

DEVELOPING PROTECTIVE HARDNESS-BASED METAL EFFLUENT LIMITATIONS

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BACKGROUND

The California and National Toxics Rules describe water quality standards for seven metals that vary as a function of hardness: (1) cadmium, (2) copper, (3) chromium III, (4) lead, (5) nickel, (6) silver, and (7) zinc. The equation describing the total recoverable regulatory criterion takes the form:

$$\text{Total Recoverable Criterion} = e^{m[\ln(H)]+b} \quad (1)$$

Where:

m = criterion-specific constant

H = hardness

b = criterion-specific constant

The constants “m” and “b” are specific to both the metal under consideration, and the type of total recoverable criterion water quality standard under consideration (i.e., acute standards or chronic standards).

The California Toxics Rule is very clear that the hardness to be used when implementing Equation 1 is not to exceed 400 mg/L without determination of a corresponding water effect ratio [§131.38(c)(4)(i)]. The rationale provided is that at hardness in excess of 400 mg/L, the relationships between hardness and other important inorganic constituents (e.g., alkalinity, pH) may not correspond with the relationships present in the dilution waters used for development of the criteria. The preamble to the California Toxics Rule states that should the effluent cause the hardness to exceed 400 mg/L, then “the hardness used in the hardness equation is the hardness of upstream water that does not contain the effluent.”

The guidance provided by the California Toxics Rule is less clear under conditions whereby the hardness is less than 400 mg/L. The California Toxics Rule states that with waters with a hardness of 400 mg/L or less, the actual ambient hardness of the surface water shall be applied [§131.38(c)(4)(i)] and that the hardness values used shall be consistent with the design discharge conditions established for design flows and mixing zones [§131.38(c)(4)(ii)]. This regulatory guidance has been applied with considerable variability in California’s Central Valley Region (Region 5). For example, historical methods used to implement this guidance include use of the lowest effluent hardness (e.g., Order No. 5-01-122), use of the lowest receiving water hardness (e.g., Order No. 5-01-120), use of a variable limit making use of the actual hardness observed after the discharge and receiving water mix (e.g., Order No. 5-01-242), estimates of what might constitute a reasonable hardness (e.g., Order No. 5-00-171), or any methodology adopted by a state in implementation of standards (e.g., 85th

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percentile lowest hardness of the ambient receiving water³). The variability in the manner by which hardness is applied to Equation 1 is likely because the term “ambient” is not defined by statute and “ambient” is simply defined as “all around; surrounding; encompassing⁴.”

Because of the non-linearity of Equation 1, some of the methodologies referenced above may be inconsistent with federal and state narrative toxicity objectives (i.e., “All waters shall be maintained free of toxic substances that produce detrimental physiological responses in human, plant, animal, or aquatic life”) because they result in the formation of toxicity after the mix of effluent into a receiving water when no toxicity may have been initially present in either the receiving water or whole effluent. In the sections that follow, it will be demonstrated that the methodology for assigning protective fixed (non-varying) effluent limitations must account for the non-linearity of Equation 1.

The purpose of this paper is to describe a methodologies for assigning fixed effluent limitations for hardness based metals that will be protective under all dilution conditions when the final mixed receiving water/effluent hardness is less than 400 mg/L, without being overly restrictive. Unless otherwise stated, the equations presented herein were developed for occasional effluent dominated conditions (i.e., an effluent discharge can constitute up to 100 percent of stream flow at times) and no use of environmental assimilative capacity (i.e., receiving water contaminant concentrations at water quality objectives prior to discharge of effluent). The methodologies can be easily modified to account for restricted ranges of fractional effluent to be present in a receiving water or to allow use of environmental assimilative capacity.

THEORY

The mixing of an effluent discharge into surface water under the wide variation of flow conditions that might be present (e.g., both low flows during the summer and high background flows during winter storm events) and the ensuing concentration is important when defining a protective water quality objective for use in assigning effluent limitations. The hardness of both the receiving water and effluent discharge water are typically different and variable, with neither always having the higher value. Reasons include use of groundwaters for municipal supply with subsequent discharge to surface waters, the import of water from other watersheds, the discharge to agricultural drains, or because municipal use of surface water increases hardness by approximately 75 to 225 mg/L⁵.

