STRINGENT HEAVY METALS LIMITS FOR MUNICIPAL PLANTS. WHAT ARE YOUR OPTIONS?

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Recently NJ DEP started to enforce Surface Water Quality Standards for heavy metals and other toxic pollutants. Consequently, most permit renewals issued in past two years or so have stringent limits for some heavy metals (copper, zinc, sometimes silver mercury and lead, also cyanide). In some cases limits for some organic toxic pollutants were also proposed; specifically chloroform (a chlorination byproduct) and Bis (2-Ethylhexyl) Phthalate (see insert). The good news is that the new, Water Quality Based Effluent Limits (WQBEL) have a 5 year (59 months, to be specific) compliance schedule. Table 1 provides a partial list of newly imposed limits for a number of discharges in several watersheds in Northern New Jersey. Some of these are, at the time of writing, proposed in draft permit form; and most of those, which were finalized, are being challenged. In some cases, notably for Lead, Mercury and Cyanide, the calculated limits are lower than the present official Quantification Limit (equal to the Recommended Quantification Level, or RQL). While the calculated limits will be imposed in the Permit, the enforceable concentration limit (and corresponding mass loading limit) will be based on the present, more lenient RQL (just as it is in the case of CPO).

Table 1.
New WQBEL Imposed Recently on Dischargers in Northern NJ.
All concentrations are in µg/L (ppb)

	Zinc	Lead	Copper	Mercury	Cyanide
Recommended Quantification Level = Enforceable Limit	*30*	*10*	*10*	*1*	*40*
Bernards	145	15.25	23	-	-
Caldwel	-	-	15.7	-	9.62
E. Windsor	-	-	15.3	-	-
JTBOE - Stanlick School	116	-	18.7	-	-
MCJM	112	-	18	-	8.8
Woodland (Morris Township)	-	-	18.7	-	-
Warren Stage	68.75	-	7.64	0.012	5.2
Warren Stage IV	-	-	29.08	-	-
Chatham Township	100(*)	-	10(*)	-	-

(*) Approximate, the exact value not yet proposed.

Who Gets the Limit?

First, NJ DEP identifies any parameter (heavy metal or organic priority pollutant) that has been detected more than 3 times in the plant's effluent in the last 5 years or so. For parameters found to be present, the Waste Load Allocation (WLA) is calculated, based on:

- numerical value of Surface Water Quality Criterion (SWQC) for the given pollutant (a function of hardness for many metals),
- dilution available in the receiving stream.

The WLA is calculated for all criteria applicable for the given pollutant, which in the case of many metals includes three different criteria (protection of aquatic life from acute and chronic effects and human health protection). If the maximum effluent concentration on record is greater than any of the applicable WLA, the limit is imposed (so called "Cause Analysis" is positive).

> **NOTE:** If the receiving stream is classified as impaired for a given parameter in the Integrated List of Waterbodies, no dilution is allowed and Water Quality Criterion is applied end-of-the-pipe. For example, segments of the Passaic River upstream of the Pompton River are classified as impaired for several parameters including copper, zinc and cyanide!

Permit Limit Derivation

Once the need for imposing a limit has been established, the actual maximum daily limit is calculated. In almost all cases the toxic pollutant is monitored only once per month, so the monthly average is equal to the daily maximum. Several factors/variables are involved in derivation of the numerical value of the limit, including:

- multiple Surface Water Quality Criteria (acute, chronic, human health),
- multiple stream design flows (dilution),
- soluble to total recoverable translators,
- effect of hardness for most of the metals,
- effluent variability (CV).

Not surprisingly, limit calculations tend to be quite involved and prone to errors.

> **NOTE:** Several dischargers had multiple detects in their effluent of Bis (2-Ethylhexyl) Phthalate (BEHP), a Base/Neutral compound. Consequently, limits were originally proposed/ imposed. In several cases it was subsequently documented that BEHP was contamination from vinyl tubing in automatic effluent samplers. To prevent contamination, use Teflon coated tubing for sampler lines and silicone tubing in the peristaltic pump heads, particularly when sampling for Base/Neutrals. To convince NJ DEP that past detects were a result of contamination, specially designed side-by-side testing may be needed.

