

Environmental and Public Health Engineering

TECHNICAL MEMORANDUM

TO: Mike Conner, EBDA

FROM: Ray Goebel, Tom Hall and EBDA staff

DATE: September 12, 2016

SUBJECT: NPDES Permit Reissuance - Chlorine Residual Issue

Introduction

Nearly every POTW that discharges to the Bay disinfects its effluent with chlorine (a small number use ultraviolet light). NPDES Permits for POTWS adopted by the RWQCB contain chlorine residual effluent limits of 0.0 mg/L, expressed as an instantaneous maximum, consistent with Table 4-2 of the Basin Plan. Self-monitoring programs typically allow monitoring of dechlorinated effluent to be conducted either continuously or by grab samples every one to two hours. Given the high toxicity of chlorine to aquatic life, RWB staff believe that effluent chlorine residual should be continuously monitored.

It is well known in the industry that it is difficult to continuously and precisely balance chlorination and dechlorination processes and that occasional low level, short duration exceedances of residual chlorine in the discharge can occur. This is the case even in well operated and maintained systems applying dechlorinating agent in excess of the amount mathematically required to neutralize the measured chlorine residual. As a result, most Bay agencies add excess amounts of sodium bisulfite (1-2 ppm or more) beyond that theoretically needed to neutralize the remaining measured chlorine residual to ensure the absence of TRC in their discharge.¹

EBDA adds approximately 1.5-2.0 million pounds of bisulfite to its effluent each year. EBDA's pre-dechlorination chlorine residual concentrations are generally lower than most agencies given the configuration of its extensive effluent transport system from the six contributing POTWs in southern and eastern Alameda County (Attachment A). Therefore EBDA's bisulfite dosages may underestimate those used at other POTWs. Conservatively extrapolating from EBDA to all the Bay Area POTWs suggests that approximately 10-20 million pounds of sodium bisulfite (SBS) are added to Bay Area POTW effluents each year to meet the regulatory requirement for TRC. Although non-toxic at the concentrations normally present in POTW effluents, excess dechlorinating agents consume oxygen in the receiving water. Reductions in the levels of excess dechlorinating agent would thus provide a direct environmental benefit.

Continuous on-line chlorination/dechlorination monitoring and control systems are considerably more complex than simple laboratory measurements of grab sample chlorine residual samples. Limited information exists upon which to determine a minimum level that constitutes a "real"

¹ Excess SBS is required to compensate for inaccuracies in on-line TRC analyzers and limitations of those analyzers and the associated SBS feed systems to respond immediately to changing TRC levels. Higher SBS residuals provide a greater buffer against those limitations and reduce the likelihood of TRC effluent violations.



chlorine residual excursion above 0.0 mg/L with on-line analyzers. If a non-zero reporting level were established, operators might be less compelled to protect against spurious low-level chlorine residual "blips" by dosing excessive levels of dechlorinating agent. Since January 1, 2000 (effective date of SB709), POTWs have been subject to mandatory minimum penalties (minimum \$3,000 each) for exceedances of the 0.0 mg/L chlorine residual effluent limit including transient and/or potentially false positive readings.

Based on limited information from a late 1990s national survey of laboratory amperometric titrator based chlorine residual measurements, the reliable reporting limit for grab samples under laboratory conditions was found to be approximately 0.2 mg/L. An equivalent reporting level for on-line analyzer systems would be higher than one derived under laboratory conditions given the additional complexity and variables inherent in continuous on-line measurement systems. The capabilities and performance of the overall system need to be addressed in developing a credible minimum reporting level value; one cannot simply rely on a manufacturer's analyzer specifications.

Three possible approches to address the "zero chlorine residual" and excessive SBS dosing issues outlined above are described below. The first is based on establishing a non-zero TRC effluent limit based on TRC decay rates that still satisfies the Basin Plan effluent limit of $0.0 \, \text{mg/L}$ TRC prior to the effluent reaching the receiving water. The second is based on achieving the EPA water quality criterion for TRC based on calculated concentrations after release from the diffusers, at the edge of the zone of initial dilution. The third is based on establishing a realistic reporting limit (RL) for use with continuous monitoring on-line analyzer systems for purposes of evaluating and reporting compliance with Basin Plan TRC effluent limit.