Because of the non-linearity of Equation 1, the relationship can be either concave downward or concave upward depending on the criterion-specific constants. The most appropriate, and protective, methodology is dependent on the type of relationship. Discussion pertaining to the appropriate methodology for assigning effluent limitations when the relationship is concave downward or concave upward is presented in the following sections.

³ United States Environmental Protection Agency (1991) **Technical Support Document for Water Quality-Based Toxics Control**, PB91-127415, Office of Water Enforcement and Permits, Office of Water Regulations and Standards, Washington, D.C.

⁴ Barnhart, C. L. and R. K. Barnhart (1980) **World Book Dictionary**, World Book-Childcraft International, Inc., Chicago.

⁵ Tchobanoglous, G. and Schroeder, E. D. (1985) **Water Quality**, Addison-Wesley Publishing Company, Reading, MA.

Concave Downward Criteria

For those contaminants whereby the regulatory criteria exhibit a concave downward relationship as a function of hardness (e.g., acute and chronic copper, chromium III, nickel, and zinc and chronic cadmium), use of the effluent hardness for establishment of water quality objectives is fully protective of all beneficial uses regardless of whether the effluent or receiving water hardness is higher. The rationale is most easily explained by example. Copper will be presented as an example for illustration purposes.

Effluent Hardness Higher Than Receiving Water Hardness. Assume that the minimum observed hardness of an effluent is 211 mg/L. A chronic water quality objective of 18 $\mu\text{g/L}$ corresponds with a hardness of 211 mg/L. Assume that the minimum hardness of the receiving water was 36 mg/L. A chronic water quality objective of 3.9 $\mu\text{g/L}$ corresponds with a hardness of 36 mg/L. If both the effluent and receiving water contain copper at exactly their water quality objectives, then no assimilative capacity would be present in either water prior to mixing, but both waters would be in compliance with their respective water quality objectives. The condition that would occur upon any mix of these two waters is illustrated in Figure 1.

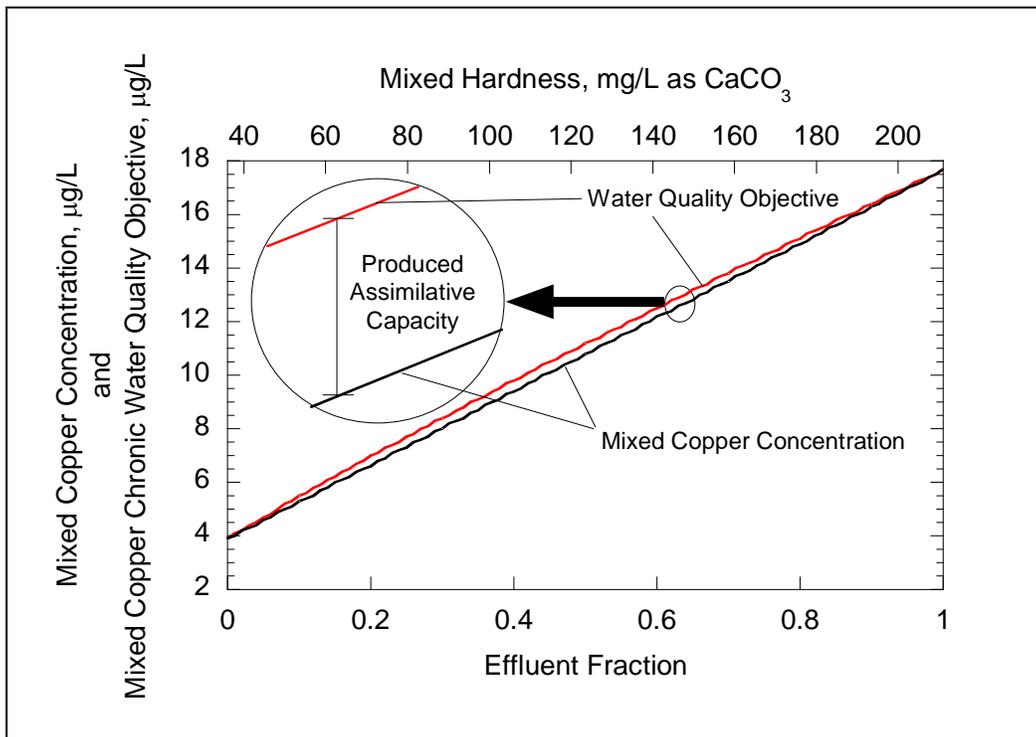


Figure 1
Illustration of the Assimilative Capacity that is Always Produced Upon Mixing Two Different Hardness Waters when the Regulatory Relationship is Concave Downward.

