

DATE: *draft*

TO:

FROM: Jim Schmidt - WR/2

SUBJECT: Evaluation of Hardness Values in the Calculation of Effluent Limitations Based Upon NR 105 Chronic Toxicity Criteria

The attached draft report summarizes an investigation by Tom Mugan (WW/2) and myself of the potential for using mix hardness values to calculate weekly average effluent limitations for several metals with NR 105 chronic toxicity criteria related to hardness. Up to now, the Department has typically used receiving water hardness to calculate chronic toxicity criteria (CTC) and effluent hardness to calculate acute toxicity criteria (ATC) because the former considers mixing zones in the generation of limits, while the latter does not. Based on our findings, there may be situations in Wisconsin which justify the use of a "mix" hardness value for the CTC calculations. This justification is supported through the investigation of general water chemistry issues, but will only make a significant difference in the CTC calculations and the resulting effluent limitations in selected situations. Where those situations occur, though, this may significantly impact WPDES permit recommendations relating to the need to included CTC-based limits in those permits, as well as just the calculated limits.

The situations where mix hardness evaluations are likely to be appropriate are as follows:

- 1) Mix hardness must be significantly different from the background water hardness, meaning the effluent hardness must be significantly different from (greater or less than) background.
- 2) The effluent flow must be fairly high compared to the applicable river flow, meaning relatively little dilution is available on a percentage basis. This doesn't mean the receiving water must be effluent-dominated, however.
- 3) Hardness added through the effluent is not likely to be "lost" through chemical reactions when mixed with the receiving water, meaning the likelihood of precipitation of calcium carbonate or biological uptake will be reduced. This is most likely to occur in areas of low pH and/or low hardness in background waters.

The attached report discusses this evaluation in more detail, including a summary of general examples for determining when the mix hardness consideration is appropriate and some speculation on where the affected discharges are likely to occur. I would like to thank David Webb of the Bureau of Water Resources Management, Tom Mugan of the Municipal Wastewater Section and Kathy Bartilson of NWD for their contributions in generating the supporting documentation.

**EVALUATION OF THE USE OF MIX POINT HARDNESS VALUES IN THE
CALCULATION OF WEEKLY AVERAGE EFFLUENT LIMITATIONS
BASED UPON NR 105 CHRONIC TOXICITY CRITERIA**

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INTRODUCTION

Several substances have water quality criteria in ch. NR 105 that are related to water hardness. These substances, which include cadmium, chromium, copper, lead, nickel, silver and zinc, are less toxic in harder waters. Chemical characteristics of hard water, as defined by calcium carbonate concentrations, have a significant effect upon the following conditions:

1. Chemical/ionic speciation of the metal in the surrounding water,
2. Strength and extent of binding and/or chelation of the metal in the surrounding water, and
3. Cellular calcium content in the effected organism.

In most cases, speciation, binding, and cellular calcium content control the extent to which metals are able to traverse gill membranes or other biological tissues leading to bioavailability and toxicity. Because of this relationship, water quality criteria may be significantly different between the northern and western parts of Wisconsin, where water is relatively soft, and the eastern and southern parts of the state where water is harder.

Along with the difference in the relative criteria, one must also consider the impact of these differences on effluent limitations. Acute toxicity criteria (ATC) do not factor in any sort of mixing zone evaluation besides the LC50/LC1-based 2:1 ratio that is used in ch. NR 106 to calculate daily maximum limitations, unless there is a zone of initial dilution, but that is somewhat rare. As a result, the only difference in these effluent limitations from one part of the state to another is in the applicable hardness, which has commonly been represented by the mean effluent hardness since mixing zones are not typically considered in terms of ATC. The common sense approach of using effluent hardness to calculate ATC has not been questioned since NR 105 and 106 were first published in 1989, except in certain cases where a Zone of Initial Dilution (ZID) is used to calculate ATC-based limits because those situations are unusual in that mixing zones are considered, but mixing takes place rapidly.

When considering chronic toxicity criteria (CTC), not only does hardness impact the calculations and WPDES permit recommendations, but in addition, background levels of the metals being evaluated play a part in the evaluation process along with the relative dilution rate within the so-called mixing zone. To that end, ch. NR 106 is somewhat silent regarding the hardness value to be used in the CTC calculation.

Until now, the common approach has been to use the background hardness in calculating CTC because of the common notion that the criteria should be considered independently of the existence of mixing zones due to the fact that they are only applicable outside of those mixing zones.