I. Decay of Residual TRC in EBDA's Combined Effluent Outfall

TRC is almost always measured at the same location that is used for collecting other effluent compliance samples, which for practical purposes is after all treatment processes (including dechlorination) but before the effluent enters the outfall. For EBDA this is monitoring location M-001, defined in the NPDES Monitoring and Reporting Program (MRP) as "At any point in the EBDA Common Outfall Outfall at which all waste tributary to that outfall is present after final dechlorination at the Marina Dechlorination Facility."

However, measuring TRC at this location can dramatically overestimate the amount of TRC potentially present, if not dechlorinated, that would actually reach the Bay. Any TRC present decays significantly while being transported through effluent transport pipelines, outfall pipeline and diffusers. The interior of these pipes are coated with both inorganic constituents and with biofilms that rapidly react with chlorine. These chemical reactions very quickly convert the reactive chlorine into the harmless chloride ion, which is already present in estuarine waters at 30,000 fold higher concentrations. TRC concentrations have been demonstrated in multiple laboratory and field studies to decrease over time during transport through effluent pipelines where detention time (i.e. contact time with biofilms) is based on the pipeline length, diameter, and flow rate. This detention time determines the rate at which the TRC is transformed to chloride ions.

TRC decay during pipe transport frequently measured in drinking water distribution systems to ensure that systems are operated to maintain a measureable residual to protect against potential recontamination in the event of a pipeline break or cross connection. Huang et al., 1997 modified these drinking water decay models to to evaluate TRC decay in wastewater discharges in South

Florida. They adopted the basic assumptions from the drinking water models that include 1) pipe flow is steady state and plug flow; 2) chlorine decay is a first-order kinetic process; 3) the decay is due to reactions in both the bulk flow and in the biofilm at the pipe wall; and 4) the rate of wall reaction is affected by the rate at which chlorine can be transported from the bulk flow to the pipe wall and is represented by a film resistance model of mass transfer.

Based on these assumptions, the steady-state, one dimensional, mass-conservation equation for effluent TRC in an outfall pipe is U dC/dx = -KC where x= distance along the pipe; C= TRC concentration; U= mean velocity of pipe flow, and K= overall decay constant. The decay constant reflects chlorine consumption in the bulk flow and the chlorine consumption by the biofilm at the pipe wall. The solution to the equation with the boundary condition $C=C_0$ at x=0 is $C/C_0=e^{-Kt}$ where t=t the detention time.

The decay rate within the EBDA outfall could, in theory, be most accurately measured by allowing chlorinated effluent of various concentrations to travel through the pipe and using a diver to measure the concentration inside the diffuser just before release. In the absence of making such a challenging direct measurement, EBDA simulated a calculation of this decay rate for the outfall by consulting its data base of measurements of TRC in its on-land transport system in the effluents from each of member agencies. Each of the EBDA treatment plants disinfects its effluent and measures TRC at its point of discharge into the EBDA interceptor system. EBDA continuously measures the TRC entering the Marina Dechlorinatin Facility (MDF) from both the northern and southern parts of its system to allow it to accurately dose the amount of sodium bisulfite necessary to eliminate the TRC in the combined discharge prior to conveyance to the EBDA outfall.