As depicted, because of the concave downward relationship between the copper water quality objective and hardness, assimilative capacity is always produced when two waters of differing hardness are mixed. Therefore, it is appropriate and protective to assign copper (and any other contaminant exhibiting a concave downward relationship) water quality objectives based on the hardness of the effluent. Further, the establishment of mixing zones is unnecessary because at any mixed or intermediate partially mixed condition, toxicity is never exerted.

Effluent Hardness Lower Than Receiving Water Hardness. Under conditions whereby the receiving water exhibits a higher hardness than does the effluent to be discharged into it, it remains appropriate to assign effluent limits based on the hardness of the effluent, even though it might feel intuitive to use the receiving water hardness. By way of example, assume a receiving water contains hardness at 36 mg/L and contains copper at its corresponding water quality criterion of 3.9 $\mu\text{g/L}$ and the effluent to be discharged into it contains hardness at 211 mg/L and also contains copper at its corresponding water quality criterion of 18 $\mu\text{g/L}$. As illustrated in Figure 2, any mix of these two waters will contain copper at a concentration below the corresponding mixed hardness water quality objective.

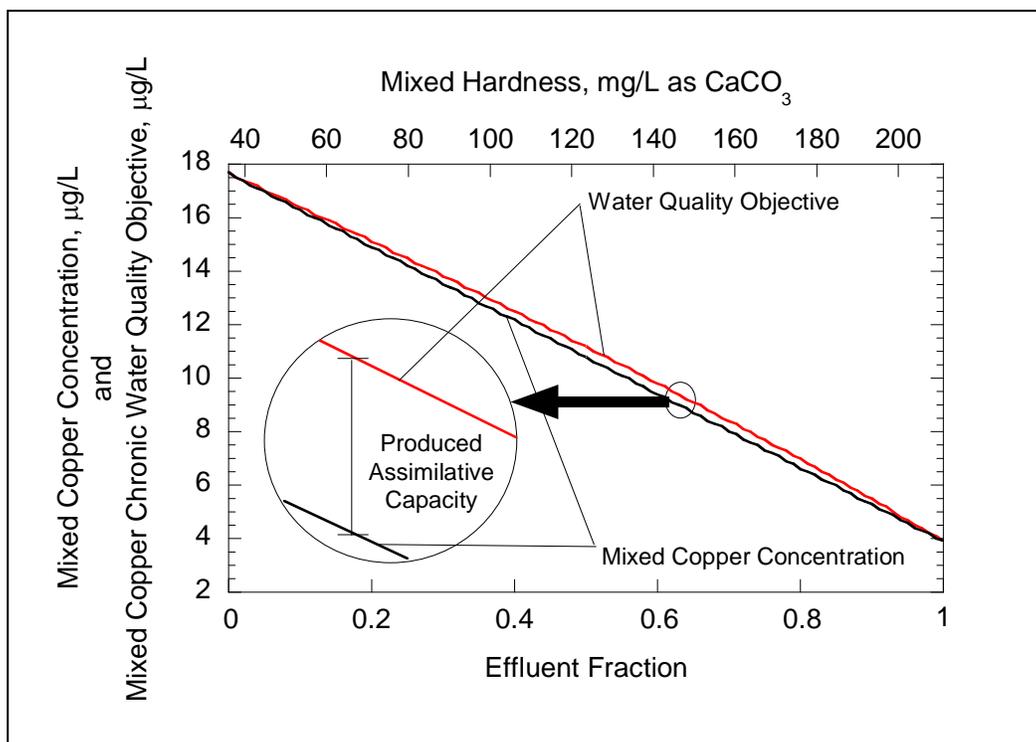


Figure 2
Illustration of the Assimilative Capacity that is Always Produced Upon Mixing Low Hardness Effluent Into a High Hardness Receiving Water

Concave Upward Criteria

For those contaminants whereby the regulatory criteria exhibit a concave upward relationship as a function of hardness (e.g., acute cadmium, acute and chronic lead, acute silver), a water quality objective based on either the effluent hardness or the receiving water hardness would not be protective under all mixing scenarios. Rather, an effluent limitation that accounts for both the hardness of the receiving water and the effluent is required. Discussion follows.

