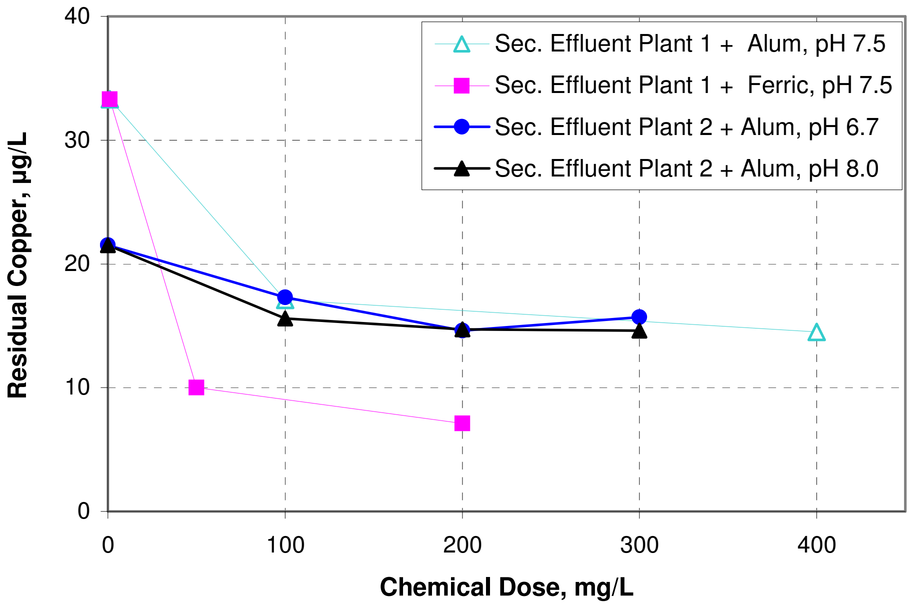

Figure 1. Effect of Chemical Dose and pH on Residual Copper

Zinc Removal

Similarly as for copper, and probably for the same reasons, aluminum or ferric salts were not effective in reducing the residual, soluble zinc concentration beyond the small, initial effect due to coagulation of the particulate/colloidal fraction.

However, tests with mixed liquor from two different facilities without primary clarification documented that zinc concentration in the secondary effluent is controlled by the pH at which the activated sludge process operates. This is illustrated in Figure 2, where the residual zinc concentration is a function of mixed liquor pH, regardless of chemical addition. Although such effect could be expected from the basic properties of the metal ions (solubility), such behavior has not been reported in the literature, including recent WERF Report on that topic (Sedlak *et al.*, 2004). The activated sludge appears to serve as a depository of zinc, and variations in the process pH result in a transfer of zinc between the sludge and solution. Activated sludge from separate sludge nitrification facility (following primary clarification and trickling filters) did not demonstrate such zinc release-adsorption phenomenon upon pH manipulations. Relation of these pH effects to the EDTA complexation reported by Sedlak *et al.* (2004) warrants further investigation.