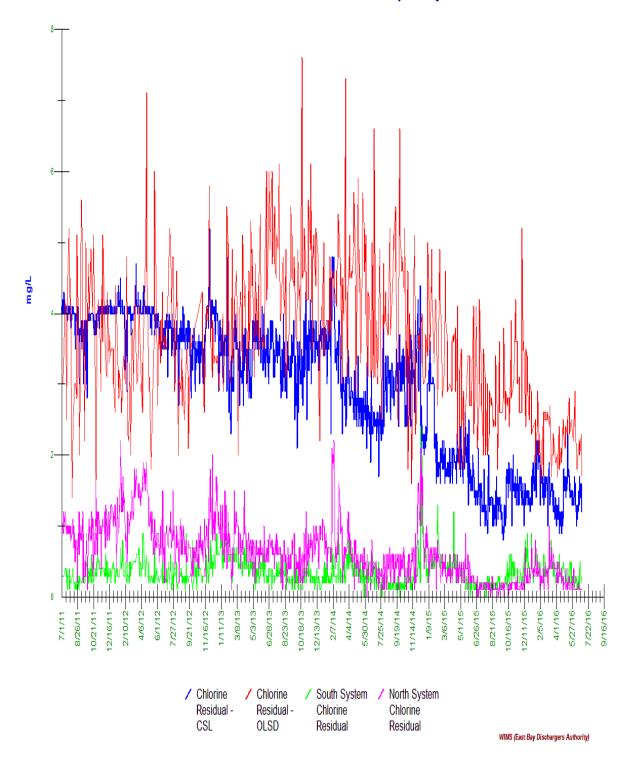
Figure 1 shows measured TCR concentrations from July 2011 through June 2016 in; City of San Leandro (CSL) effluent (blue line), Oro Loma Sanitary District (OLSD) effluent (orange line), South System combined effluent flows entering the MDF (green line), and North System flows entering the MDF (purple line). It can be seen that the CSL TRC concentrations are generally in the 2-4 mg/L range while the OLSD TRC concentrations are slightly higher and more variable in the 3-6 mg/L range. Both CSL and OLSD concentrations trend lower during this time period.

Despite these differences, it can be seen that chlorine decay is similar within the transport system both north and south of the MDF. The north system TRC at MDF is slightly higher (1 - 1.5 mg/L) than in the south system in the first portion of this monitoring period. Both systems then track fairly closely in the 0.5 to 1 mg/L range, or below, for the latter portion of the period.



Figure 1. TRC at the Nearest Treatment Plants North and South of the MDF.

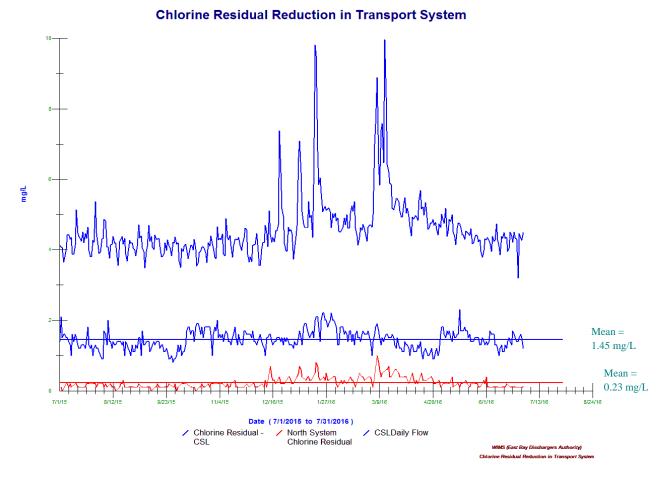
Chlorine Residual Reduction in Transport System





It should be noted that flows from the south are more complicated since they include inputs from three EBDA treatment plants and two LAVWMA treatment plants (City of Livermore and Dublin San Ramon Services District). To simplify these representations of TRC decay Figure 2 shows TRC from the north system only with TRC leaving the CSL plant (lower blue line), TRC arriving at the MDF facility, along with the amount of effluent discharged last year (upper blue line in mgd). The average decay from CSL to MDF during this period was approximately 1.22 mg/L.

Figure 2. TRC and Flows at at San Leandro and TRC Reaching MDF During FY 2016



Discharge flows were fairly consistent during the dry season, with more variability during the wet season as the result of storm events. For this reason, two different comparisons were made: 1) wet season from November 15 to March 31 (Figure 3), and 2) dry season from April 1 to June 30 (Figure 4). As shown in the two figures, the TRC ratio calculated as that measured at the CSL pump station effluent discharged / MDF influent received (consistent with the Huang et al., 1997 equation (C_o/C)) was about 4.4 during the wet season and about 7 during the dry season.