Effluent Hardness Higher Than Receiving Water Hardness. The following example illustrates how making use of the effluent hardness for determining water quality criteria (as was done for the concave downward criteria) can result in receiving water toxicity. The descriptive equation for the silver acute water quality objective (i.e., the Criterion Maximum Concentration, or CMC, as presented in the California Toxics Rule) is provided as Equation 2:

$$\text{Silver CMC} = e^{[1.72\ln(H)] - 6.52} \quad (2)$$

where the reported values of “m” and “b”⁶ for silver have been inserted into Equation 1 and “H” is as defined in Equation 1.

Should two different waters each containing silver at the regulatory criterion be mixed, then the resulting blend will contain silver at a concentration that exceeds the resulting mixed-hardness based acute water quality objective (CMC). For example, suppose an effluent exhibited a hardness of 211 mg/L and contained 15 µg/L of silver. This effluent would be in compliance with the CMC standard (Equation 2) associated with its hardness. Furthermore, suppose the receiving water exhibited a hardness of 36 mg/L and contained 0.70 µg/L of silver. This receiving water, too, would be in compliance with the CMC standard associated with its hardness. However, any mix of these two waters would not be in compliance with the CMC standard associated with the resulting hardness mix. This phenomenon is illustrated in Figure 3.

To ensure that the mixed concentration complies with the acute water quality objective, a water quality objective must be developed that is more restrictive than that based on the effluent hardness. Because the mixing of two different waters results in a linear contaminant concentration relationship, the final contaminant concentration in the mixed waters can be determined by:

$$\text{Mixed Concentration} = K_1x + K_2 \quad (3)$$

Where:

K_1 = slope of the mixing relationship

K_2 = initial receiving water contaminant concentration

x = contributory fraction of effluent

⁶ Environmental Protection Agency (2000) “Numeric Quality Standards; Establishment of Numeric Criteria for Priority Toxic Pollutants for the State of California; Rule,” 40 CFR Part 131, **Federal Register**, Vol. 65, No. 97

