Bay Area Clean Water Agencies

Preparing for Your Next NPDES Permit Renewal

September 24, 2010

Calculating Ammonia Effluent Limits for Bay Dischargers

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Ammonia Limits:

Development Process

1. Water Quality Objectives
2. Total vs. Un-ionized Ammonia
3. Reasonable Potential Analysis
4. Calculating Effluent Limits

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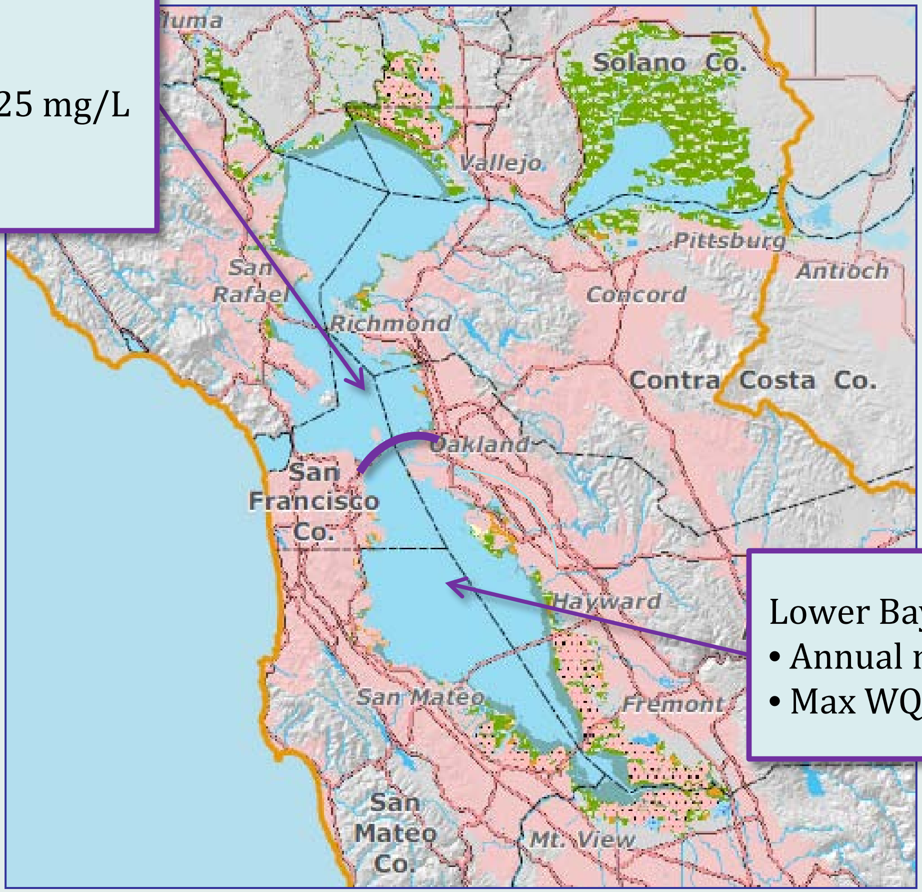
Water Quality Objectives

Basin Plan §3.3.20

Central Bay and Upstream:
- Annual median WQO = 0.025 mg/L
- Max WQO = 0.16 mg/L



Lower Bay:
- Annual median WQO = 0.025 mg/L
- Max WQO = 0.4 mg/L

Water Quality Objectives

Older Permits

C. RECEIVING WATER LIMITS

1. The discharge of waste shall not cause the following conditions to exist in waters of the State at any place:

   a. Floating, suspended, or deposited macroscopic particulate matter or foam;

   b. Bottom deposits or aquatic growths to the extent that such deposits or growths cause nuisance or adversely affect beneficial uses;

   c. Alteration of temperature, turbidity, or apparent color beyond present natural background levels;

   d. Visible, floating, suspended, or deposited oil or other products of petroleum origin; and/ or

   e. Toxic or other deleterious substances to be present in concentrations or quantities that cause exceedence of the narrative toxicity objective contained in the Basin Plan.