Figure 3. Wet season TRC at San Leandro Discharge and the North System Influent at MDF

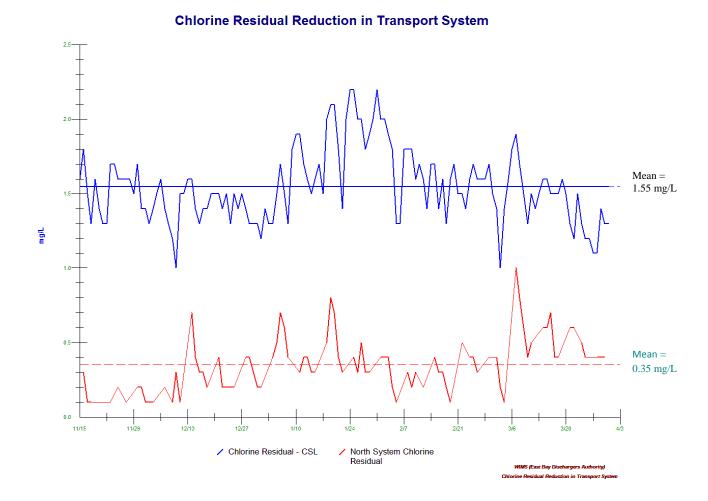
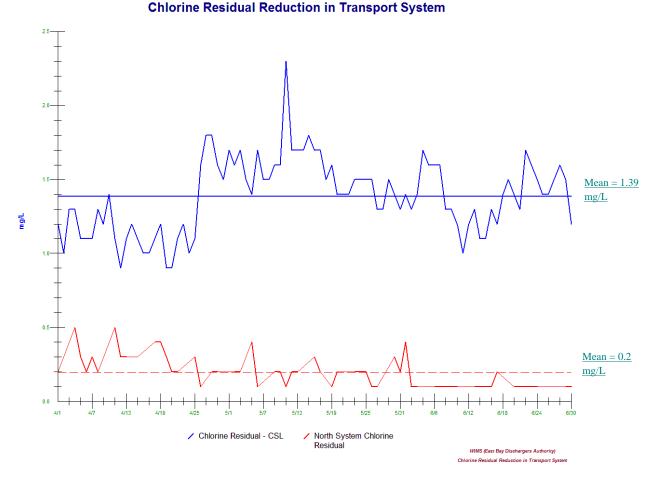




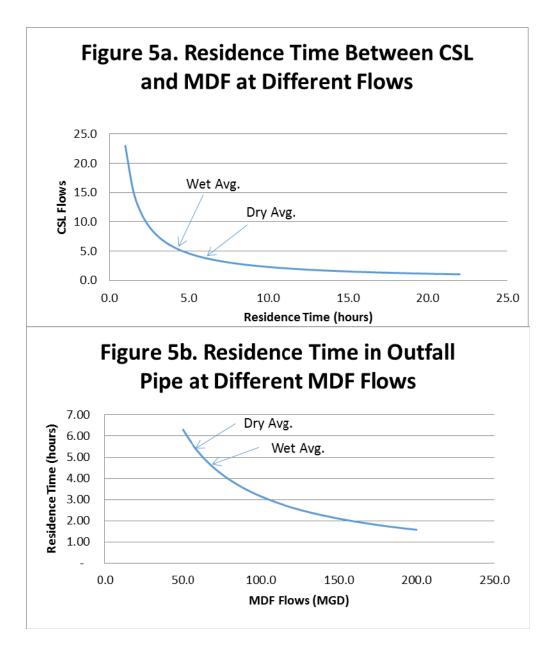
Figure 4. Dry season TRC at San Leandro discharge and the North system influent at MDF.



Pipe residence times were estimated by dividing the flow rate by the total pipe volume, which in the wet season was approximately 4.5 hours, and 5.4 hours in the dry season. The relationship between residence time and flow is illustrated in Figure 5a. Fitting these data to the equation developed by Huang et al., 1997 (and taking the natural log of both sides yields $\ln(4.4)/280 \, \text{min.} = K$) yielded an overall decay constant of 0.0053 min⁻¹ (wet season) and 0.0061 min⁻¹ (dry season). In their data from South Florida, Huang et al., 1997 determined a higher decay constant (0.0136 min⁻¹) in a cast iron pipe 54 inches in diameter, but their comparison to other data showed a range that overlaid the EBDA data.