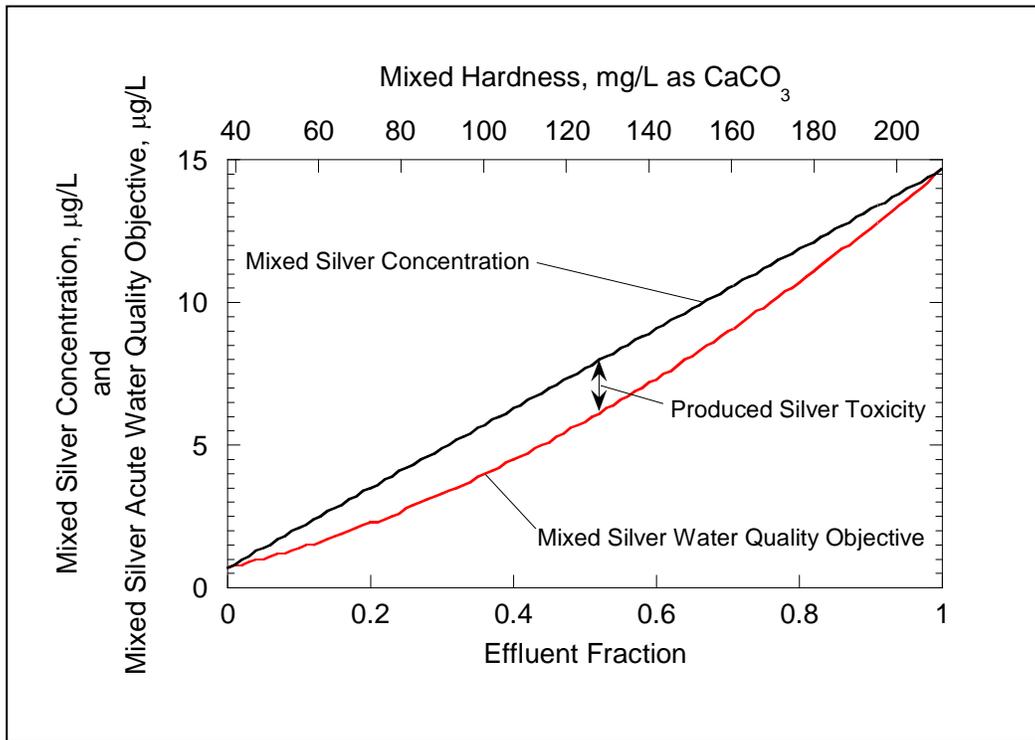


Figure 3
Impact of Mixing on the Development of Silver Toxicity

The constant K_1 can be determined by finding the derivative of the regulatory equation (illustrated in Figure 3) at $x = 0$ (i.e., ambient receiving water hardness). To determine the derivative, first define H as follows:

$$H = x(H_e) + (1-x)H_{rw} \quad (4)$$

Where:

H_e = hardness of the effluent

H_{rw} = hardness of the receiving water

and the other terms as defined previously. Combining Equation 4 with Equation 1 yields:

$$\text{Total Recoverable Criterion} = e^{m\{\ln[(x)(H_e) + (1-x)H_{rw}]\} + b} \quad (5)$$

The derivative of Equation 5 yields:

$$\left(\frac{\text{Total Recoverable Criterion}}{\text{Criterion}} \right)' = K_1 = \left(e^{m\{\ln[(x)(H_e) + (1-x)H_{rw}]\} + b} \right) \left(\frac{m}{(x)(H_e) + (1-x)(H_{rw})} \right) (H_e - H_{rw}) \quad (6)$$

Evaluating the derivative at $x = 0$ yields K_1 as follows:

$$K_1 = \left(\frac{m(H_e - H_{rw}) \left(e^{m\{\ln(H_{rw})\}+b} \right)}{H_{rw}} \right) \quad (7)$$

The constant K_2 is simply the water quality objective corresponding with the hardness of the receiving water (i.e., $x = 0$):

$$K_2 = e^{m\{\ln(H_{rw})\}+b} \quad (8)$$

Inserting Equations 7 and 8 into Equation 3, and evaluating at $x = 1$ (i.e., effluent limitations are assigned at 100 percent effluent) yields:

$$\text{Water Quality Objective} = \left(\frac{m(H_e - H_{rw}) \left(e^{m\{\ln(H_{rw})\}+b} \right)}{H_{rw}} \right) + e^{m\{\ln(H_{rw})\}+b} \quad (9)$$

Returning to the silver acute criterion example, a protective water quality objective when the lowest effluent and receiving water hardness is 211 and 36 mg/L, respectively, is calculated as follows:

$$\text{Water Quality Objective} = \left(\frac{1.72(211-36) \left(e^{1.72\{\ln(36)\}-6.52} \right)}{36} \right) + e^{1.72\{\ln(36)\}-6.52} = 6.6 \mu\text{g/L}$$

An illustration of the impact of mixing a receiving water with a hardness of 36 mg/L and a silver concentration of 0.7 $\mu\text{g/L}$ with an effluent with a hardness of 211 mg/L and a silver concentration of 6.6 $\mu\text{g/L}$ is illustrated in Figure 4, together with the applicable acute regulatory criteria. As shown, the developed fixed effluent limitation prevents an exceedance of the acute criteria regardless of the mixing condition and, therefore, is protective under all mixing conditions.