However, it has been noted that there are cases in which the "edge-of-mixing-zone" hardness value is not the same as the background value, that some form of intermediate level is achieved in these isolated cases. Are there cases in which the effluent hardness, the background hardness, a "mix" value, or some other alternative value is appropriate? The purpose of this report is to summarize an investigation of these situations and project them into real-world situations in Wisconsin where alternatives may be more appropriate. If these alternative values are significantly different than background, this could have a significant impact on both the water quality-based effluent limitations calculated by the Department and the occasions in which those limitations are included in WPDES permits.

THE CHEMISTRY OF "HARDNESS"

For the most part, hardness can be considered a conservative parameter of the ranges of values seen in the State of Wisconsin. Hardness of inland waters may vary from approximately 25 ppm in northwestern Wisconsin (upper reaches of the Black, Chippewa and Wisconsin River basins), to about 75 ppm in Lake Superior, to 100 - 200 ppm in the Wolf River, Fox (Wisconsin), Mississippi River, and lower Wisconsin River basins as well as Lake Michigan, to 200 - 300 ppm in some of the streams feeding into Lake Michigan between Green Bay and Milwaukee, and in the 300 - 400 ppm range in the Rock, Fox (Illinois), and Des Plaines River basins. These ranges have a significant impact on the NR 105 CTC for several metals, with criteria in hard waters (350 ppm) being 5 to 29 times the same criteria in soft waters (25 ppm):

Table 1 - Hardness-to-CTC relationship

<u>Substance</u>	NR 105 CTC (in ug/L) at Hardness of:				<u>Variation over range</u>
	<u>25 ppm</u>	<u>100 ppm</u>	<u>200 ppm</u>	<u>350 ppm</u>	
Cadmium:					
GL & CW	0.61	1.82	2.80	2.80	4.6 X
WWSF & others	0.68	2.02	3.11	3.11	4.6 X
Chromium (+3)	17.37	54.60	95.37	139.78	8.0 X
Copper	3.12	11.51	22.12	37.48	12.0 X
Lead	1.73	10.09	24.38	49.70	28.7 X
Nickel	20.47	66.13	118.9	155.14	7.6 X
Silver	0.39	1.99	4.48	6.08	15.6 X
Zinc	15.32	49.59	89.23	143.36	9.4 X

The above example criteria are the same for all classifications except for cadmium as noted (Aug. 1995 version of NR 105). For cadmium, criteria above a hardness of 173 ppm are the same as at 173 ppm.

With the extreme variation in the criteria over the above hardness range, selection of the appropriate hardness value in criteria and limits calculations is extremely important. The term "hardness" is defined as the sum of the calcium and magnesium concentrations, and hardness may be determined either by calculation from separate determinations of calcium and magnesium or by EDTA titration.

After mixing of a discharge and a receiving water, the only changes (other than through uptake or release by organisms) which could occur that would potentially alter hardness levels are dissolution or precipitation of minerals that contain calcium and magnesium.

DISSOLUTION

In the part of the state where we would likely apply the mix hardness calculation, there is little carbonate rock from which to dissolve calcium or magnesium ions. If dissolution of calcium or magnesium would occur, hardness levels would rise. This would not be a concern in those cases because metals are less toxic in harder waters.

PRECIPITATION

If hardness levels added to the receiving water were sufficiently high, precipitation of minerals would occur. Calcium carbonate would form as a white precipitate which would cause dissolved hardness levels to decrease, or be less than the levels calculated using a straight mass balance approach. This does not typically occur with respect to municipal effluents, so this may be more of a concern in industrial effluents or in municipalities where a significant portion of the discharge consists of industrial contributions. Since industrial contribution percentages vary from community to community, the precipitation issue should be investigated and considered at all locations where mix hardness is significantly different from the background value. Of course, if the mix and background values are not significantly different, the mix hardness process will likely have a minimal effect on effluent limitations.

In southern Wisconsin, surface water hardness values of 200 to 350 ppm are not uncommon. Because much of this hardness is in the form of carbonate hardness (which imparts alkalinity to the water), pH levels are also relatively high. In southern Wisconsin, pH ranges of 7.5 to 8.5 are typical (usually in the upper half of that range). In northern Wisconsin, hardness levels are generally much lower and, in turn, pH levels are also much lower except in impounded waters.