2. The discharge of waste shall not cause the following limits to be exceeded in waters of the State any one place within one foot of the water surface:

   a. Dissolved Oxygen: 5.0 mg/L, minimum

      The median dissolved oxygen concentration for any three consecutive months shall not be less than 80% of the dissolved oxygen content at saturation. When natural factors cause concentrations less than that specified above, then the discharge shall not cause further reduction in ambient dissolved oxygen concentrations.

   b. Dissolved Sulfide: 0.1 mg/L, maximum

   c. pH: Variation from normal ambient pH by more than 0.5 pH units.

   d. Un-ionized Ammonia: 0.025 mg/L as N, annual median

      0.16 mg/L as N, max.

   e. Nutrients: Waters shall not contain biostimulatory substances in concentrations that promote aquatic growths to the extent that such growths cause nuisance or adversely affect beneficial uses.

Water Quality Objectives

Recent Permits

- Increased interest in regulating ammonia
- Implementation of ammonia WQOs for Bay discharger effluent limits was directed by State Water Board.
  - Included in Remand Order for EBMUD Wet Weather Facilities
  - Prepared on State Water Board’s own initiative.

Water Quality Objectives

Recent Permits

- Permit renewals now include:
  - Reasonable Potential Analysis (RPA) for ammonia
  - Effluent limits for total ammonia (if triggered)

Example:

Parameter	Units	Effluent Limitations [1,2] AMEL	MDEL
Copper	µg/L	33	46
Cyanide	µg/L	20	54
Dioxin-TEQ [3]	µg/L	1.4×10^{-8}	4.4×10^{-8}
Chlorodibromomethane	µg/L	340	680
Bis(2-ethylhexyl)phthalate	µg/L	59	120
Total Ammonia	mg/L N	150	490

Footnotes for Table 7:

(1) a. Limitations for toxic pollutants apply to the average concentration of all samples collected during the averaging period (daily = 24-hour period; monthly = calendar month).

b. All metals limitations are expressed as total recoverable metal.

(2) A daily maximum or average monthly value for a given constituent shall be considered noncompliant with the effluent limitations only if it exceeds the effluent limitation and the Reporting Level for that constituent. The Regional Standard Provisions (Attachment G) provide Minimum Levels (MLs) for compliance determination purposes. An ML is the

Ammonia Limits:

Development Process

1. Water Quality Objectives
2. **Total vs. Un-ionized Ammonia**
3. Reasonable Potential Analysis
4. Calculating Effluent Limits

Total vs. Un-ionized

Un-ionized Ammonia

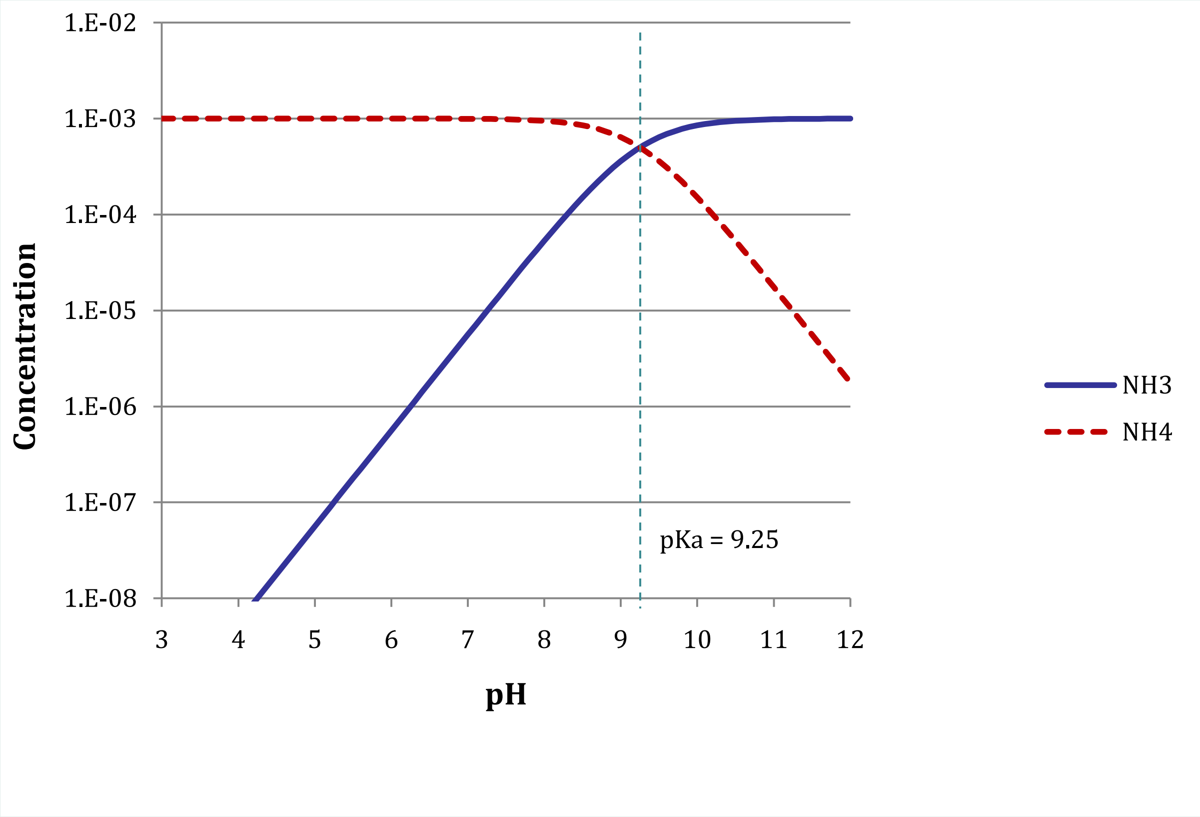
- $NH_4^+ \leftrightarrow NH_3 + H^+$
- Total Ammonia = $NH_3 + NH_4^+$
- $K_a = \frac{\{NH_3\}\{H^+\}}{\{NH_4^+\}}$