Avenues for Challenging/Complying with WQBEL for Heavy Metals

There are several avenues for dealing with the proposed or imposed WQBEL limit, grouped into three major categories:

I. Modification on technical/scientific grounds, which strives to demonstrate that a more lenient limit (or no limit at all) is justified.

II. Compliance with the limit by source control and/or improved treatment.

III. Challenge to the limit on legal grounds (we leave this one to lawyers).

I. Modification on Technical Grounds

A number of the steps could be taken prior to finalization of the limit (during the comment period on the draft permit or even when applying for a permit renewal):

- challenge inclusion of more than 5-year old or otherwise in-applicable data in determination of "pollutant present analysis,"
- exclude outliers or high results, which can be documented as sampling or analytical errors,
- present effluent and stream hardness data, if available (default =100 mg/L as $CaCO_3$),

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- verify stream design flow from USGS (include flows from upstream plants!),
- verify statistical calculations presented by DEP in the Fact Sheet of the Draft Permit.

After imposition of the WQBEL, with a 59-month long compliance schedule, there are a number of ways to relax/remove the limit. Some of these options are actually specified in the permit itself (Part IV) and include:

1. Non-presence. Present 2 years of monthly data showing non-presence of the parameter at a detection level no higher than the RQL.

2. No Reasonable Potential. Alternatively, when the pollutant is detected, but at concentrations lower than WQBEL, the permittee could demonstrate that the pollutant has no reasonable potential to exceed the future, calculated permit limit. A small consolation is that the Department is presently allowing use of 95 % statistics in such "no reasonable potential analysis," which is more lenient that the traditionally used 99% statistics.

3. Better Hardness Data. For most heavy metals, the critical, aquatic life protection SWQC are a strong function of hardness (in the stream downstream from the discharge, at critical low flow conditions). If site-specific data are not available, NJ DEP uses a default hardness of 100 mg/L as CaCO3. For several tested dischargers in the Passaic Basin, effluent hardness was > 200 mg/L. The USGS data indicate that the Passaic River hardness is approximately 180 mg/L or more under low flow conditions, which is expected as the Passaic River is dominated by treated effluents at dry weather flows. Under such circumstances the SWQ criterion for metals such as copper and zinc could be close to double the default (see Table 2). In some other watersheds hardness could be lower (e.g. 45 mg/L in the Millstone River). It may be necessary to conduct an approved stream Water Quality Study to demonstrate a more favorable hardness.

Table 2. Effect of Hardness on Acute Water Quality Criteria

	Hardness - 100 mg/L as CaCO3 (Default)	Hardness - 20 mg/L as CaCO3
Copper Acute SWQC, µg/L	17	33
Zinc, Acute SWQC µg/L	114	206

4. Stream Design Flow. In calculating the available dilution, the Department relies on official MA7CD10 flow values provided by the USGS. These flow values are sometimes much lower than a sum of dry weather discharges from upstream municipal treatment plants, which are generally known to discharge continuously. This is probably due to the fact that USGS includes into its statistical calculations data generated prior to recent land development and treatment plant construction. Consequently that database does not take into account the present level of groundwater extraction and inter-basin potable water transfers. In at least 3 cases, USGS increased its determination of the design flow values (and thus available dilution) upon petitioning.

5. Translator. Aquatic life protection SWQC for most heavy metals is expressed as dissolved metal concentration. In turn, NJ Regulations require that NJPDES permit limits be expressed as total recoverable metals. During permit limit calculations, in order to translate from dissolved to total form, a "Translator" is used, which basically is a ratio of dissolved to total metal concentration. When no site-specific data for Translator determination are available, a default Translator specified in the Surface Water Quality Standards is used. The actual ratio of soluble to total recoverable metal could be lower than the default, giving an advantage. Table 3 provides data from an on-going translator study, which indicates that approximate 15% increase in the limit could be expected.

