WATER EFFECT RATIO – AN EFFECTIVE TOOL IN MODIFYING/REMOVING COPPER LIMITS.

An update on Mitigating Stringent Limits for Heavy Metals and Toxic Pollutants

by

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Limits Imposition

From early 2000', NJ DEP started to enforce Surface Water Quality Standards for heavy metals and other toxic pollutants. Consequently, almost all dischargers in NJ have received in recent years stringent limits for some heavy metals (copper and zinc in particular, sometimes silver, mercury, arsenic and lead, also cyanide). In some cases, limits for some organic toxic pollutants were also proposed; specifically for:

- Trihalomethanes (THMs) – present sometimes in chlorinated effluent as a chlorination byproducts, and,
- Bis (2-Ethylhexyl) Phthalate (usually detected in the effluent as a result of sampling/laboratory contamination).

In the paper published in the Winter 2005 issue of Effluents, we have discussed options available for dischargers faced with very stringent effluent limits. In this update we discuss our recent experience with mitigating impacts of these proposed limits. Such limits were typically challenged and modified/stayed and all dischargers we are familiar with avoided (so far) compliance problems by various means. A review of the various approaches and alternatives used for minimizing exposure of dischargers is presented below.

Who Gets the Limit?

First, however, let us review briefly procedures used by NJDEP in imposing the limits. These limits are Water Quality Based (WQB) limits (or WQBL), based on a numerical value of Surface Water Quality Criterion (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 derivation of the numerical value of the limit, including:

1. multiple Surface Water Quality Criteria (acute, chronic, human health),
2. multiple stream design flows (dilution),
3. soluble to total recoverable translators,
4. site-specific hardness for most of the metals,
5. effluent variability as measured by coefficient of variation (CV)
6. water effect ratio (WER)

NOTE: 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 detection of the pollutant at any level, even at concentration lower than the DEP-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.

How could the Limit be Modified or Removed?

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 Department only if a study to determine background (upstream of the discharge) concentration of the pollutant is conducted as well (if there are insufficient existing data). This is because in the default limit calculation mode, a 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 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) 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, 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

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limit includes what is discharged upstream, this is not fair. The Department is presently working on guidelines on how to address 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 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 percent confidence interval around the mean is calculated. The "design" hardness for downstream of the outfall is then calculated from 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 Department. As the SWQC for some metals (such as copper and zinc) are 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. Water Effect Ratio (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.

NOTE: If the receiving stream is classified as impaired for a given parameter in the Integrated List of Waterbodies (303d List), no dilution is allowed and SWQC are applied end-of-the-pipe. Prior to 2006, segments of the Passaic River upstream of the Pompton River were classified as impaired for copper and zinc, among others. The 2006 303d List removed that classification, allowing calculation of a much more favorable limit for a number of dischargers.

It is important that any facility, which receives an objectionable or difficult to meet WQBL for a toxic pollutant, in particular for a heavy metal, initiates the process of developing the site specific information without delay. While the compliance schedule for these limits is usually 59 months, the process of preparing the required Work Plan(s) for DEP's approval, execution of the sampling programs and studies, preparation of the resulting reports for submittal to DEP for review and approval 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 be completed in advance of the original limit becoming effective, as a delay could invoke significant complications related to antidegradation and anti-back-sliding regulations.

Water Effect Ratio Studies for Copper

A Water Effect Ratio (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 Water Quality Criteria (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. 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 and the appropriate permit limit is 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 1.

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. The scope, approvals and sampling for the WER studies listed in Table 1 was conducted by HMM with laboratory work performed by Great Lakes Environmental Center.

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

	Hardness		WER (default WER=1)	Status of the Copper Limit Modification Process
	Originally Used by DEP (1)	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	Significant increase or 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	Significant increase or removal of the limit expected
Livingston Township WPCF	100	215	1.9 (2)	Significant increase or removal of the limit expected
Office Complex	100	N/A	7 (2)	Significant increase or removal of the limit expected

(1) Based on available data or a default value of 100 mg/L
(2) Result from the first sample (study in progress)

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Biotic Ligand Model and WER. Another possible tool of 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, 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 to date, the water chemistry data were 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, in some others significant discrepancies were observed. 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 conductance of an empirical WER study.

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 LC50/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

Compliance with Limit through Source Control and/or Treatment

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. An update of the important findings and recommendations in that area is provided below.

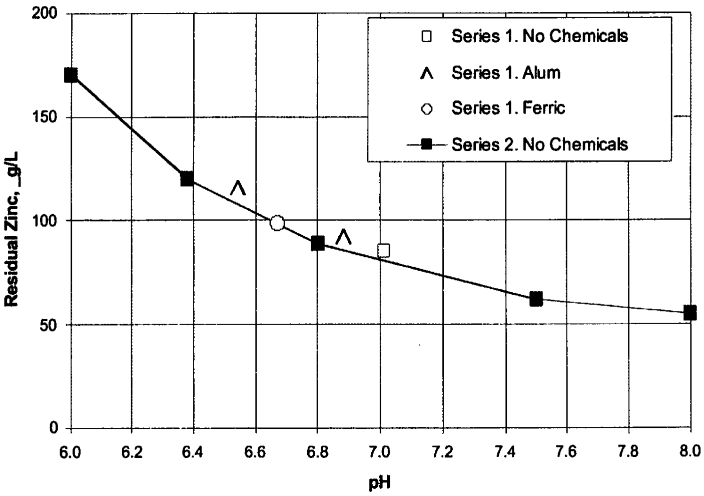
1. Source Control. A major source in raw wastewater of metals of particular concern for most municipal dischargers, i.e. copper and zinc, is the potable water supply. Copper (as well as lead and to some extent zinc) originates mostly from residential plumbing corrosion. A major source of zinc could be zinc orthophosphate-based corrosion inhibitors, which are used by some water purveyors at a dose of up to 0.3 mg/L (300 _g/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.

2. Treatment. During conventional biological treatment, a significant fraction of heavy metals present in raw wastewater can be removed by adsorption and incorporation into the waste sludge. Data from New Jersey facilities and literature information indicate that the removal of heavy metals could normally be expected to be in a range from 50 to 90%, with copper typically being at the upper end and zinc at the lower end of this scale. However, conventional wastewater treatment plants are not designed for removal of the trace heavy metals and the operator has no real control over these removal rates. Some degree of additional removal of copper and zinc could be induced by chemical addition and pH changes, which are practicable at existing conventional treatment plants. Tests conducted at New Jersey plants indicate that operating activated sludge at a higher pH (caustic addition) could be effective in somewhat increasing zinc retention in the sludge, but at substantial cost (see Figure 1). Another possibility is use of ion-specific resins, which could remove part of residual metals such as copper and zinc from the effluent. While initial jar tests conducted by HMM are promising, it is clear that this technology could be practical only for very small dischargers, where capital and maintenance costs of such treatment could be relatively small compared to the overall budget of the facility.

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.

Figure 1. Effect of Activated Sludge Process pH on Effluent Zinc



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 WER.

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