pH

Ammonium Ion

Dependent on:
- Salinity
- Temperature

Total vs. Un-ionized



Concentration of ammonia species as a function of pH

Converting WQOs

$$\text{WQO}_{(\text{total})} = \frac{\text{WQO}_{(\text{un-ionized})}}{(\text{fraction un-ionized})}$$

Calculating Fraction NH_3

Marine and estuarine

$$\text{Un-ionized fraction} = \frac{1}{1+10^{(pK-pH)}}$$

Where:

$$pK = 9.245 + 0.116*(I) + 0.0324*(298-T) + \frac{0.0415*P}{T}$$

$$I = \frac{19.9273*(S)}{1000-1.005109*(S)}$$

S = receiving water salinity (ppt)

T = receiving water temperature (Kelvin)

P = receiving water pressure (one atmosphere)

Calculating Fraction NH_3

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S = receiving water salinity (ppt)

T = receiving water temperature (Kelvin)

P = receiving water pressure (one atmosphere)

Calculating Fraction NH_3

Freshwater

$$\text{Un-ionized fraction} = \frac{1}{1+10^{(pK-pH)}}$$

Where:

$$pK = 0.09018 + \frac{2729.92}{T}$$

T = temperature (Kelvin)

Converting WQOs

Summary

1. **Receiving water:** pH, salinity, and temperature data

2. Calculate fraction NH_3 for each sample

3. Determine median and 90th percentile of fractions NH_3

4. $WQO_{(un\text{-}ionized)}$ → $WQO_{(total)}$

Converting WQOs

An Example – Step 1

Receiving Water Data

Date	RMP Station	Salinity (ppt)	Temperature (K)	pH
01/27/97	BD20	0.4	283.5	7.6
04/21/97	BD20	22.9	288.9	7.7
08/04/97	BD20	22.2	293.1	7.7
02/02/98	BD20	4.2	284.3	7.6
04/14/98	BD20	3.7	287.1	8.3
07/27/98	BD20	14.5	294.2	8.0
02/08/99	BD20	6.9	283.4	7.6
04/19/99	BD20	12.2	288.8	7.9
07/19/99	BD20	20.7	291.9	7.9
02/07/00	BD20	10.5	284.9	7.8
07/17/00	BD20	22.4	292.2	7.9
02/12/01	BD20	19.0	282.5	8.0
08/06/01	BD20	25.2	293.6	8.0