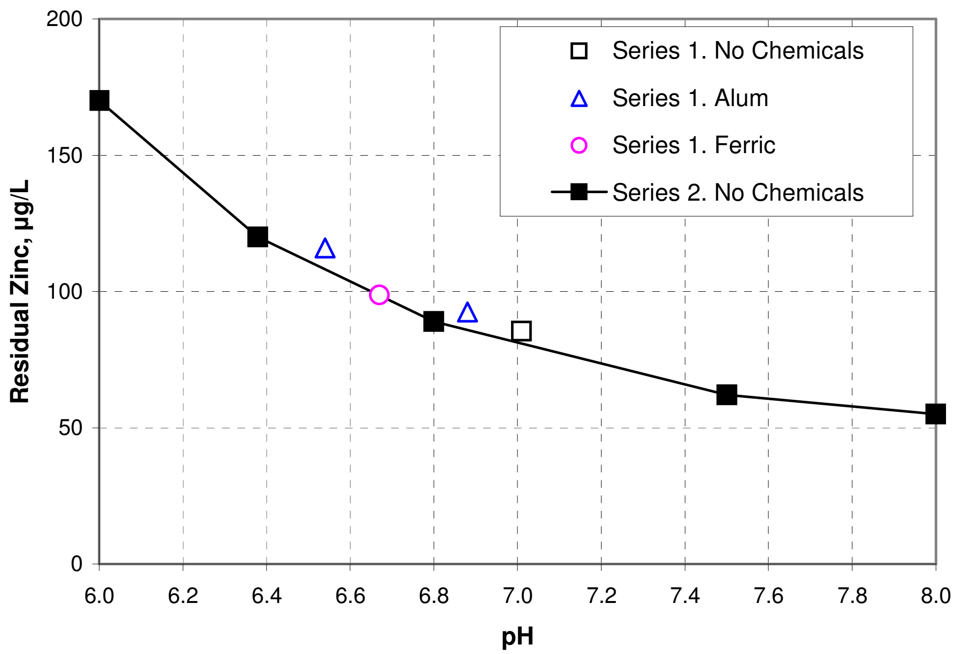

Figure 2. Effect of Activated Sludge Process pH on Effluent Zinc

WATER EFFECT RATIO STUDIES FOR COPPER

A WER study is designed to demonstrate that copper (or other metal) toxicity to aquatic life in a stream dominated by plant effluent is much lower than in the laboratory water, which was originally used to develop SWQC (and permit limits). A WER study consists of a series of bioassays conducted on plant effluent and stream water, mixed in proportions equal to the dilution available at the plant design flow and low flow conditions for the stream (MA7CD10) with appropriate controls. The solutions are spiked with a known concentration of copper to determine copper toxicity in simulated stream water downstream of the discharge. This toxicity is compared to copper toxicity in laboratory water, in a battery of bioassays performed side by side. The ratio of copper toxicity (appropriately adjusted for hardness) in the site water to that in the laboratory water is the WER. Following EPA's streamlined WER procedure for dischargers of copper, the laboratory tests should be performed at least twice, on samples collected at least one month apart. Additionally, copper toxicity in the simulated site water is compared to that of the literature database and the more conservative of the two is selected as the site-specific WER.

The appropriate water quality criterion for aquatic life protection is then multiplied by the WER (a ratio) to develop a site-specific SWQC. The appropriate permit limit is then recalculated using any new or site-specific information including, in particular, hardness. The site-specific value of WER has a practical effect of increasing the appropriate limit by the same factor, as the default value of the WER used by the Department in calculating the original limit, is equal to one.

Table 1 provides results of several WER studies conducted recently for New Jersey dischargers. As indicated, for all municipal dischargers the resulting WER value was at least twice the default. The single exception is a small treatment plant servicing a school, with wastewater composition and disproportionate use of chemicals for treatment and sanitization likely affecting the outcome.

Table 1. Results of Hardness and Water Effect Ratio Studies for Copper

	Hardness, mg/L as $CaCO_3$		WER (default =1)	Status of the Copper Limit Modification Process
	Originally Used by DEP	Developed from Site-specific Study		
East Windsor MUA	40	43	2.4	Limit has been removed
Jefferson Township, White Rock STP	100	144	3.9	Removal of the limit expected
Bernards Township SA	120	133	4.8	Limit has been removed
Jefferson Township BOE, Stanlick School	100	147	1.04	Significant increase of the limit expected
Borough of Caldwell WTP	100	219	2.2	Removal of the limit expected
Livingston Township WPCF	100	215	1.98	Removal of the limit expected
Office Complex	100	105	4.02	Significant increase or removal of the limit expected

Biotic Ligand Model and WER. Another possible tool for arriving at site-specific SWQC for heavy metals is the Biotic Ligand Model (BLM). This computational method relies on the fact that toxicity of heavy metals to aquatic life depends on the site water chemistry, and in particular on water pH and concentration of ions such as calcium, magnesium (hardness!) sodium, and potassium, as well as soluble organic matter. The BLM integrates impacts of all these variables and calculates the expected metal toxicity (and resulting SWQC) based on detailed information on the site water chemistry. During several WER studies conducted in New Jersey, the water chemistry data was used to calculate the expected copper toxicity using the BLM. Theses values are compared in Table 2 with the actual copper toxicity as measured in the site water by bioassay tests. While in some cases the agreement was very good, significant discrepancies were observed in others. Similar to that observed for several sites in New Jersey, the BLM has generally been a good predictor of toxicity elsewhere. However, as found in the New Jersey example, there have been cases when there has not been good agreement. In a study in which 39 samples were collected at 18 different stream sites in the Upper Peninsula of Michigan, the BLM consistently over-estimated the observed toxicity to *Ceriodaphnia dubia* (Figure 3). It appears that while BLM could be a useful and inexpensive tool in predicting variations in copper toxicity for a given site (as opposed to a battery of bioassays required otherwise), development of an absolute value of a site-specific SWQC for a new site requires that an empirical WER study is conducted.