Calcium carbonate (CaCO_3) is only slightly soluble ($K_{sp} = 4.7 \times 10^{-9}$). However, at the normal pH of surface waters, most of the inorganic carbon is the form of the highly soluble bicarbonate ion (HCO_3^-), so we see levels of calcium which are much higher than would be predicted by the solubility product. At lower pH, less carbonate (CO_3^{2-}) is present. Therefore, one could claim that the "hardness capacity" of the lower pH waters in northern Wisconsin would be even higher than in southern Wisconsin and, therefore, precipitation would not be a problem in terms of this analysis and application.

However, as mentioned earlier, pH levels in impounded waters can climb relatively high, even in northern parts of the state. In addition, there are other water quality parameters such as total dissolved solids (TDS) and alkalinity which may impact the "hardness capacity" of natural waters. One method used in the water supply industry to determine if a given water is saturated with respect to calcium carbonate is to calculate what is called the Langelier Index (LI).

$$\text{LI} = \text{pH} - \text{pH}_s$$

Where: pH is the measured pH in the water and
 pH_s is the calculated saturation pH of the water.

A negative LI indicates a water which is undersaturated with respect to calcium carbonate, while a positive LI indicates a water which is oversaturated with respect to calcium carbonate. Another way of saying this is that **if the saturation pH is greater than the measured pH (negative LI), the water is undersaturated and calcium carbonate will not precipitate.** In critical situations where the use of mix hardness is being considered, the saturation pH should be calculated and compared to measured pH values to determine if precipitation will potentially occur, because if precipitation potentially occurs, mix hardness is not likely to be encountered in the environment and, if used, may underestimate the metals toxicity potential of the water in question.

Following the procedure given in Process Chemistry for Water and Wastewater Treatment by Benefield, Judkins, and Weand, saturation pH may be calculated using the following equation which is applicable over a pH range of 6.5 to 9.5:

$$\text{pH}_s = \text{pK}'_2 + \text{pCa}^{2+} - \text{pK}'_s - \log(2[\text{Alk}]) - \log \gamma_m$$

Where: pK'_2 = the second equilibrium constant in the carbonic acid system adjusted for temperature and ionic strength,
 pCa^{2+} = the negative log of the calcium ion concentration,

$pK'_s =$ the solubility equilibrium constant for calcium carbonate adjusted for temperature and ionic strength,

Alk = alkalinity in moles per liter, and

$\gamma_m =$ an additional correction for ionic strength.

The following table provides example values for pK'_2 , pK'_s , and γ_m for various levels of TDS of the water. Since the solubility of calcium carbonate decreases with increasing temperature, the most critical condition is assumed to be 25°C, the default summer temperature used in Wisconsin waters. Since low-flow conditions typically occur in mid-summer when temperature is highest, this critical condition assumption is reasonably protective of conditions during the remainder of the year. In addition, the ionic strength at 25°C is assumed to be equal to $2.5 \times 10^{-5} \times \text{TDS}$. For other TDS concentrations, values may be interpolated from those in the table.

Table 2
Values of pK'_2 , pK'_s , and γ_m at various TDS concentrations and 25°C

TDS (mg/L)	$\log(\gamma_m)$	pK'_2	pK'_s
50	-0.0111	10.29	8.24
100	-0.0239	10.23	8.14
200	-0.0330	10.20	8.07
400	-0.0450	10.15	7.97
1000	-0.0659	10.07	7.80

To obtain pCa^{2+} , use the measured hardness values (in mg/L as calcium carbonate) even though magnesium may account for some of the hardness. This is a conservative approach with respect to water quality since the solubility of magnesium carbonate is much greater than the solubility of calcium carbonate.

$$pCa^{2+} = -\log(\text{hardness} \times 10^{-5})$$

Alkalinity in the saturation pH equation must be expressed in units of moles per liter. To convert from alkalinity values given in units of mg/L as calcium carbonate to units of moles per liter, multiply by 10^{-5} .

$$\text{Alk (in moles/L)} = \text{Alk (in mg/L)} \times 10^{-5}$$

EXAMPLES

In order to evaluate the applicability of mix hardness calculations using the previous discussion, the following actual information is required:

EFFLUENT FLOW

RECEIVING WATER FLOW (for this, the portion of the $7Q_{10}$ or $4Q_3$ used to calculate CTC-based limits)

RECEIVING WATER pH

EFFLUENT HARDNESS

RECEIVING WATER HARDNESS

RECEIVING WATER ALKALINITY (this shouldn't be much different than hardness, so hardness may be used if alkalinity isn't available)