In summary, the EBDA calculated pipe decay rates of TRC appear to be within the range of literature reported values. Figure 5 also shows a simplifying assumption that abstracts from the San Leandro transport pipe decay rates to the combined outfall decay rates whereby the dry season detention times in both systems is quite similar. While the San Leandro flow is about ~7% of the EBDA flow, its pipe diameter is one half that of the EBDA outfall pipe (one fourth the cross-sectional area) and the distance travelled is about one third the distance to the first EBDA diffuser. As a result, detention time in the two lines are very similar and thus TRC decay rates would be expected to be similar. Decay rates would arguably be faster in the outfall given the likely presence of organic matter on the pipeline inner circumference that would be grown and maintained in the dechlorinated effluent environment versus in the chlorinated CSL effluent pipeline environment.





The final step is to multiply these wet and dry decay ratios (4.4 and 7) by a detection limit used to define "no measureable amount". Using 0.05 ppm as a very optimistic estimate for a reliable detection limit for the on-line residual analyzer would result in a dry season TRC limit of 0.35 ppm and a wet season TRC limit of 0.22 ppm as meeting the Basin Plan requirement of no discharge of chlorine to the Bay.²

² A laboratory amperometric TRC analyzer typically has a method detection limit (MDL) of ~0.03 mg/L in clean water samples. The MDL for a wastewater effluent measured by an on-line analyzer would most certainly be higher. The 0.05 mg/L value was chosen as an optimistic estimate for the latter.



II. Applying the EBDA Outfall Actual Dilution to the EPA TRC Criteria

In its 2006 draft Chlorine Residual Policy the State Water Resources Control Board (SWRCB) proposed to adopt EPA's TRC water quality criteria (WQC) of 0.019 mg/L (as a 1-hr average) and 0.011 mg/L (as a 4-day average) for freshwater discharges. Saltwater discharges would be governed by objectives for chlorine-produced oxidants (CPO), whose values were 68% of the corresponding TRC objectives. All of these values are very close to (and with appropriate rounding, equivalent to) the Basin Plan's 0.0 mg/L TRC instantaneous maximum effluent limit. For purposes of this discussion, the 0.019 mg/l 1-hour average value is used to represent the water quality objective for TRC.

The procedure for calculating water quality based effluent limits (WQBELS) for NPDES perrmits is described in the SWRCB's Policy for Implementation of Toxics Standards for Inland Surface Waters, Enclosed Bays, and Estuaries in California, commonly referred to as the State Implementation Policy, or SIP. The procedure utilizes the applicable water quality objective, the discharger's receiving water dilution credit (where applicable) corrected for background concentration of the pollutant, and other statistical factors to derive maximum daily and average monthly effluent limits. SF Bay RWB policy generally caps the deepwater dilution factor at 10:1, although in the case of the "conventional" non-conservative pollutant ammonia, a POTW's actual dilution credit is used to calculate effluent limits.

The Anti-Degradation Analysis for Proposed Wastewater Treatment Plant Discharge Modification (June 2, 2006), that was previously submitted and accepted as part of the 2006 and 2012 NPDES permit reissuances, contains a summary of the results of the EBDA dilution study demonstrating an acute initial dilution of 79:1 at the design ADWF of 119.1 mgd. That study also found an acute initial dilution of 95:1 at the prior permitted design ADWF of 97.1 mgd (under Order No. R2-2000-0087, August 2000). Currently, the actual initial dilution being achieved will be considerably greater than 79:1 and 95:1 given the much lower recent (2015) ADWF rates of approximately 60 mgd (one-half of the approved design flow).

Following the SIP procedure, a maximum daily effluent limit (MDEL) for TRC was calculated based on the 0.019 mg/L EPA 1-hour average objective, the dilution factor (D = initial dilution – 1 per RWB convention) for the EBDA outfall (78:1 at design flow), a background concentration of zero, and the default coefficient of variation (CV) value of 0.6. The resulting MDEL value was 1.5 mg/L. (Note that if a dilution factor of 94:1 were used, the resulting MDEL would be 1.8 mg/L). The relevant calculations are included in Attachment A. This approach demonstrates that because of the high dilution rate achieved by the EBDA outfall, this TRC effluent limit for would be protective of receiving water quality. It is recognized that the EPA TRC WQC have not yet been adopted by the SWB or RWB.