Converting WQOs

An Example – Step 2

Calculate Fraction NH_3

Date	RMP Station	Salinity (ppt)	Temperature (K)	pH	Fraction Un-ionized
01/27/97	BD20	0.4	283.5	7.6	**0.022**
04/21/97	BD20	22.9	288.9	7.7	**0.012**
08/04/97	BD20	22.2	293.1	7.7	**0.023**
02/02/98	BD20	4.2	284.3	7.6	**0.030**
04/14/98	BD20	3.7	287.1	8.3	**0.010**
07/27/98	BD20	14.5	294.2	8.0	**0.015**
02/08/99	BD20	6.9	283.4	7.6	**0.032**
04/19/99	BD20	12.2	288.8	7.9	**0.007**
07/19/99	BD20	20.7	291.9	7.9	**0.024**
02/07/00	BD20	10.5	284.9	7.8	**0.026**
07/17/00	BD20	22.4	292.2	7.9	**0.007**
02/12/01	BD20	19.0	282.5	8.0	**0.013**
08/06/01	BD20	25.2	293.6	8.0	**0.018**

Converting WQOs

An Example – Step 3

Date	RMP Station	Salinity (ppt)	Temperature (K)	pH	Fraction Un-ionized
01/27/97	BD20	0.4	283.5	7.6	**0.022**
04/21/97	BD20	22.9	288.9	7.7	**0.012**
08/04/97	BD20	22.2	293.1	7.7	**0.023**
02/02/98	BD20	4.2	284.3	7.6	**0.030**
04/14/98	BD20	3.7	287.1	8.3	**0.010**
07/27/98	BD20	14.5	294.2	8.0	**0.015**
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07/19/99	BD20	20.7	291.9	7.9	**0.024**
02/07/00	BD20	10.5	284.9	7.8	**0.026**
07/17/00	BD20	22.4	292.2	7.9	**0.007**
02/12/01	BD20	19.0	282.5	8.0	**0.013**
08/06/01	BD20	25.2	293.6	8.0	**0.018**
				Median:	**0.019**
				90th Percentile:	**0.0321**

Fraction NH_3 Stats

Converting WQOs

An Example – Step 4

Date	RMP Station	Salinity (ppt)	Temperature (K)	pH	Fraction Un-ionized
01/27/97	BD20	0.4	283.5	7.6	**0.022**
04/21/97	BD20	22.9	288.9	7.7	**0.012**
08/04/97	BD20	22.2	293.1	7.7	**0.023**
02/02/98	BD20	4.2	284.3	7.6	**0.030**
04/14/98	BD20	3.7	287.1	8.3	**0.010**
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02/08/99	BD20	6.9	283.4	7.6	**0.032**
04/19/99	BD20	12.2	288.8	7.9	**0.007**
07/19/99	BD20	20.7	291.9	7.9	**0.024**
02/07/00	BD20	10.5	284.9	7.8	**0.026**
07/17/00	BD20	22.4	292.2	7.9	**0.007**
02/12/01	BD20	19.0	282.5	8.0	**0.013**
08/06/01	BD20	25.2	293.6	8.0	**0.018**
				Median:	**0.019**
				90th Percentile:	**0.0321**
				Annual Median WQO for Un-ionized Ammonia:	**0.025**
				Maximum WQO for Un-ionized Ammonia:	**0.16**
				Chronic WQO for Total Ammonia:	**1.3**
				Acute WQO for Total Ammonia:	**5.0**

WQO (un-ionized) → WQO (total)

Converting WQOs

An Example – Step 4 (Chronic)

Date	RMP Station	Salinity (ppt)	Temperature (K)	pH	Fraction Un-ionized
01/27/97	BD20	0.4	283.5	7.6	**0.022**
04/21/97	BD20	22.9	288.9	7.7	**0.012**
02/08/99	BD20	6.9	283.4	7.6	**0.032**
04/19/99	BD20	12.2	288.8	7.9	**0.007**
07/19/99	BD20	[illegible]	291.9	7.9	**0.024**
02/07/00	BD20	[illegible]	284.9	7.8	**0.026**
07/17/00	BD20	[illegible]	292.2	7.9	**0.007**
02/12/01	BD20	[illegible]	282.5	8.0	**0.013**
08/06/01	BD20	25.2	293.6	8.0	**0.018**
				Median:	**0.019**
				90th Percentile:	**0.0321**
				Annual Median WQO for Un-ionized Ammonia:	**0.025**
				Maximum WQO for Un-ionized Ammonia:	**0.16**
				Chronic WQO for Total Ammonia:	**1.3**
				Acute WQO for Total Ammonia:	**5.0**

$$\text{Chronic WQO}_{\text{(total)}} = \frac{\text{Annual Median WQO}_{\text{(un-ionized)}}}{\text{(fraction un-ionized)}}$$