RECEIVING WATER TOTAL DISSOLVED SOLIDS (but the difference between total solids and total suspended solids may be used to represent TDS, STORET may refer to these parameters as total residue and total non-filtrable residue, respectively)

EFFLUENT TOTAL DISSOLVED SOLIDS (This is generally unknown because it's not reported on DMRs. It may be available from a treatment plant operator, but it may be estimated if EFFLUENT HARDNESS and EFFLUENT CHLORIDES are known. The estimated TDS in mg/L equals the hardness plus 1.65 X chlorides in mg/L. This formula may also be used to estimate receiving water TDS if unknown, but the collection of actual data should be encouraged, particularly for effluent.)

MIX TOTAL DISSOLVED SOLIDS (calculated from effluent and receiving water)

No defaults should be accepted, this process should encourage the collection and reporting of actual data (particularly hardness, pH and, where possible, TDS) as a means of justifying the "mix hardness" consideration. Other parameters referenced earlier in this report can either be calculated or interpolated from tables.

Examples of this approach can, therefore, only be evaluated where this information is available (STORET is an example source), though there may be situations where one can rule out mix hardness as a viable alternative immediately. Those situations may be deduced from the examples shown here. These examples will also serve to illustrate the likely locations where mix hardness may be considered in general. Please note that the hardness, pH, and TDS values referenced here represent receiving water values.

1) City of Medford (low dilution, low hardness, low pH)

Effluent flow = 1.45 MGD (2.24 cfs)

$7Q_{10} = 0.86$ cfs (100% of the $7Q_{10}$ is used for mixing, $IWC = 2.24/3.10 = 72\%$)

Effluent hardness = 190 ppm

Receiving water hardness = 78 ppm
 Calculated mix hardness = 158.9 ppm
 Rec. water alkalinity = hardness (at Neillsville, which is downstream of Medford, hardness = 59.5 ppm and alkalinity = 58 ppm, so this assumption is reasonable)
 Rec. water total solids = 121.6 mg/L
 Rec. water suspended solids = 5.7 mg/L
 Calculated receiving water TDS = 121.6 - 5.7 = 116 mg/L
 Effluent chlorides = 20 mg/L (from water supply data)
 Effluent TDS = 223 mg/L
 Mix TDS = 193 mg/L
 Rec. water pH = 7.3

From Table 2:

$$\begin{aligned}
 pK'_2 &= 10.20 \\
 pCa^{2+} &= -\log(158.9 \times 10^{-5}) = -(-2.80) = 2.80 \\
 pK'_s &= 8.07 \\
 \log(2[Alk]) &= \log(2 \times 158.9 \times 10^{-5}) = \log(3.178 \times 10^{-3}) = -2.50 \\
 \text{[In the above, assume mix alkalinity = mix hardness since the receiving water values were similar. In reality, alkalinity will be slightly less than hardness, so } \log(2[Alk]) \text{ will be slightly greater than } \log(2[Hardness]). \text{ The effect of this would be to slightly reduce LI, which probably won't affect the conclusions much.]} \\
 \log \gamma_m &= -0.0324 \\
 \text{Saturation pH} &= 10.20 + 2.80 - 8.07 + 2.50 + 0.0324 = 7.46 \\
 \text{Measured pH} &= 7.3 \\
 \text{LI} &= 7.3 - 7.46 = -0.16 < 0
 \end{aligned}$$

Since $LI < 0$, precipitation is unlikely and the mix hardness may be used to calculate limits. It may be concluded that **where background hardness is relatively low and little dilution is available, mix hardness is more appropriate to be used to calculate CTC since precipitation is less of a concern.**

2) City of Wausau (high dilution, low hardness, low pH)

Effluent flow = 8.2 MGD (12.7 cfs)
 7Q10 = 850 cfs (25% of the 7Q10 is used for mixing, $IWC = 12.7 / 225.2 = 5.6\%$)
 Effluent hardness = 107 ppm
 Receiving water hardness = 44 ppm
 Calculated mix hardness = 48 ppm
 (NOTE: Since mix hardness is close to receiving water hardness, this exercise is probably pointless for a facility like Wausau, but I'll finish it anyway)
 Rec. water alkalinity = 30 ppm
 Estimate effluent alk. = effluent hardness = 107 ppm, so mix alk. = 34 ppm
 Rec. water total solids = 103 mg/L

