

Cyanide Attenuation Study

Use of Trace-Level Cyanide Method
to Determine Attenuation of
Discharged Cyanide in Lower South
San Francisco Bay

Paradox



...although the origins of terrestrial life appear to have been dependent in part on the presence and chemical reactivity of HCN and its derivatives, paradoxically it is toxic to the majority of living matter (Timothy C. Marrs and Bryan Ballantyne)

Regulatory Driver for Study

- EPA Cyanide Criterion is 1.0 $\mu\text{g/L}$
- Proposed S. F. Bay SSO is 2.9 $\mu\text{g/L}$
- Most Shallow-Water Dischargers cannot meet this limit

Compliance Strategies

- Water-Effect Ratio study: results $\cong 1$
- Spiking study
- Translator Study
 - Free:Total cyanide
 - EPA criteria based on free cyanide
 - MDL for free cyanide too high
- Fate and transport study
 - Need trace total cyanide method

Attenuation Study

- F & T Most Reasonable Strategy for Relief
 - Attenuation = dilution + degradation
- Based on low levels of Total Cyanide
- Need Lower Reporting Limit
- Another type of “Translator”

Trace Cyanide Method Development

- MDL for conventional method : 1-2 $\mu\text{g/L}$
- Proposed SSO requires MDL of $< 0.5 \mu\text{g/L}$
- Trace method adapted from Standard Methods, 18th edition- 4500 CN-B,C &E

Method Modifications

- Concentration Factor increased from two to six fold
- Increased distillation time
- Use of a 10 cm Cell for color determination
- Use of Nitrogen as a carrier gas

Methodology

- Preliminary Treatment of samples
 - to remove interferences
- Distillation
 - to liberate cyanide as gaseous HCN from the matrix background. HCN is collected as CN^- in the NaOH scrubbing solution
- Colorimetric Determination of Cyanide
 - UV-VIS Spectrophotometer

Distillation Apparatus

- Heating Mantles
- Distillation Flasks
- Cold Finger Condenser
- Sparger
- Sparger Vessel
- Nitrogen Gas

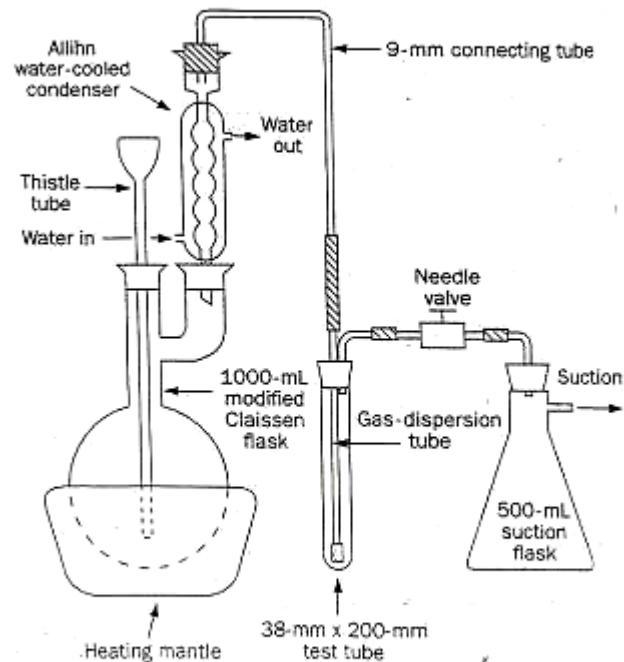


Figure 4500-CN-1: Cyanide distillation apparatus.

Distillation Procedure

- Sample Volume: 700 ml
- Reagents:
 - 70 ml 0.04N NaOH
 - PbCO₃
 - MgCL₂, NH₂SO₃H
 - H₂SO₄
- Spikes: 2-5ug/L (1ug/ml std) KCN
- Nitrogen Flow Rate
 - 2-4 air bubbles/sec