Median for Chronic WQO

0.025 ÷ 0.019 = 1.32

Converting WQOs

An Example – Step 4 (Acute)

$$\text{Acute WQO}_{\text{(total)}} = \frac{\text{Max WQO}_{\text{(un-ionized)}}}{\text{(fraction un-ionized)}}$$

90th Percentile for Acute WQO

Date	RMP Station	Salinity (ppt)	Temperature (K)	pH	Fraction Un-ionized
01/27/97	BD20	0.4	283.5	7.6	**0.022**
04/21/97	BD20	22.9	288.9	7.7	**0.012**
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	**.023**
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	**.030**
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	**.010**
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	**.015**
02/08/99	BD20	6.9	283.4	7.6	**0.032**
04/19/99	BD20	12.2	288.8	7.9	**0.007**
07/19/99	BD20	[illegible]	291.9	7.9	**0.024**
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02/12/01	BD20	[illegible]	282.5	8.0	**0.013**
08/06/01	BD20	25.2	293.6	8.0	**0.018**
				Median:	**0.019**
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				Annual Median WQO for Un-ionized Ammonia:	**0.025**
				Maximum WQO for Un-ionized Ammonia:	**0.16**
				Chronic WQO for Total Ammonia:	**1.3**
				Acute WQO for Total Ammonia:	**5.0**

$0.16 \div 0.032 = 5.0$

Ammonia Limits:

Development Process

1. Water Quality Objectives
2. Total vs. Un-ionized Ammonia
3. **Reasonable Potential Analysis**
4. Calculating Effluent Limits

Two Approaches for Ammonia

- State Implementation Policy (SIP) – Adopted by State Water Board in 2000
- Technical Support Document (TSD) – Published by USEPA in 1991

RPA – SIP Approach

Maximum total ammonia effluent concentration (MEC)	>	Most stringent converted $WQO_{(total)}$	?