[CONTINUED ON NEXT PAGE]

unless pH values are high (such as to impoundments)

Rec. water suspended solids = 7 mg/L
 Calculated receiving water TDS = 96 mg/L
 Effluent chlorides = 10 mg/L (from water supply data)
 Estimated effluent TDS = 123 mg/L
 Mix TDS = 98 mg/L
 Rec. water pH = 7.2

From Table 2:

$$\begin{aligned}
 pK'_2 &= 10.23 \\
 pCa^{2+} &= -\log(48 \times 10^{-5}) = -(-3.32) = 3.32 \\
 pK'_s &= 8.14 \\
 \log(2[\text{Alk}]) &= \log(2 \times 34 \times 10^{-5}) = \log(6.8 \times 10^{-4}) = -3.17 \\
 \log \gamma_m &= -0.0237 \\
 \text{Saturation pH} &= 10.23 + 3.32 - 8.14 + 3.17 + 0.0237 = 8.60 \\
 \text{Measured pH} &= 7.2 \\
 LI &= 7.2 - 8.60 = -1.4 < 0
 \end{aligned}$$

Again, mix hardness may be considered here, but since the relative dilution is so high, it makes a very small difference in the calculated chronic toxicity criteria. A better example for a low hardness, low TDS river like the Wisconsin would be in a situation where as little dilution as possible was available, such as downstream at Wisconsin Rapids where a discharge exists having high flow and hardness.

3) Consolidated Papers - Wisconsin Rapids (joint treatment center)

Effluent flow = 27.9 MGD (43.2 cfs)
 7Q10 = 999 cfs (25% of the 7Q10 is used for mixing and the CPI water is withdrawn from the river, IWC = $43.2 / 249.75 = 17.3\%$)
 Effluent hardness = 250 ppm
 Receiving water hardness = 63 ppm (Biron data)
 Calculated mix hardness = 95 ppm
 Rec. water alkalinity = 50 ppm (estimated)
 Estimate effluent alk. = effluent hardness = 250 ppm, so mix alk. = 85 ppm
 Rec. water total solids = 150 mg/L
 Rec. water suspended solids = 11 mg/L
 Calculated receiving water TDS = 139 mg/L
 Effluent chlorides = 5 mg/L (estimated as equal to river)
 Estimated effluent TDS = 258 mg/L
 Mix TDS = 160 mg/L
 Rec. water pH = 7.2

From Table 2:

$$\begin{aligned}
 pK'_2 &= 10.21 \\
 pCa^{2+} &= -\log(95 \times 10^{-5}) = -(-3.02) = 3.02
 \end{aligned}$$

$$\begin{aligned}
pK'_s &= 8.10 \\
\log(2[\text{Alk}]) &= \log(2 \times 85 \times 10^{-5}) = \log(1.7 \times 10^{-3}) = -2.77 \\
\log \gamma_m &= -0.0294 \\
\text{Saturation pH} &= 10.21 + 3.02 - 8.10 + 2.77 + 0.0294 = 7.93 \\
\text{Measured pH} &= 7.2 \\
\text{LI} &= 7.2 - 7.93 = -0.7 < 0
\end{aligned}$$

It appears that when background pH is very low, there's a good chance that a mix hardness calculation will be appropriate because it won't be likely that precipitation will occur. The next examples look at harder water situations, though.

4) City of Peshtigo

Effluent flow = 4.2 MGD (6.5 cfs)
 7Q10 = 150 cfs (50% of the 7Q10 is used for mixing based on a study and the City gets 90% of its flow from Badger Paper's pulp mill whose water is withdrawn from the river, IWC = $6.5 / 75.65 = 8.6\%$)
 Effluent hardness = 501 ppm
 Receiving water hardness = 135 ppm
 Calculated mix hardness = 166 ppm
 Rec. water alkalinity = 117 ppm
 Estimate effluent alk. = effluent hardness = 501 ppm, so mix alk. = 150 ppm
 Rec. water total solids = 176 mg/L
 Rec. water suspended solids = 6 mg/L
 Calculated receiving water TDS = 170 mg/L
 Effluent chlorides = unknown
 Estimated effluent TDS = 501 mg/L (no chlorides data from Badger Paper, which makes up 90% of the POTW flow, so to be conservative TDS is set equal to hardness)
 Mix TDS = 198 mg/L
 Rec. water pH = 7.8