Table 2. Comparison of Experimental and Biotic Ligand Model-derived Toxicity Values

	Sample 1			Sample 2		
	Copper LC50 in Test Sample, ug/L		Ratio Measured LC_{50}/BLM	Copper LC50 in Test Sample, ug/L		Ratio Measured LC50/BLM
	Measured	Calculated from BLM		Measured	BLM	
Jefferson Township, White Rock STP	163	76.9	2.12	93.9	72.7	1.29
Bernards Township SA	117	127	0.92	148	123	1.20
Jefferson Township BOE, Stanlick School	48.8	32.5	1.50	53.7	37.4	1.44
Borough of Caldwell WTP	104	96.8	1.07	133	145	0.92
Livingston Township WPCF	128	187	0.685	46.9	83.4	0.562
Office Complex	93.0	133	0.699	95.8	98.3	1.03

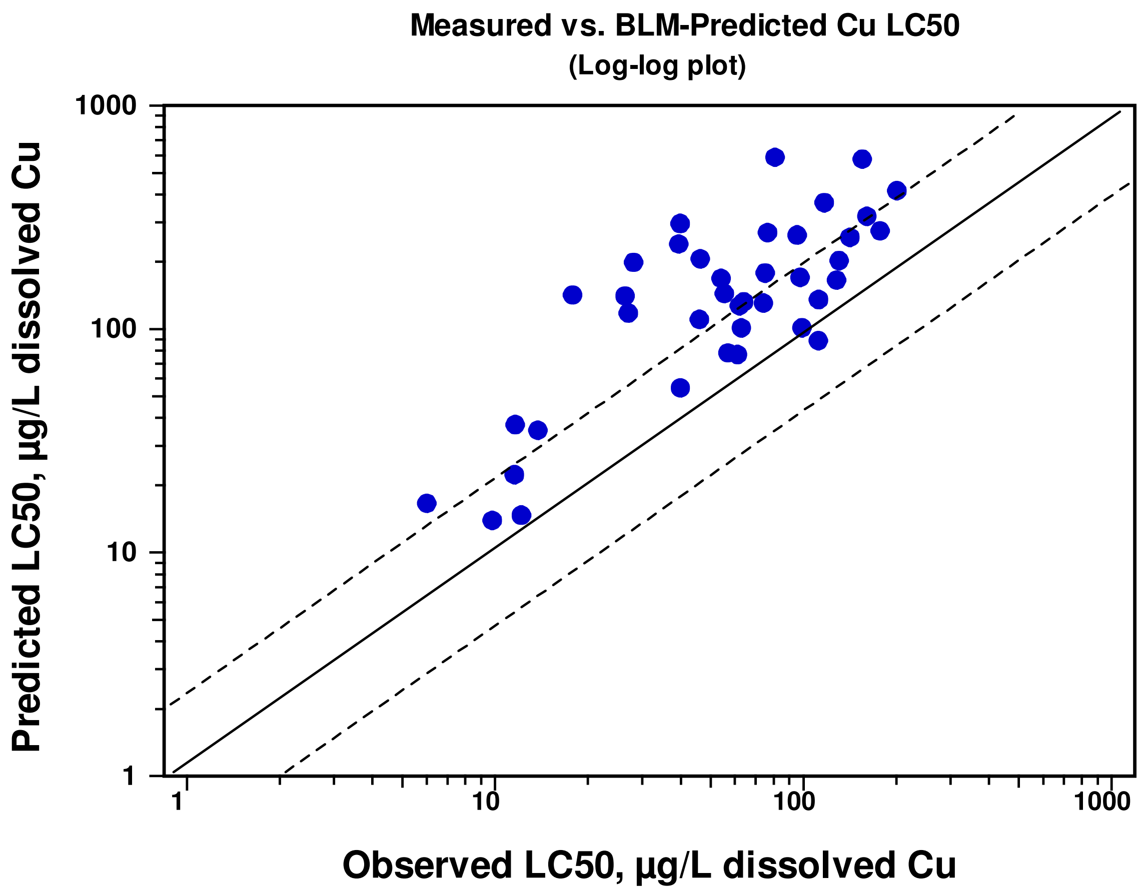

Figure 3. Log-log plot of measured versus BLM-predicted Cu LC_{50} values for stream samples collected in Michigan's Upper Peninsula. Solid line represents the theoretical line of equality; dashed lines indicate when BLM-predicted values are within a factor of two.

CONCLUSIONS

1. Permittee could undertake a number of measures in order to minimize its potential exposure to stringent limits for toxic parameters, including water quality studies, source control, and improved treatment.

2. Review of available options and initiation of water quality studies should be performed without delay to finalize the process of limits modification before they become effective, in order to avoid antibacksliding complications.

3. The majority of copper and zinc in most municipal plants influents originates from potable water, including zinc-containing compounds added for corrosion control.

4. Removal of residual copper and zinc in effluent from conventional treatment plants can be improved by use of conventional chemicals (alum/ferric), but only to a limited extent.

5. Zinc concentration in the secondary effluent is impacted by the pH in the activated sludge process.

6. BLM is a useful, but not always reliable, predictor of toxicity.

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