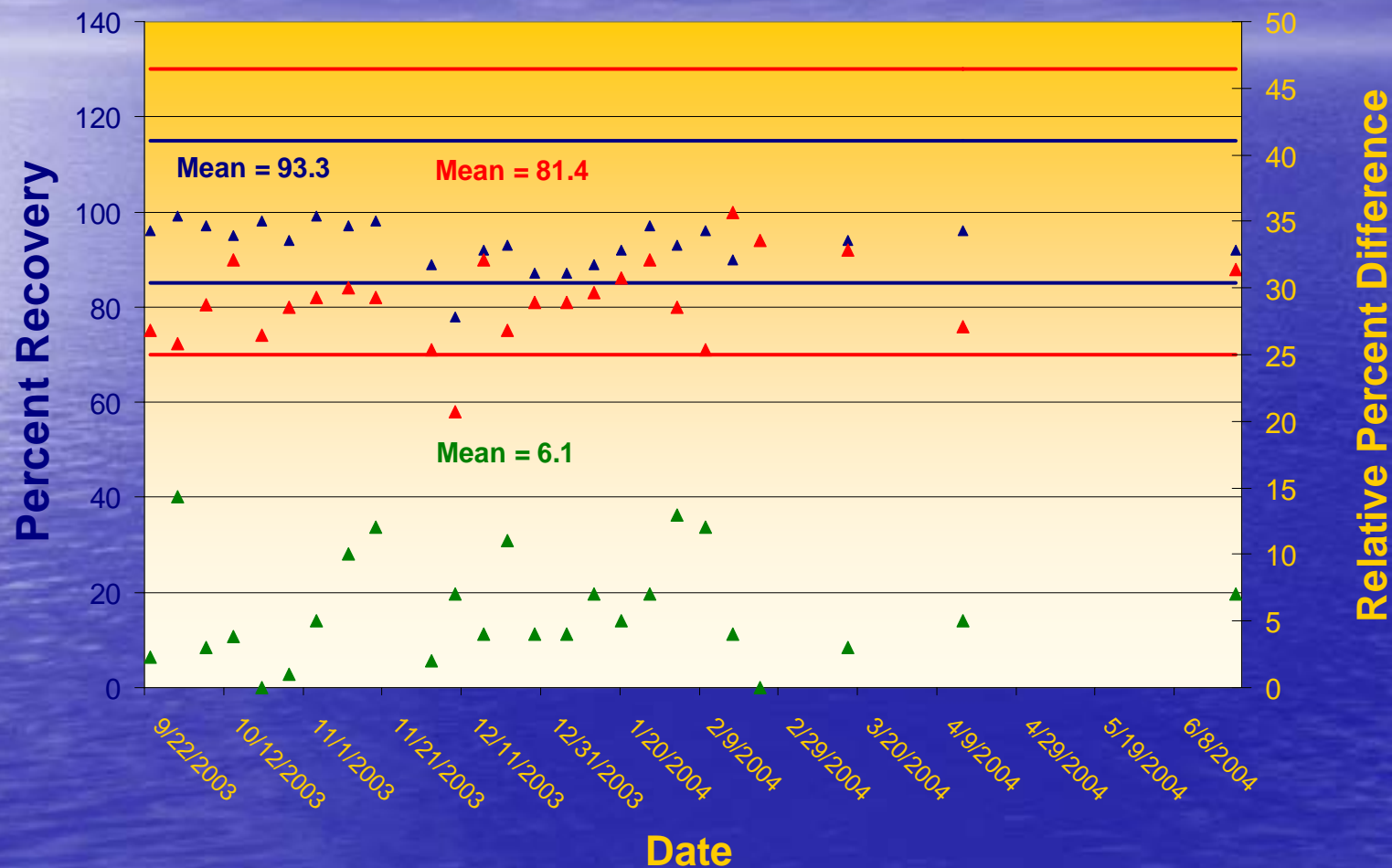


MDL Studies

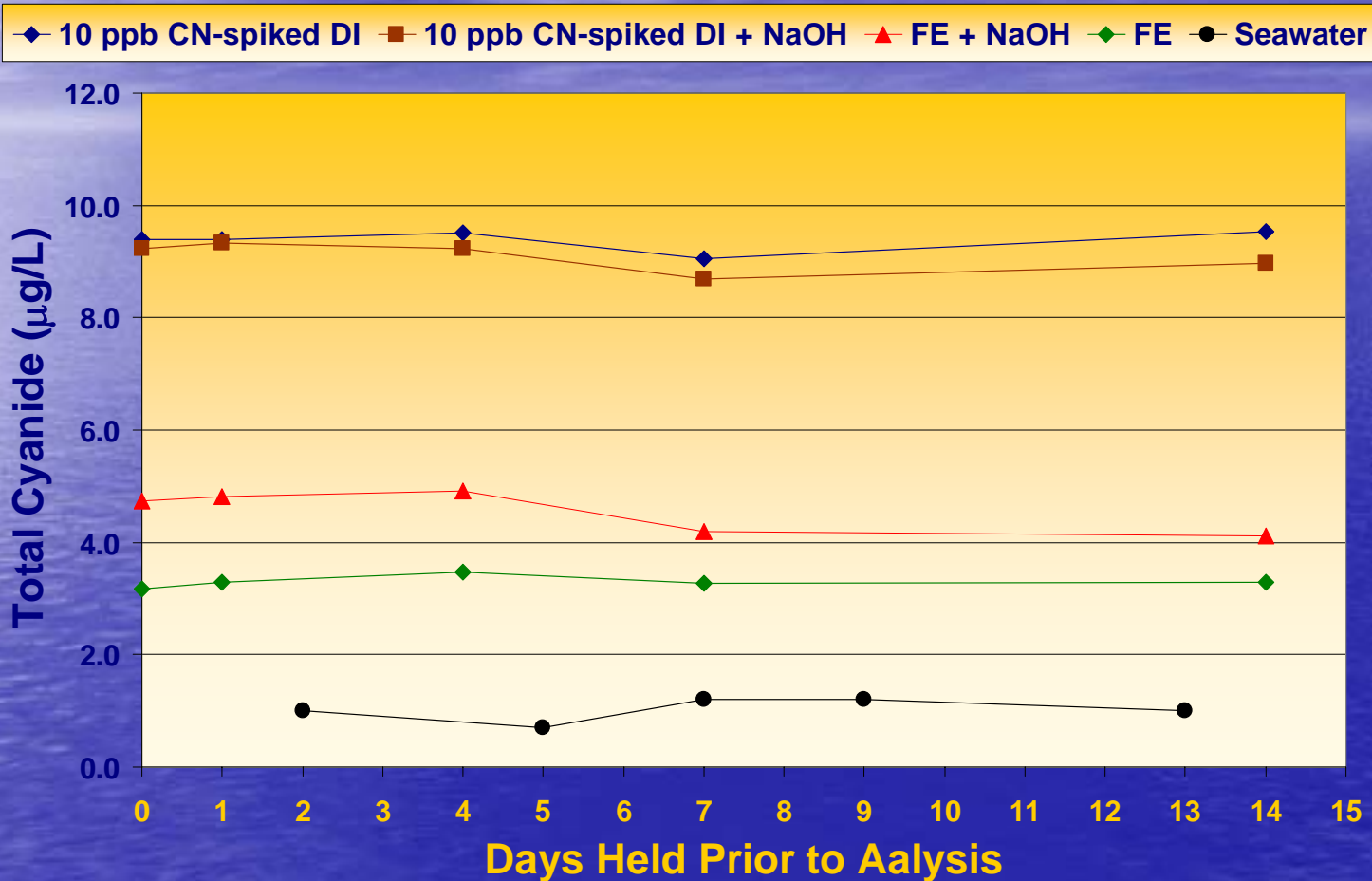
Matrix	Distilled Water	Final Effluent	Seawater
MDL ($\mu\text{g/L}$)	0.06	0.2	.06