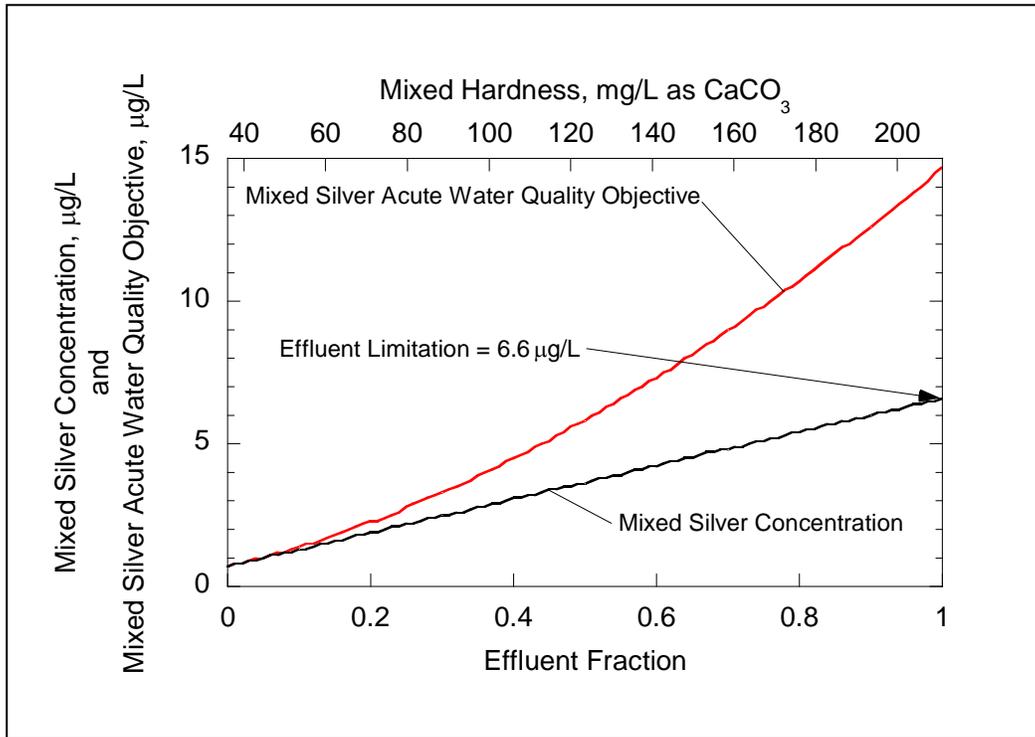


Figure 4
Impact of the Proposed Effluent Limitation Development Methodology on Silver Toxicity

Effluent Hardness Lower Than Receiving Water Hardness. The use of Equation 9 for deriving protective water quality criteria is not limited to the application of discharges of high hardness effluent to low hardness receiving waters. The use of Equation 9 when developing water quality criteria remains valid when applied to low hardness effluent discharging to high hardness receiving water. However, some further discussion is warranted because water quality criteria derived will be more restrictive than suggested directly by CTR, and in some cases may be negative (i.e., a negative concentration will be derived).

An example is provided in Figure 5. When determining the acute silver water quality criterion associated with discharging an effluent containing 60 mg/L of hardness into a receiving water containing 200 mg/L of hardness, use of Equation 9 yields a silver water quality criterion of -2.7 µg/L. Insofar as concentrations cannot be negative, such a result is actually a statement that the mixing of the effluent with such a low hardness, regardless of the effluent silver concentration, will decrease the receiving water hardness such that the silver already present within the surface water will exert toxicity. Thus, the discharge would cause or contribute to silver aquatic life toxicity via the reduction of hardness in addition to any toxicity that might occur due to the addition of silver. In this instance neither the use of the receiving water hardness nor the effluent hardness alone in Equation 1 would have been sufficient to prevent aquatic life silver toxicity.