Table. 3 Translator Study Results for Zinc (no dilution available)

Data Point	Total Recoverable µg/L	Dissolved, µg/L	Ratio (Translator)
1	119	101	0.85
2	65.4	53.6	0.82
3	67.8	56.1	0.83
4	56.2	48.2	0.86
5	106	76.5	0.72
6	118	114	0.97
Averge	88.4	74.9	**0.84**
		Default Translator	~ **0.98**

6. Development of Site Specific Criteria. One other possibility of modifying the WQBEL is the development of site-specific SWQC for the parameter of concern. There are several types of EPA-approved studies, which could result in the development of a more appropriate limit. Studies of this type have not been previously conducted in NJ although several are presently underway.

Water Effect Ratio (WER) Study. This is a series of bioassays 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. Treated municipal effluent is believed to contain complexing agents, which chelate dissolved metal ions, making it biologically non-available and thus non-toxic. In an on-going study in central New Jersey, a WER of at least 2 for copper is expected, resulting in a commensurate (i.e. 2-fold) increase in the effluent limit for copper.

Recalculation Procedure. The objective of this type of study is to demonstrate that the most sensitive aquatic species, upon which the criterion for the particular toxic parameter was based, is not or could not be present in the receiving stream. The procedure usually requires a field species survey and habitat evaluation. One such study is presently under way in the Passaic River basin.

Resident Species Procedure. This is another type of EPA approved method, which is essentially a combination of the two procedures discussed above.

II. Compliance with Limit Through Source Control and/or Treatment

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 (notably NJAWC - Short Hills reservoir) at a dose of up to 0.3 mg/L (300 mg/L) as zinc. Table 4 provides data from a wastewater treatment facility, which service area is supplied by NJAWC. These data indicate that, indeed, potable water could easily account for the majority of the copper and zinc found in raw wastewater at this

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location. 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 highly variable concentration) potential industrial or commercial source is indicated and should be investigated.

Table 4. Zinc and Copper in Wastewater

Location \ Metal	Zinc	Copper
Potable Water, µg/L (*)	462	160
Raw Wastewater, µg/L (**)	374	80.3
Final Effluent, µg/L (**)	98	6.6
Percent Removal at Treatment plant, %	72	92

(*) Average from data collected on two occasions from several taps in the service area. "First flush" effect and limited data could be responsible for relatively high concentrations as compared to raw wastewater.
(**) Average from long-term monitoring results.

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. Table 4 indicates that approximately 70 % of zinc and 90 % of copper is being removed in this fashion at the tested facility. Literature data indicate that the removal of other heavy metals could normally be expected to be in a range from 50 to 90%. 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. Results from a series of tests conducted recently at several New Jersey facilities are summarized below.

Copper. Addition of coagulants such as alum or ferric, which are commonly used for phosphorus precipitation, will remove part of the residual copper from activated sludge effluent. Figure 1 presents typical results from jar tests indicating that ferric was somewhat more effective than alum in copper reduction at an equivalent metal ion dose. Another observation was that further increase of alum or ferric dose did not result in significant additional decrease of the residual copper. This is likely due to the presence of complexing agents in the treated effluents, which prevent residual copper from being precipitated/adsorbed by ferric salts (this is the same mechanism which makes copper non-available biologically, as discussed under the Water Effect Ratio procedure above). Consequently, these "standard" technologies may not be capable of removing the residual copper reliably to the levels required by some of the new permits.

Zinc. Addition of alum or ferric salts to activated sludge was not effective in reducing the residual zinc concentration, as illustrated on Figure 2. However, subsequent tests at several different facilities documented that the critical issue for effluent zinc concentration is

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the pH at which the activated sludge process operates (not the final effluent pH). This is shown on Figure 3, where the residual zinc concentration is a strong function of mixed liquor pH, with or without chemical addition. As shown in Table 4, 70% of the zinc is being removed at this facility. That zinc is incorporated into the biomass, thus sludge in the aeration basin naturally serves as a reservoir of zinc. As the zinc solubility is a strong function of pH in the moderate pH range, a decrease in the process pH can cause a transfer of zinc from sludge to solution, according to chemical equilibrium. An increase in pH causes zinc precipitation and incorporation into the sludge.

It should be noted that copper is also sensitive to process pH but at a much higher pH range, beyond what could be tolerated by activated sludge (and by standard pH permit limits). Another note is that an increase in the mixed liquor (aeration basin) pH requires typically much more caustic than a similar pH adjustment of the treated effluent.