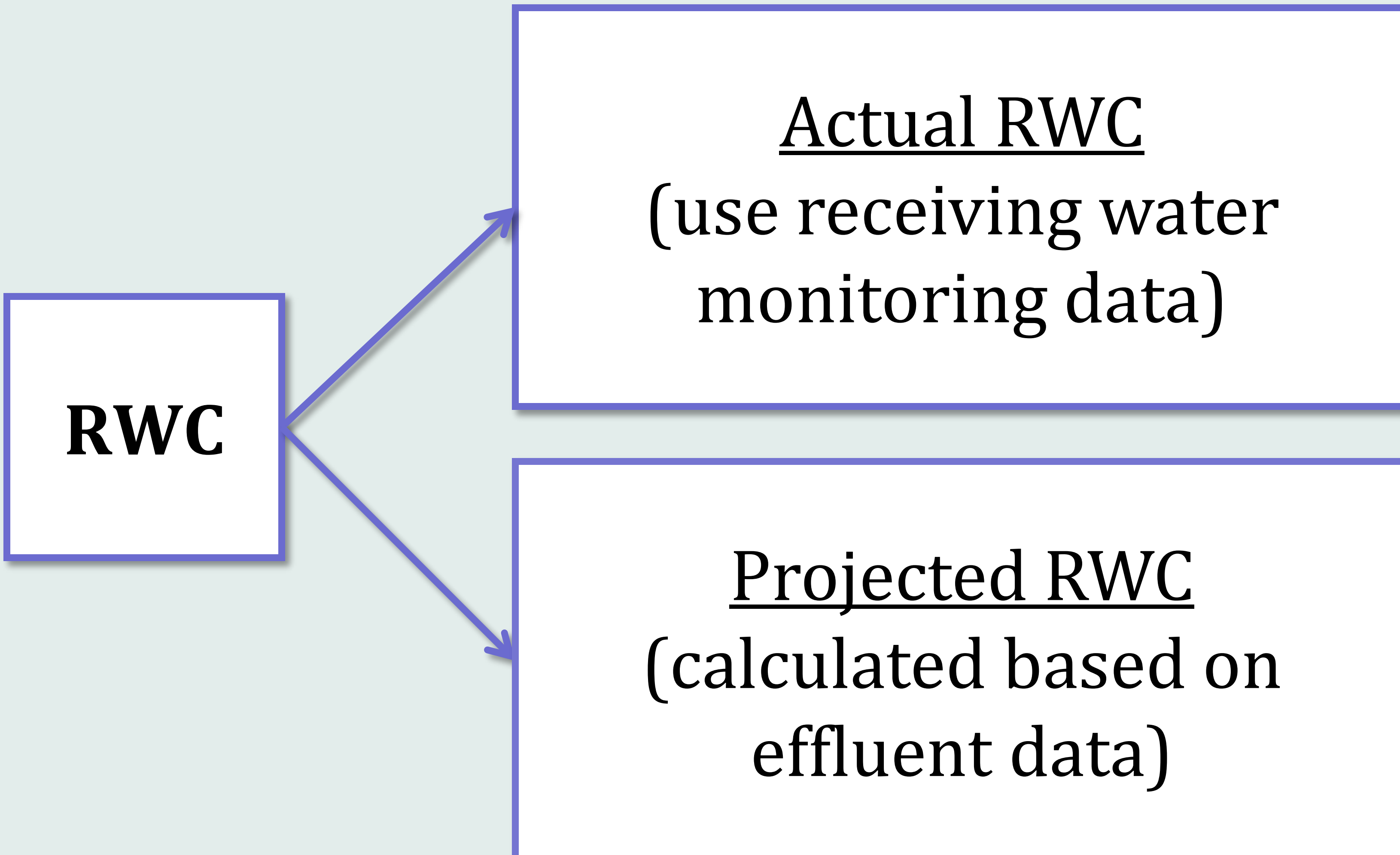
RPA – TSD Approach

Evaluate Both WQOs

Median un-ionized ammonia RWC	>	Annual median $WQO_{(un\text{-}ionized)}$	?
Maximum un-ionized ammonia RWC	>	Maximum $WQO_{(un\text{-}ionized)}$	?

RPA – TSD Approach

Evaluate Both Receiving Water and Effluent Data



RPA: TSD Approach

Actual RWC

Receiving Water: collect total ammonia, pH, salinity and temperature data

↓

Calculate ***concentration*** of NH_3 for each sample

↓

Determine median and maximum concentrations

↓

Is median RWC > annual median $WQO_{(un\text{-}ionized)}$?

Is maximum RWC> maximum $WQO_{(un\text{-}ionized)}$?

RPA: TSD Approach

Projected RWC

Effluent: collect total ammonia, pH, and temperature data

↓

Calculate concentration of NH_3 for each sample

↓

Determine projected median & maximum RWC

↓

Is median projected RWC > annual median $WQO_{(un\text{-}ionized)}$?

Is maximum projected RWC > maximum $WQO_{(un\text{-}ionized)}$?

RPA: TSD Approach

Projected RWC

Effluent: collect total ammonia, pH, and temperature data

↓

Calculate concentration of NH_3 for each sample

↓

Determine projected median & maximum RWC

↓

Is median projected RWC > annual median $WQO_{(un\text{-}ionized)}$?

Is maximum projected RWC > maximum $WQO_{(un\text{-}ionized)}$?