Actual dilution is routinely used for calculating chlorine residual and bacterial effluent limits for ocean dischargers pursuant to the SWB Ocean Plan. As an example, the North San Mateo County Sanitation District (NSMCSD) Wastewater Treatment Plant NPDES permit (Order No. R2-2012-0013) contains the following TRC effluent limits based on an initial dilution of 70:1 (per antibacksliding from the 2006 permit) and the Ocean Plan TRC WQOs:



- 6-month median = 0.14 mg/L
- Daily Maximum = 0.57 mg/L
- Instantaneous Maximum = 4.3 mg/L

The NSMCSD enterococcus effluent limits also based on an initial dilution value of 70:1 are:

- 30-day geometric mean = 2,500 MPN/100 mL
- Single sample maximum = 7,400 MPN/100 mL

The current EBDA permit contains a 5-sample monthly geometric mean enterococcus limit of 242 MPN/100 mL based on an initial dilution of 10:1. An equivalent enterococcus limit based on an initial dilution of 79:1 (D=78) would be 1,829 MPN/100 mL. Such a modified enterococcus limit would allow required chlorine residual dosages to be reduced considerably, along with the amount of dechlorinating agent needed to be added. There would also be additional ancillary environmental benefits achieved by reducing the amounts of these chemicals that need to be produced, purchased, transported, stored, and handled by EBDA staff. Finally, reduced application of chlorine would result in reduced production of potentially toxic disinfection byproducts in the effluents at each of the six WWTPS discharging to the EBDA system.

III. Adopting a Realistic Reporting Limit for TRC

An alternative approach to addressing the "no chlorine discharge" goal is through establishment of realistic reporting limits (RL or ML) for on-TRC line analyzers, in addition to the effluent limitation, as is done for other pollutants. EBDA NPDES permit Provision VII.A. Compliance Determination states in part the following:

"For purposes of reporting and administrative enforcement by the Regional and State Water Boards, the Discharger shall be deemed out of compliance with effluent limitations if the concentration of the priority pollutant in the monitoring sample is greater than the effluent limitation and greater than or equal to the reporting level (RL)." (emphasis added)

Although most POTWs are currently reporting TRC values of zero for compliance purposes, it is widely understood that the on-line analyzers cannot reliably measure TRC down to that level. However, unlike laboratory benchtop analyzers, there is no widely accepted method for determining the reporting limit for an on-line analyzer. In an effort to support the development of its proposed 2006 Chlorine Residual Policy, the State Board conducted a study in 2007, in which EBDA and four other Bay area POTWs participated, of continuous measurement of chlorine and sulfite in wastewaters (California State Water Resources Control Board, Division of Water Quality. April 2008. Draft Report. *Investigation of Continuous Online Measurement of Chlorine and Sulfite in Wastewaters: Implications for Water Quality Regulation*).

The objective of the SWRCB study was to determine the lowest feasible reporting level for continuous monitoring of TRC and SO3 (sulfite) in complex wastewater matrices. The study consisted of three test types: 1) spike recovery of TRC and SO3 standards, 2) response time in TRC and SO3 online measurements, and 3) comparisons between benchtop and online TRC analyzers. TRC and SO3 were measured in batch-mixed effluents from each of the test facilities. Batch-mixed TRC effluent samples were obtained by mixing the facility's final chlorinated effluent with



concentrated sodium bisulfite (SBS) and/or the facility's final dechlorinated effluent, which contains SBS. This process provided low concentrations of analyte in varied wastewater matrices.