PQL ($\mu\text{g/L}$)	0.3	1.0	0.3

Cyanide Recoveries

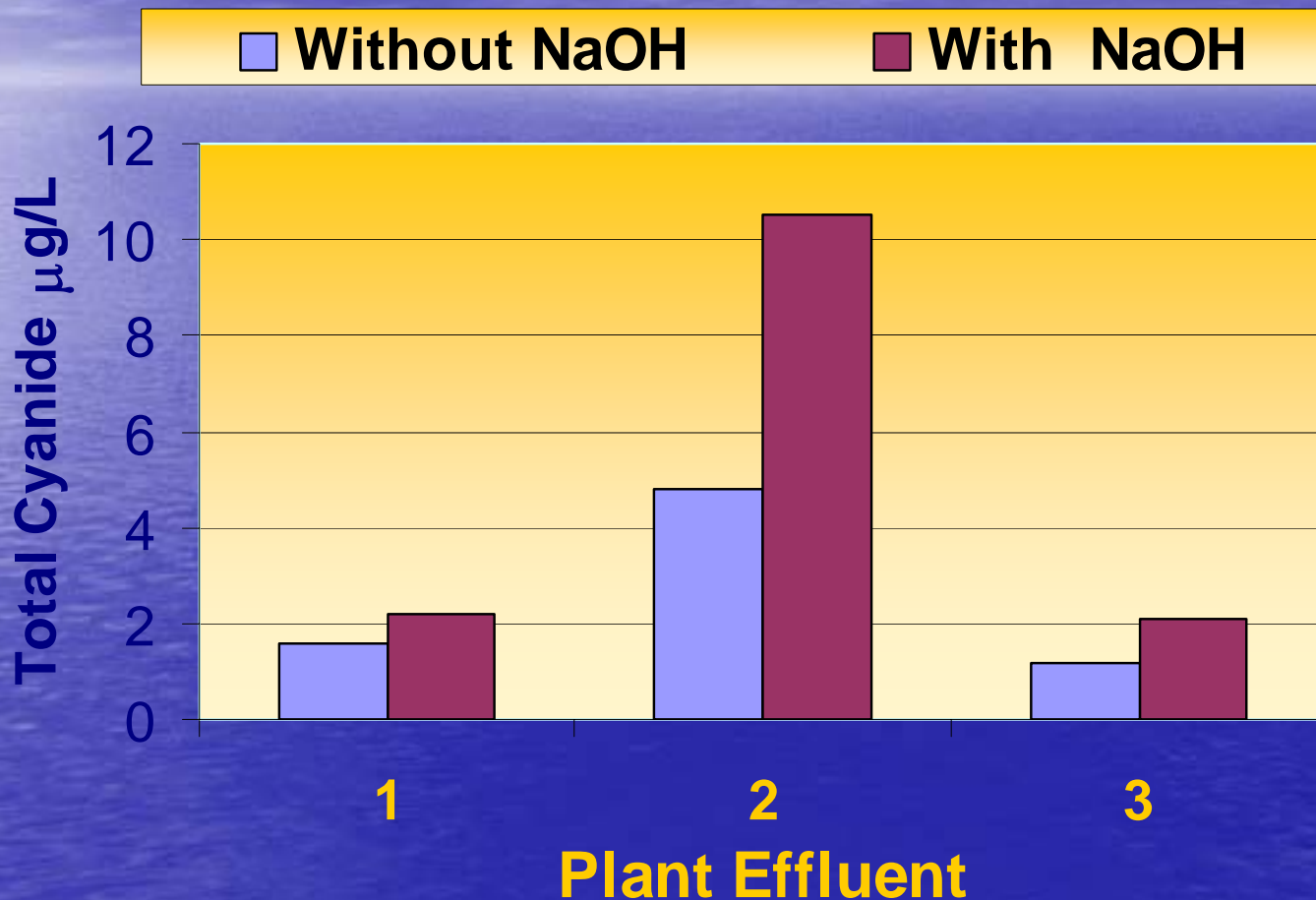
▲ Blank Spike — Blank - Low & High ▲ Matrix Spike — Matrix - Low & High ▲ % RPD