RPA: TSD Approach

Projected RWC

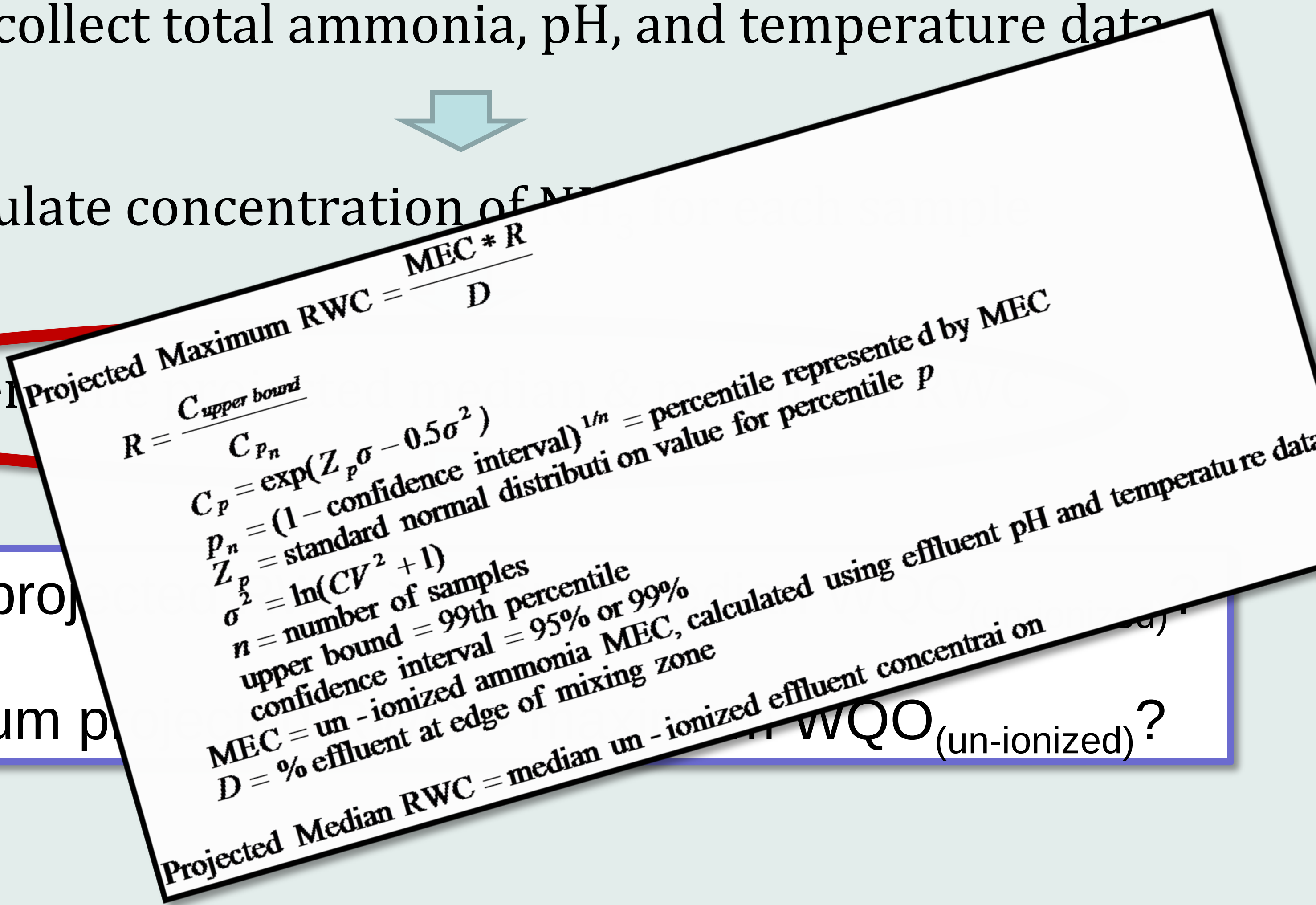
Effluent: collect total ammonia, pH, and temperature data

Calculate concentration of N…

Deter…

Is median pro… …d)?

Is maximum p… … WQO$_{(un\text{-}ionized)}$?



$$\text{Projected Maximum RWC} = \frac{MEC * R}{D}$$

$$R = \frac{C_{upper\ bound}}{C_{p_n}}$$

$C_p = \exp(Z_p\sigma - 0.5\sigma^2)$

$p_n = (1 - \text{confidence interval})^{1/n}$ = percentile represented by MEC

Z_p = standard normal distribution value for percentile p

$\sigma^2 = \ln(CV^2 + 1)$

n = number of samples

upper bound = 99th percentile

confidence interval = 95% or 99%

MEC = un-ionized ammonia MEC, calculated using effluent pH and temperature data

D = % effluent at edge of mixing zone

Projected Median RWC = median un-ionized effluent concentration

Ammonia Limits:

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4. **Calculating Effluent Limits**

Calculating Limits

- Effluent limits are currently calculated using only the SIP.
- Modifications needed because “chronic” WQO for ammonia is annual median (instead of 4-day average):
  - Averaging period = 365 days
  - Sampling frequency (max) = 30 days/month
  - Median background concentration is used

Calculating Limits

Total Ammonia WQBEL Calculations (mg/L N)		
	ACUTE	CHRONIC
Dilution Factor	0	0
No. of Samples per Month	4	30
Acute WQO	4.70	
Chronic WQO		1.30
Background Concentration	0.16	0.07
ECA acute	4.7	
ECA chronic		1.3
Avg of Effluent Data Points	4.1	4.1
Std Dev of Effluent Data Points	3.7	3.7
CV	0.90	0.90
ECA acute mult99	0.22	
ECA chronic mult99		0.90
LTA acute	1.05	
LTA chronic		1.17
Minimum of LTAs	1.05	1.05
MDEL mult99	4.47	4.47
AMEL mult95	1.85	1.29
MDEL	~~4.70~~	4.70
AMEL	~~1.95~~	1.36