The State Board did not issue a final version of that report (or of the proposed Chlorine Residual Policy) and although the report cautions "do not cite or quote" (because of its draft status), this peer-reviewed study nevertheless represents the most relevant evaluation of low-level TRC measurement in wastewater effluent currently available. The study concluded the following regarding an appropriate reporting level for TRC in wastewater effluent:

This study found that the measurement of very low-concentrations of TRC in wastewater effluents is not a feasible method to demonstrate compliance with the proposed 0.011 and 0.019 mg/L TRC Objectives. Even in pure water, a number of TRC spike-recoveries failed in the range of 0.18 to 0.21 mg/L TRC. In TRC effluents, all TRC spike recoveries that used an initial (unspiked) TRC effluent concentration below 0.17 mg/L TRC failed, and all of the failed samples had an initial TRC concentration ≤ 0.25 mg/L. The TRC benchtop-online comparison tests found a high degree of variation in measurements of the same batch-mixed effluent, including between TRC analyzers that had passed the spike-recovery criteria in both pure water and effluent.

The variability associated with measurements at or below 0.2 mg/L TRC extends below the concentrations of the proposed TRC objectives. However, the variability associated with the measurement of 0.3 mg/L does not extend below the proposed Objectives. This data indicates that measurements of 0.3 mg/L TRC and above will reliably represent the presence of TRC in wastewater effluent. Therefore, the data from both the spike-recovery tests and the comparison tests support the use of 0.3 mg/L as a reporting level for TRC in wastewater effluent. (emphasis added)

Summary

Three approaches for identifying defensible non-zero effluent limits for TRC limit were examined as a means to moderate the normal POTW practice of overdosing dechlorinating agent (sodium bisulfite) in the final effluent, which is done to ensure compliance with the current 0.0 mg/L TRC effluent limit.

The first approached utilized the fact that TRC decays in the effluent outfall line between the point of measurement and the actual discharge point. Applying values of TRC decay measured in the "on land" portion of the effluent line from the City of San Leandro to the EBDA final outfall, coupled with an estimate of a laboratory benchtop TRC analyzer reporting limit resulted in technically defensible TRC limits that would be protective of water quality of 0.22 and 0.35 mg/L for wet and dry season, respectively.

In the second approach, an effluent limit (MDEL) was calculated based on the State's normal (SIP based) procedure for calculating water quality-based effluent limits, using EPA's TRC objective of 0.019 mg/L coupled with actual dilution achieved by the EBDA outfall when operating a design capacity of 119.1 mgd. This approach resulted in an TRC MDEL of 1.5 mg/L.