Holding Time Experiments



Effect of NaOH Preservation



Cyanide Recoveries in Raw Sewage

Spike Conc ($\mu\text{g/L}$)	Preserved $\text{K}_3\text{Fe}(\text{CN})_6$ % Recovery	Unpreserved $\text{K}_3\text{Fe}(\text{CN})_6$ % Recovery
5	73.6	80.2
10	74.3	81.6
20	81.9	87.8
50	66.8	84.3
Average Recovery	74.2	83.5

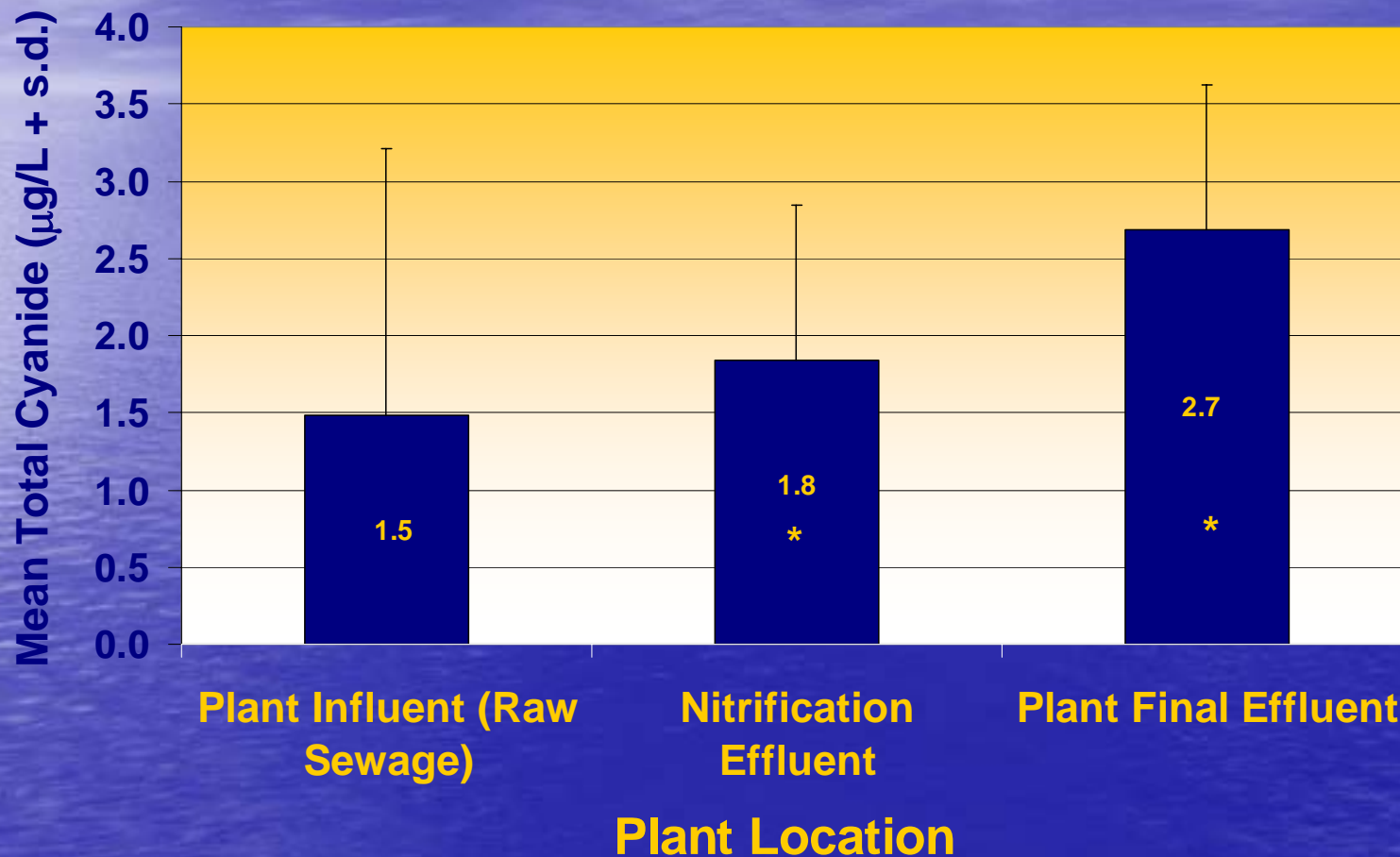
Cyanide Recoveries in Raw Sewage

- Recoveries : Independent of Spike Concentration
Higher with $\text{K}_3\text{Fe}(\text{CN})_6$ than KCN
- Average Recoveries with $\text{K}_3\text{Fe}(\text{CN})_6$:
 - 74.2% Preserved
 - 83.5% Unpreserved