Since eff H is very high (given the ind. contribution) this may be a case where we'd want eff alk data to verify the # in the calc/ability to use mg/L

From Table 2:

$$\begin{aligned}
pK'_2 &= 10.20 \\
pCa^{2+} &= -\log(166 \times 10^{-5}) = -(-2.78) = 2.78 \\
pK'_s &= 8.07 \\
\log(2[\text{Alk}]) &= \log(2 \times 150 \times 10^{-5}) = -2.52 \\
\log \gamma_m &= -0.0328 \\
\text{Saturation pH} &= 10.20 + 2.78 - 8.07 + 2.52 + 0.0328 = 7.46 \\
\text{Measured pH} &= 7.8 \\
\text{LI} &= 7.8 - 7.46 = 0.34 > 0
\end{aligned}$$

In this case, the LI calculation resulted in a positive number (Langelier Index > 0), which means the water is oversaturated with respect to calcium carbonate and

precipitation is likely to occur. As a result, a mix hardness calculation is not likely to be representative of receiving water conditions.

5) City of Janesville

Effluent flow = 17.75 MGD (27.5 cfs)
7Q10 = 200 cfs (25% of the 7Q10 is used for mixing, IWC = 27.5 / 77.5 = 35.5%)
Effluent hardness = 339 ppm
Receiving water hardness = 309 ppm
Calculated mix hardness = 320 ppm
Rec. water alkalinity = 245 ppm
Estimate effluent alk. = effluent hardness = 339 ppm, so mix alk. = 278 ppm
Rec. water total solids = 450 mg/L
Rec. water suspended solids = 41 mg/L
Calculated receiving water TDS = 409 mg/L
Effluent chlorides = 15 mg/L
Estimated effluent TDS = 365 mg/L
Mix TDS = 393 mg/L
Rec. water pH = 8.4

From Table 2:

pK'_2	=	10.15	
pCa^{2+}	=	$-\log(320 \times 10^{-5})$	= 2.49
pK'_s	=	7.97	
$\log(2[\text{Alk}])$	=	$\log(2 \times 278 \times 10^{-5})$	= -2.25
$\log \gamma_m$	=	-0.045	
Saturation pH	=	$10.15 + 2.49 - 7.97 + 2.25 + 0.045$	= 6.97
Measured pH	=	8.4	
LI	=	$8.4 - 6.97$	= 1.43 > 0

6) City of Kewaunee

Effluent flow = 0.584 MGD (0.9 cfs)
7Q10 = 6.9 cfs (25% of the 7Q10 is used for mixing, IWC = 0.9 / 2.62 = 34%)
Effluent hardness = 469 ppm
Receiving water hardness = 330 ppm
Calculated mix hardness = 378 ppm
Rec. water alkalinity = 283 ppm
Estimate effluent alk. = effluent hardness = 469 ppm, so mix alk. = 347 ppm
Rec. water total solids = 480 mg/L
Rec. water suspended solids = 12 mg/L
Calculated receiving water TDS = 468 mg/L
Effluent chlorides = 25 ppm (from water supply data)
Estimated effluent TDS = 510 mg/L [CONTINUED ON NEXT PAGE]

Mix TDS = 482 mg/L
Rec. water pH = 8.1

From Table 2:

$$\begin{aligned} pK'_2 &= 10.14 \\ pCa^{2+} &= -\log(378 \times 10^{-5}) = -(-2.42) = 2.42 \\ pK'_s &= 7.96 \\ \log(2[\text{Alk}]) &= \log(2 \times 283 \times 10^{-5}) = -2.25 \\ \log y_m &= -0.05 \\ \text{Saturation pH} &= 10.14 + 2.42 - 7.96 + 2.25 + 0.05 = 6.9 \\ \text{Measured pH} &= 8.1 \\ \text{LI} &= 8.1 - 6.9 = 1.2 > 0 \end{aligned}$$

In Cases 5 and 6, we wouldn't consider mix hardness because the measured pH exceeds the saturation pH, but it probably doesn't make much difference because both effluent and receiving water hardnesses are very high.