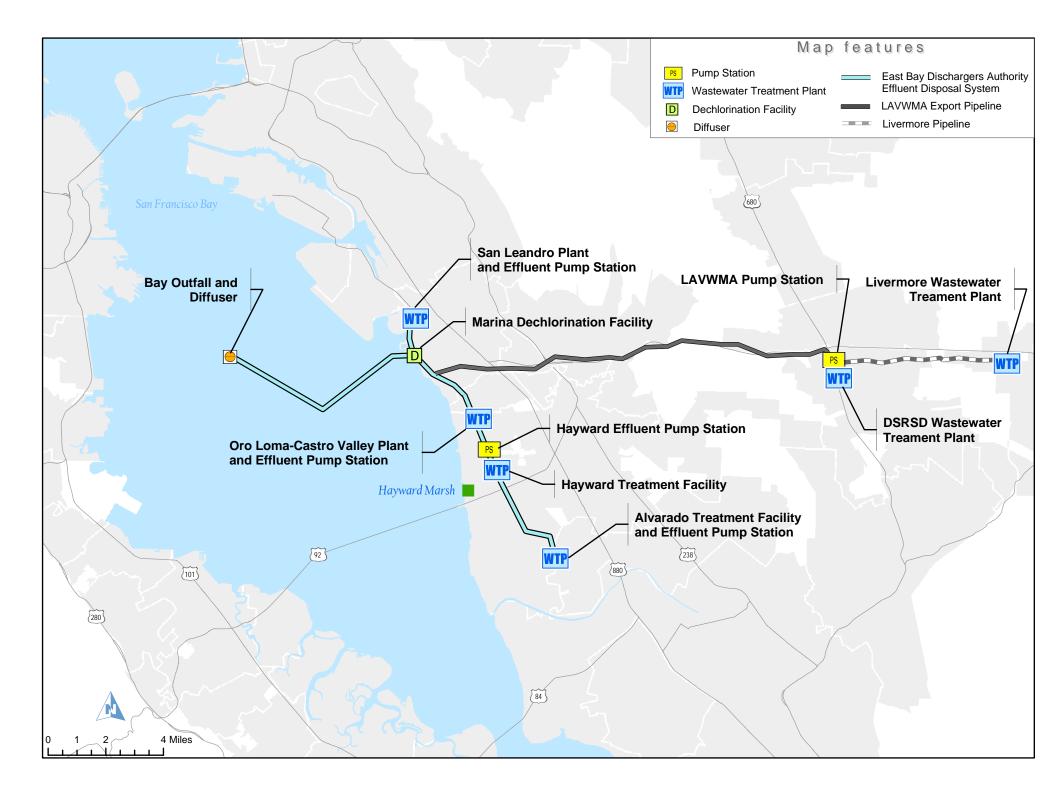


A third alternative to establishing non-zero effluent limits is available by identifying appropriate continuous monitoring reporting limits for TRC in the wastewater matrix. A 2008 study conducted by the State Board, with multi-agency participation (including EBDA) sought to identify the lowest feasible reporting limits for on-line TRC analyzers, based on spike recovery data and comparative tests of benchtop and on-line analyzers. The study results supported use of of 0.3 mg/L as a reporting level for TRC in wastewater effluent. As demonstrated by EBDA's observed TRC decay rate data or by water quality-based effluent limit calculations for TRC, the use of 0.3 mg/L as a reporting reporting limit (RL/ML) for TRC would be protective of the receiving water while allowing EBDA and other POTWs to reduce unnecessary overdosing of sodium bisultite in effluents discharged to the Bay. The ML/RL approach is consistent with current RWB practices for evaluating compliance with other toxic pollutant effluent limits.

References

Huang, H., R.E. Fergen, J. P Cooke, and G.S. Fox. 1997. Effluent Total Residual Chlorine Decay in Outfall Pipe. J. Environ. Eng., 123(8):813-816.

California State Water Resources Control Board, Division of Water Quality. April 2008. Draft Report. Investigation of Continuous Online Measurement of Chlorine and Sulfite in Wastewaters: Implications for Water Quality Regulation.



Effluent Limit Calculations

Constituent	Chlorine Residual (mg/L)
Acute Aquatic Life Water Quality	0.019
Objective (C) Chronic Aquatic Life Water	
· ·	
Quality Objective (C) Acute Translator	1
Chronic Translator	<u>'</u> 1
	·
Acute Aquatic Life Water Quality Objective (C) - Adjusted	0.019
Chronic Aquatic Life Water Quality Objective (C) - Adjusted	
Human Health Water Quality	
Objective (C)	
Dilution Credit (D)	78
Ambient Background	0
Concentration (B)	0
Acute Aquatic Life Effluent	1.50
Concentration Allowance (ECA)	1.50
Chronic Aquatic Life Effluent	NA
Concentration Allowance (ECA)	
Human Health Effluent	NA
Concentration Allowance (ECA)	
Coefficient of Variation (CV)	0.60
(о)	0.555
(σ) ₄	0.294
Z	2.326
Acute Multiplier	0.321
Chronic Multiplier	0.527
Long Term Average (Acute)	0.48
Long Term Average (Chronic)	0.40
Lowest LTAs	0.48
n	4
(σ) _n	0.294
Z(AMEL)	1.645
AMEL Multiplier	1.55
MDEL Multiplier	3.11
Average Monthly Limit (aquatic	0.75
life)	4.5
MDEL (aquatic life)	1.5
AMEL (human health)	NA NA
MDEL _(human health)	NA

Chlorine Residual (mg/L)	
0.019	
1	
1	
0.019	
94	
0	
1.81	
NA	
NA	
0.60	
0.555	
0.294	
2.326	
0.321	
0.527	
0.58	
0.58	
4	
0.294	
1.645	
1.55 3.11	
3.11	
0.90	
1.8	
NA	
NA	