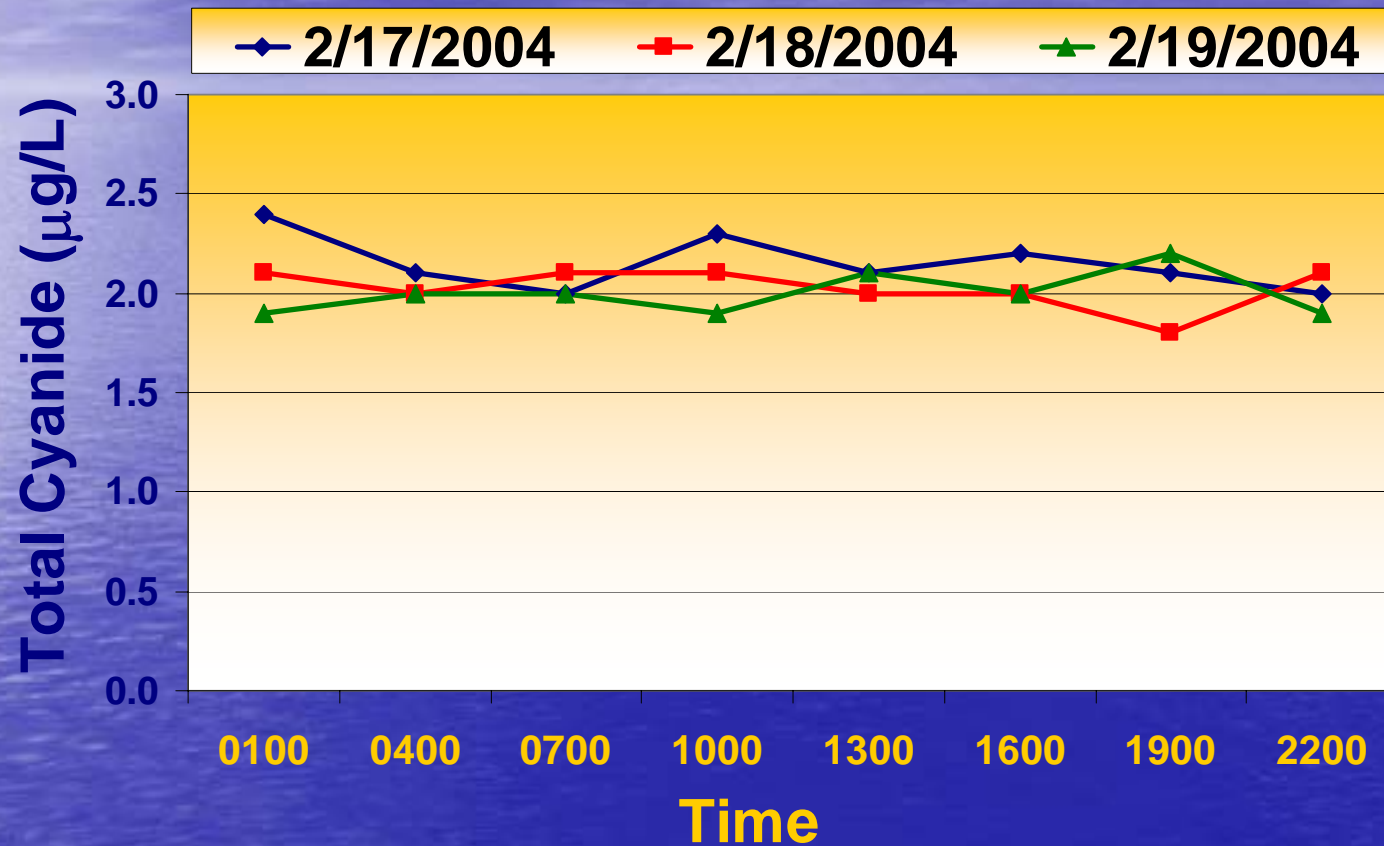
Future Research

- Cyanide Speciation Studies – Free Cyanide
- Sample Preservation Issues
- Cyanide Formation:
 - Chloramination
 - Thiocyanate