Calculating Limits

Converted WQOs

Total Ammonia WQBEL Calculations (mg/L N)		
	ACUTE	CHRONIC
Dilution Factor	0	0
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Calculating Limits

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Minimum of LTAs	1.05	1.05
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MDEL	~~4.70~~	4.70
AMEL	~~1.95~~	1.36

Calculations Adjusted for Annual Median

Calculating Limits

Total Ammonia WQBEL Calculations (mg/L N)		
	ACUTE	CHRONIC
Dilution Factor	0	0
No. of Samples per Month	4	30
Acute WQO	4.70	
Chronic WQO		1.30
Background Concentration	0.16	0.07
ECA acute	4.7	
ECA chronic		1.3
Avg of Effluent Data Points	4.1	4.1
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MDEL	~~4.70~~	4.70
AMEL	~~1.95~~	1.36

Select Lower Pair for Final Limits

Calculating Limits

Dilution Credits

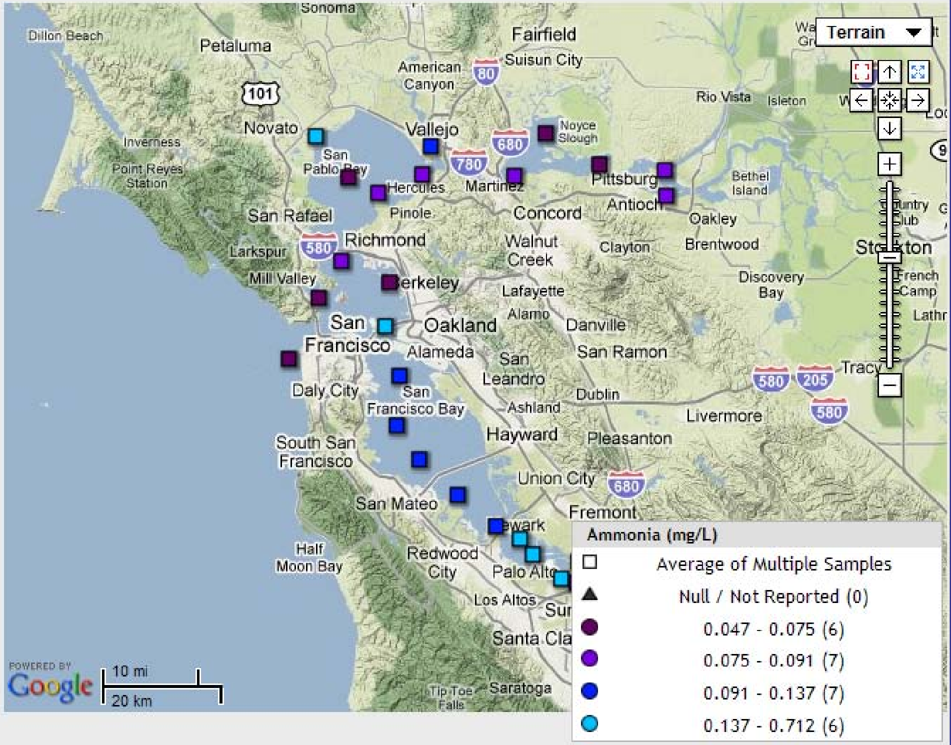
- Dilution credits are necessary for compliance in many cases
- Deepwater dischargers:
  - Currently OK to use actual initial dilution > 10:1 for ammonia
  - Need to provide dilution studies that are representative of current conditions
- Shallow water dischargers:
  - Need current dilution study
  - Need to justify a mixing zone that meets SIP conditions

Preparing for Ammonia Limits

6-12 months before permit application is due:

- Conduct dilution study
- Identify recommendations to Regional Water Board staff to ensure compliance
- Submit materials with Report of Waste Discharge (ROWD)

Some Ammonia Data for the Bay



SFEI RMP Web Query Tool Results

Un-ionized Ammonia at RMP Station BD20
Compared to Annual Median WQO