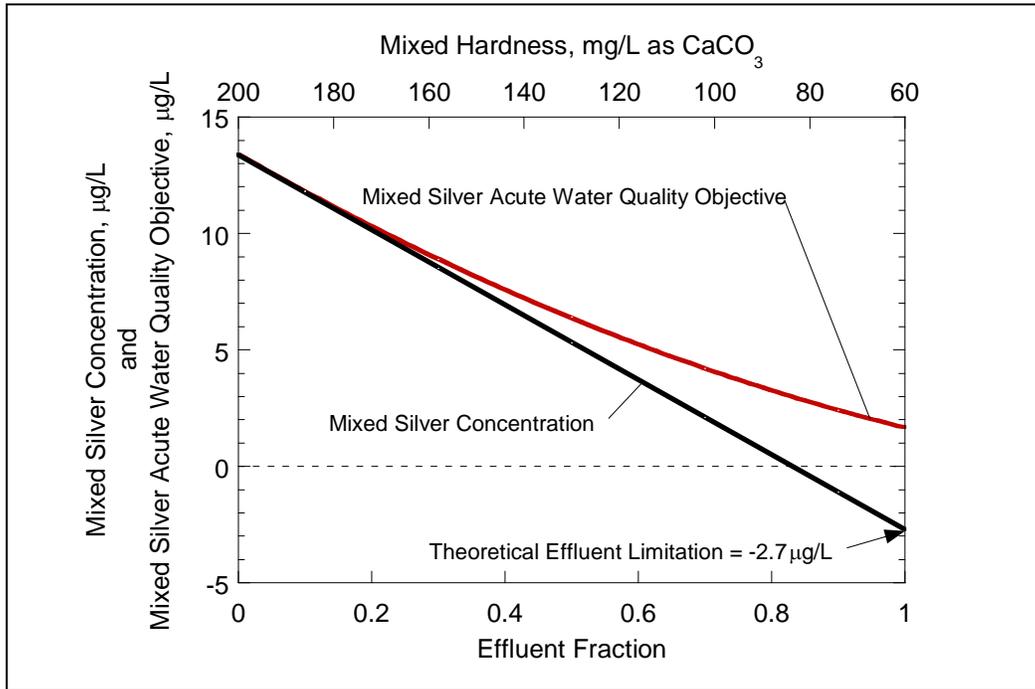


Figure 5
**Potential Impact of the Proposed Effluent Limitation Development Methodology
 When Low Hardness Effluent Is Discharged Into a High Hardness Receiving Water**

In the example illustrated in Figure 5, the significant difference in receiving water and effluent hardness leads to a condition that precludes discharge. However, the preclusion was due to the assumption that the receiving water at times contains silver up to its water quality criterion. Insofar as a high hardness condition within a receiving water may correspond with a water quality objective that is higher than maximum concentrations in the receiving water, it may be possible to discharge if data are available supporting use of a lower peak contaminant concentration for the receiving water.

The only method to allow for a discharge is to make use of some environmental assimilative capacity. To conduct a site-specific analysis that includes consideration of a lower peak receiving water contaminant concentration, use available monitoring data to assign a value to K_2 (i.e., the peak observed contaminant concentration in the receiving water). Together with the other known variables (e.g., H_e , H_{rw} , m , b), iterate a solution for “x” in Equation 10, below:

$$\frac{\left(e^{m(\ln((x)(H_e)+(1-x)(H_{rw})))} \right)^{b}}{(x)(H_e) + (1-x)(H_{rw})} + K_2 = e^{m(\ln((x)(H_e)+(1-x)(H_{rw})))} \quad (10)$$

Solve Equation 6 for K_1 at the value of “x” determined from Equation 10. The maximum allowable effluent concentration can be found by finally evaluating Equation 3 at $x = 1$. For example, assume a receiving water with 200 mg/L of hardness has been observed to contain silver as high as 12 $\mu\text{g/L}$. The solution for the appropriate water quality objective to be used to determine toxicity is illustrated in Figure 6. As shown, the effluent can contain up to 0.72 $\mu\text{g/L}$ of silver and any degree of mixing (or partial mixing) between the two waters will not exhibit toxicity.

Note that it is possible to solve Equation 10 and obtain a value of “x” that exceeds 1. Should this solution occur, it can be demonstrated that it is protective that the water quality objective be based on the effluent hardness.