Summary

1. A number of variables and factors are involved into determining the need for a limit for a heavy metal (or other toxic parameter), and into calculation of a numerical value for the limit. A permittee could undertake a number of different steps, even before the draft limits are proposed, to minimize its potential exposure to stringent limits.

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

3. Residual copper can be removed by conventional chemicals (alum/ferric) but only to a certain level.

4. Zinc removal is to a large degree governed by process pH (in activated sludge or in a polishing, tertiary step).

In summary, compliance with stringent limits for heavy metals can be challenging and costly. A thorough evaluation of all available options for limit modification and/or compliance is recommended to arrive at the most reasonable and cost effective solution.

Figure 1. Copper Removal from Activated Sludge Plant Effluent

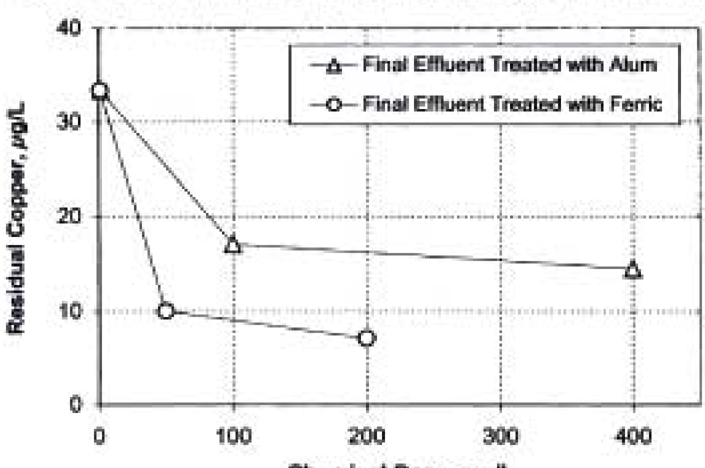


Figure 2. Effect of Coagulant Dose to Activated Sludge on Residual Zinc

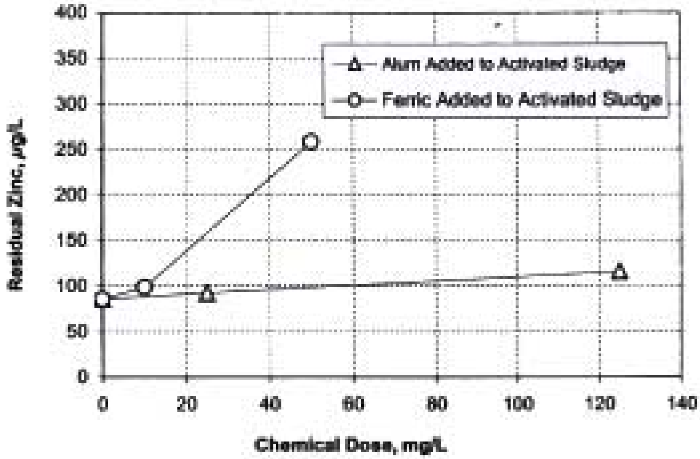
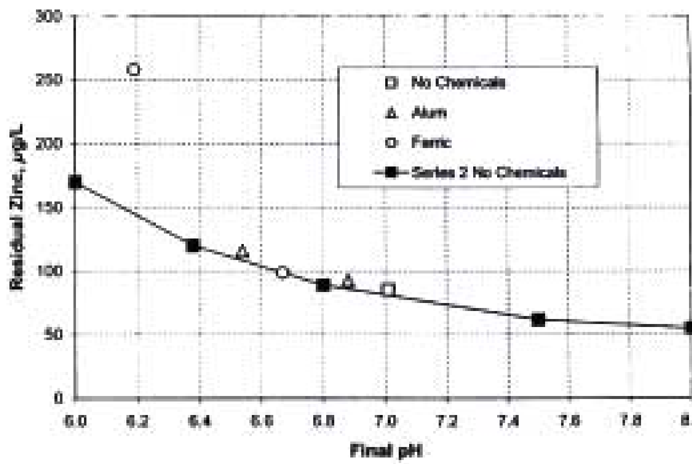


Figure 3. Effect of pH of Activated Sludge on Residual Zinc Concentration



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