7) City of Eau Claire

Effluent flow = 11.5 MGD (17.8 cfs)
7Q10 = 714 cfs (25% of the 7Q10 is used for mixing, IWC = $17.8 / 196.3 = 11\%$)
Effluent hardness = 77 ppm
Receiving water hardness = 53 ppm
Calculated mix hardness = 55 ppm
Rec. water alkalinity = 50 ppm
Estimate effluent alk. = effluent hardness = 77 ppm, so mix alk. = 52 ppm
Rec. water total solids = 75 mg/L
Rec. water suspended solids = 4 mg/L
Calculated receiving water TDS = 71 mg/L
Effluent chlorides = 2.5 ppm (from water supply data)
Estimated effluent TDS = 80 mg/L
Mix TDS = 72 mg/L
Rec. water pH = 7.3

From Table 2:

$$\begin{aligned} pK'_2 &= 10.26 \\ pCa^{2+} &= -\log(55 \times 10^{-5}) = 3.26 \\ pK'_s &= 8.2 \\ \log(2[\text{Alk}]) &= \log(2 \times 52 \times 10^{-5}) = -2.98 \\ \log y_m &= -0.017 \\ \text{Saturation pH} &= 10.26 + 3.26 - 8.2 + 2.98 + 0.02 = 8.32 \\ \text{Measured pH} &= 7.3 \\ \text{LI} &= 7.3 - 8.32 = -1.0 < 0 \end{aligned}$$

Here, mix hardness can be considered, but since the dilution is so high, the difference between background and mix is very small and will have little impact on the limits (compared to dilution, at least).

SUMMARY

The LI values calculated in the above examples are not very useful on their own except for comparing to each other and to zero (for determining if LI is positive or negative). Some generalizations may be reached from the examples, though. The conclusions reached above show that precipitation is most likely to occur where receiving water hardness is high or where receiving water pH is high. Combinations of these conditions could magnify or reduce this concern. In consideration of that, the situations where a mix hardness calculation is not as likely to result in precipitation conditions and, just as importantly, where mix hardness may have a more significant impact on the calculated effluent limitations and WPDES permit recommendations, is as follows:

- * **Mix hardness may be considered where the background hardness is relatively low and where the background pH is relatively low. The impact of TDS appears to follow the impact of hardness since you won't find low TDS where hardness is high. This will affect criteria calculations only where dilution is relatively low, though, because otherwise the mix hardness will approach background.**

These conditions are most likely to exist in fairly small streams with large discharges to them, those streams most likely need to be in the northern or western parts of the state, and the discharge site cannot be directly to lakes or impoundments or nearby downstream of those waterbodies where pH levels may be elevated. Discharges which occur in high-dilution situations, even in those parts of the state, may be "eligible" for mix hardness consideration, but the impacts on their limits will be small because of the large dilution factors.

In my estimation, communities which will most likely benefit from mix hardness evaluations include Ellsworth, Medford, Black River Falls, Abbotsford, Marshfield, Tomah and Antigo if effluent and background hardness values are dissimilar. However, communities such as Ellsworth, Abbotsford and Marshfield discharge to variance streams or streams with little or no background flow, so those are situations where effluent hardness should be considered for calculating chronic toxicity criteria along with acute anyway, a mix calculation will just result in a value equal to effluent anyway, regardless of the results obtained for the other parameters such as alkalinity, TDS, pH, or chlorides.

For the other communities with somewhat more dilution available, effluent hardness is well above background stream hardness, and these are all places with low dilution

factors (but non-zero), so the mix hardness will be very different from background. Industries in these areas may also benefit from mix hardness calculations, along with larger discharges such as some of the larger paper mills along the Wisconsin River. There may actually be some direct Great Lakes discharges which may benefit from mix hardness calculations as well because the pH in the Great Lakes waters are fairly low. Where background streamflows are close to zero, it is likely that limits have already been evaluated with chronic criteria based on effluent hardness, so some form of "mix hardness" effects have probably already been considered.

What I also noticed is that the effluent databases we currently have on the parameters which are used in the mix hardness evaluation are either small (if present at all, especially in the case of TDS or chlorides) or somewhat old. It may be a good idea to let people know that some data collection is advisable before mix hardness can be considered, but the generalizations I've made here may also provide some insight on where it is practical to pursue or consider mix hardness. For instance, it wouldn't pay to give a southern community the idea that we're considering mix hardness because they probably won't meet the requirements for eligibility (plus it probably won't help them much anyway since both effluent and receiving water hardness will be high, possibly even near the upper thresholds for the hardness ranges in NR 105 above which no further criteria adjustments are considered anyway). I think we can narrow down the areas of the state where mix hardness is a likely option, but if we know they'll be likely to get mix hardness, then there's no need to ask for a large data collection effort to verify what we already know.