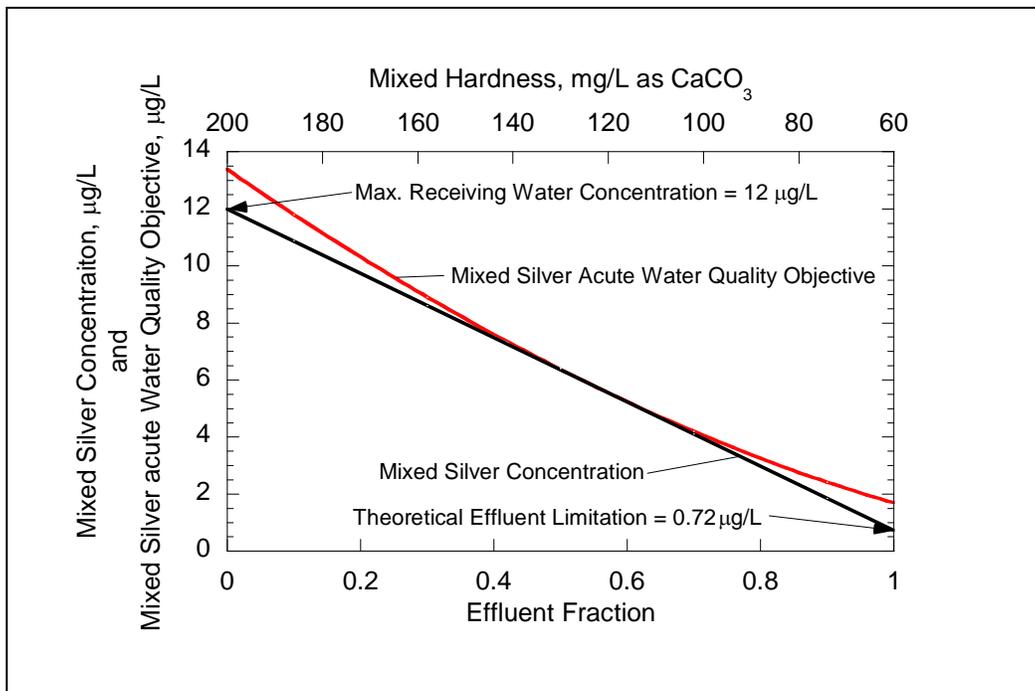


Figure 6
Illustration of the Theoretical Effluent Concentration Allowable When Discharging Low Hardness Effluent (Hardness = 60 mg/L) into a High Hardness Receiving Water (Hardness = 200 mg/L) That Contains Already 12 $\mu\text{g/L}$ of Silver.

PROPOSED IMPLEMENTATION

It is proposed to develop water quality criteria for use in conducting “reasonable potential” analyses for the assignment of effluent limitations based on the following methodology. It has

been demonstrated that the following methodology for setting fixed effluent limitations for hardness dependent metals will always be protective under all flow and mixing conditions (i.e., is independent of 1Q10 and 7Q10 design flows). In situations where maximum receiving water contaminant concentrations are less than water quality objectives or if effluent will never make up 100 percent of the stream flow, these same methodologies can be modified easily to set protective, fixed effluent limitations based on the maximum receiving water contaminant concentration or maximum percentage of effluent that will be present in the receiving water.

Concave Downward Criteria

The following methodology is directly applicable to effluent discharges that either are not to use any assimilative capacity of a receiving water or the effluent may constitute 100 percent of stream flow at times. The methodology is applicable for acute and chronic copper, acute and chronic chromium III, acute and chronic nickel, acute and chronic zinc, and chronic cadmium.

Effluent Hardness Higher Than Receiving Water Hardness. Make use of the lowest recorded effluent hardness when developing water quality objectives.

Effluent Hardness Lower Than Receiving Water Hardness. Make use of the lowest recorded effluent hardness when developing water quality objectives.

Concave Upward Criteria

The following methodology is applicable to acute cadmium, acute and chronic lead, and acute silver. A procedure for making use of some environmental assimilative capacity is also included.

Effluent Hardness Higher Than Receiving Water Hardness. Make use of the following equation, inserting the lowest recorded effluent hardness and highest recorded receiving water hardness. Note, the highest recorded receiving water hardness increases the difference between the hardness of the two waters and leads to the development of more restrictive water quality criteria.

$$\text{Effluent Limitation} = \left(\frac{m(H_e - H_{rw}) \left(e^{m \{ \ln(H_{rw}) \} + b} \right)}{H_{rw}} \right) + e^{m \{ \ln(H_{rw}) \} + b}$$

where

H_e = hardness of the effluent

H_{rw} = hardness of the receiving water

m = criterion-specific constant from CTR

b = criterion-specific constant from CTR

Effluent Hardness Lower Than Receiving Water Hardness. Assign K_2 the value of the highest receiving water contaminant concentration on record, regardless of corresponding receiving water

flow. Iterate a solution for “x” in the equation below, making use of the lowest recorded effluent and receiving water hardness:

$$\frac{\left(e^{m(\ln((x)(H_e)+(1-x)(H_{rw})))} \right)^{+b} (m)(H_e - H_{rw})(x)}{(x)(H_e) + (1-x)(H_{rw})} + K_2 = e^{m(\ln((x)(H_e)+(1-x)(H_{rw})))} + b$$

Use the value of “x” to solve for K_1 :

$$K_1 = \left(e^{m\{\ln[(x)(H_e) + (1-x)H_{rw}]\} + b} \right) \left(\frac{m}{(x)(H_e) + (1-x)(H_{rw})} \right) (H_e - H_{rw})$$

The water quality criterion is determined at “x=1:”

$$\text{Water Quality Criteria} = K_1x + K_2$$