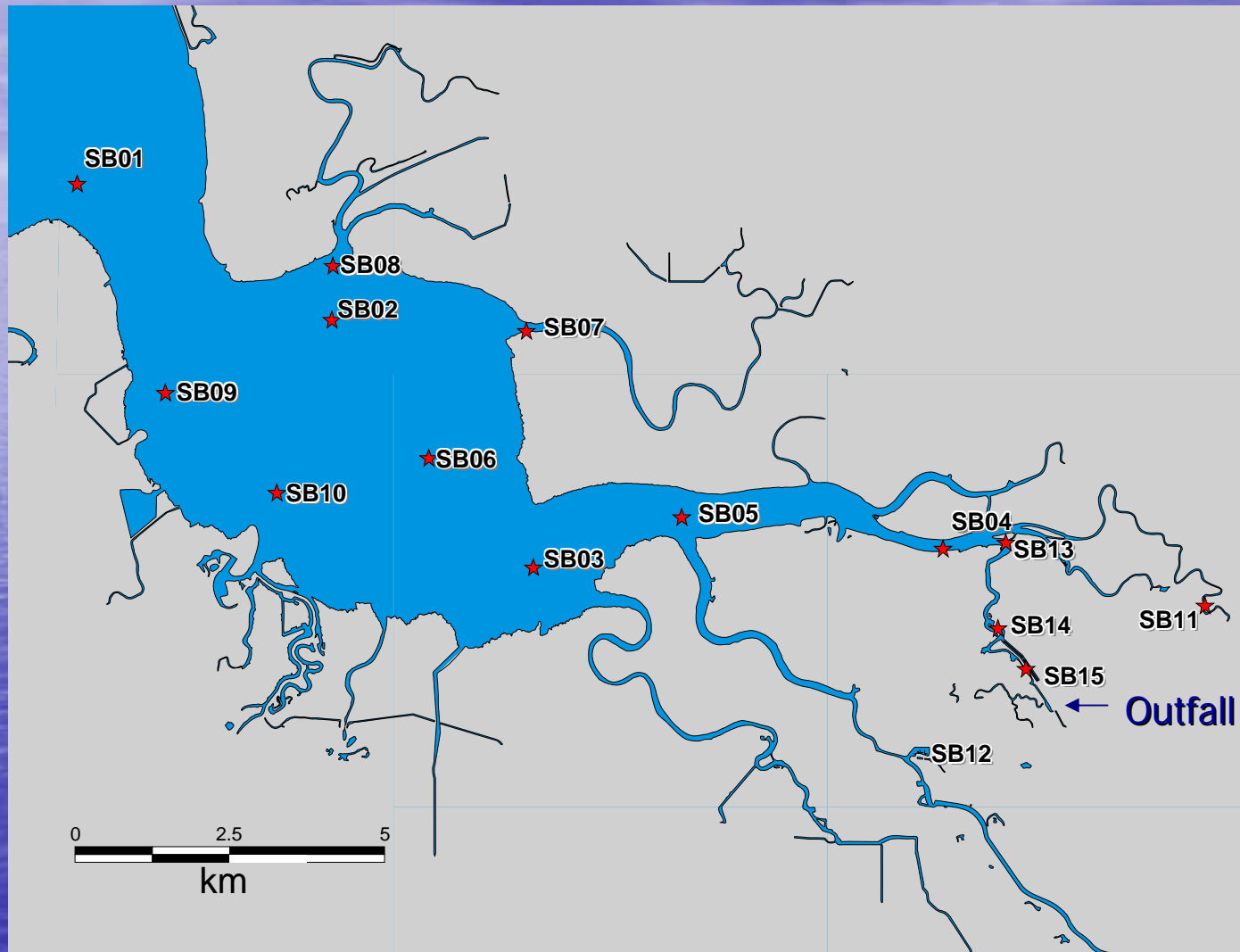
Plant Cyanide Measurements



Plant Variability Study



Cyanide Sampling Stations

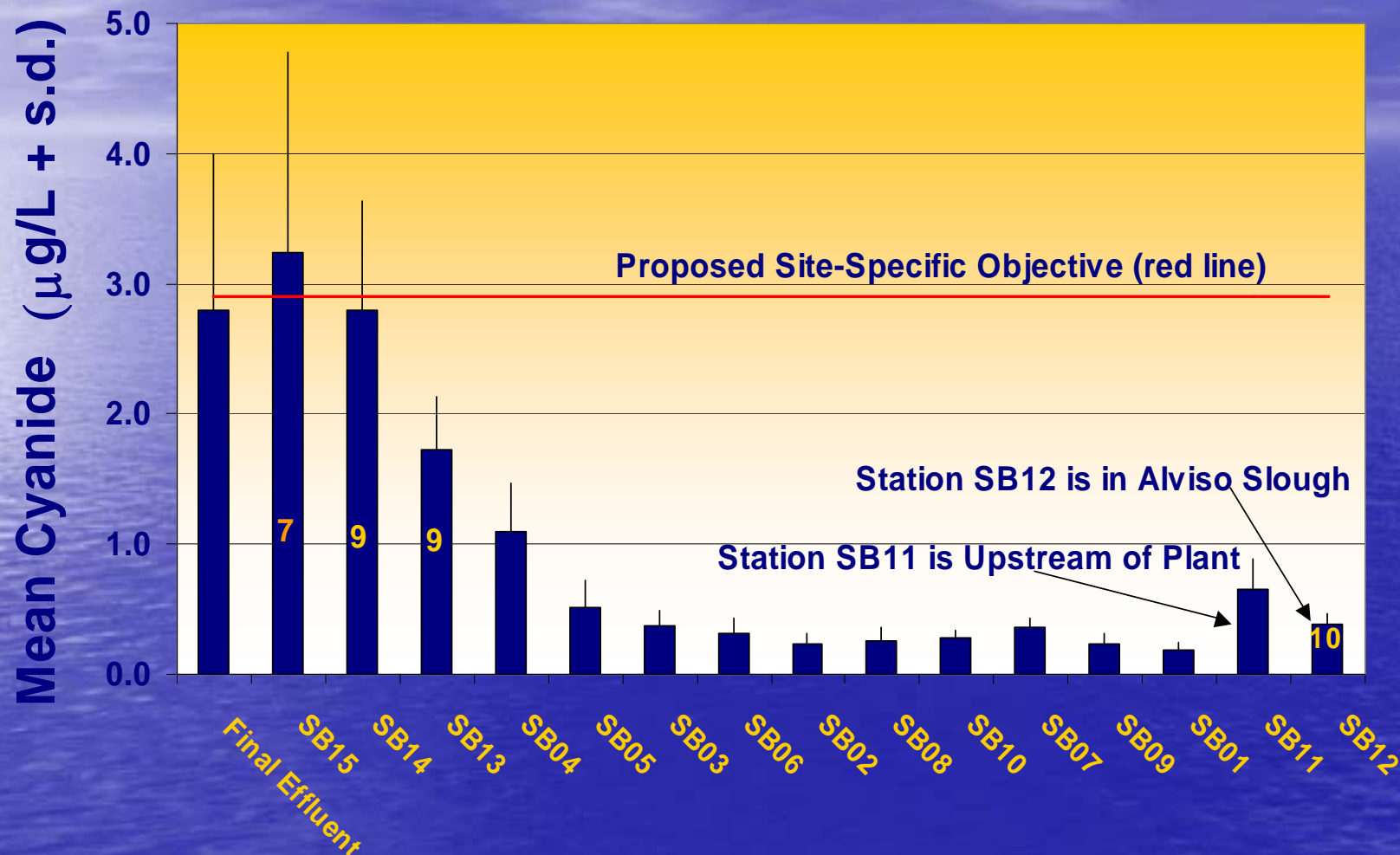








Cyanide Attenuation

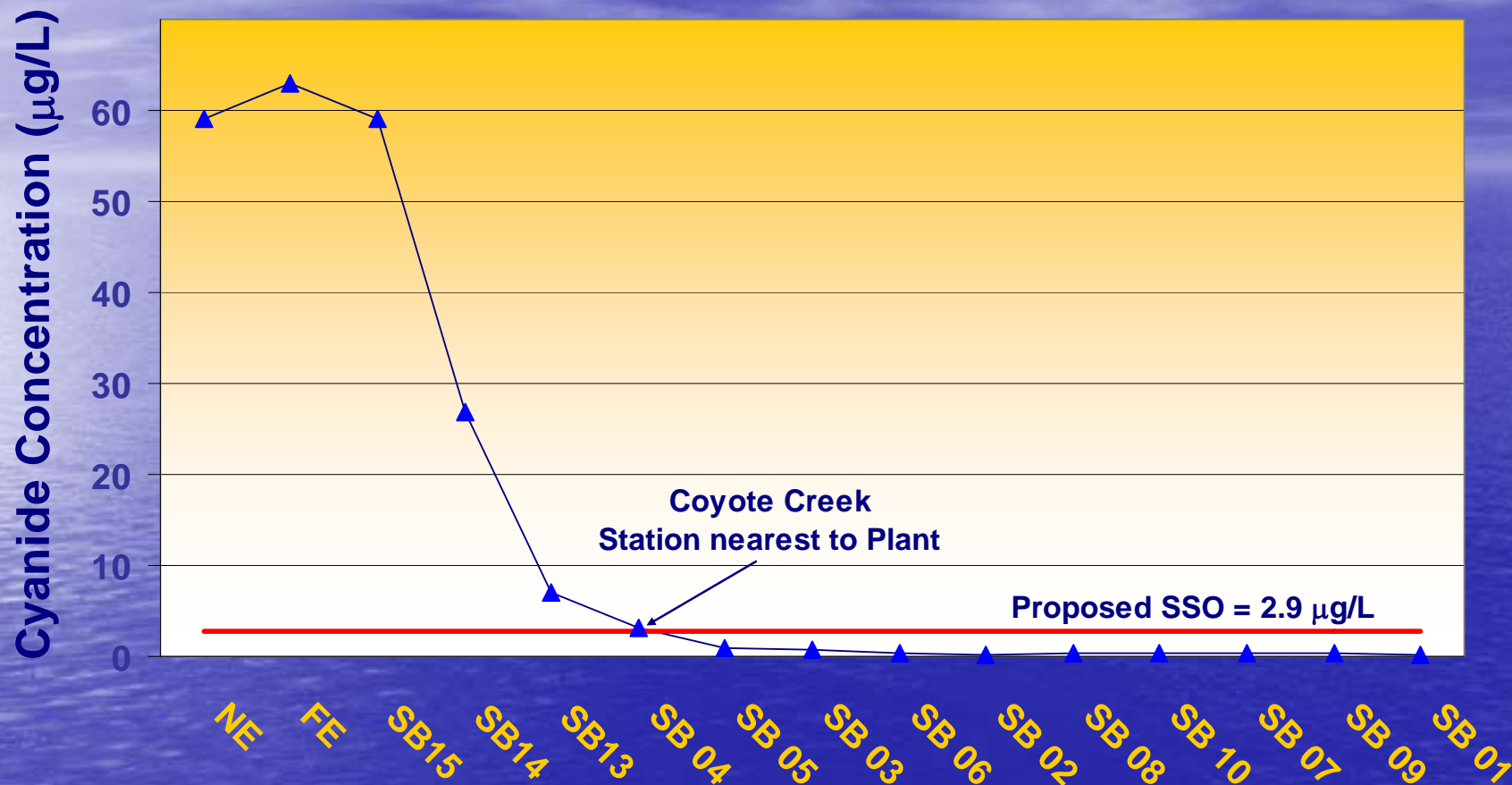


Cyanide stations going away from the Plant

Cyanide Attenuation Factors

Date	Tidal Cycle	SB04 Cyanide Concentration *	SB05 Cyanide Concentration *	Final Effluent Cyanide Concentration *	SB04 Attenuation Factor	SB05 Attenuation Factor
7/9/03	Flooding	1	0.4	1.6	1.6	4.0
8/20/03	Flooding	0.8	0.6	1.8	2.3	3.0
9/24/03	Flooding	1.2	0.5	3.5	2.9	7.0
10/15/03	Ebbing	1.8	0.9	2.3	1.3	2.6
11/19/03	Flooding	0.7	0.2	2.7	3.9	13.5
12/3/03	Ebbing	0.7	0.4	5.2	7.4	13.0
1/21/04	Flooding	1.1	0.4	1.8	1.6	4.5
2/27/04	Ebbing	0.9	0.7	2	2.2	2.9
3/17/04	Flooding	0.8	0.3	3.1	3.9	10.3
4/16/04	Flooding	1.7	0.4	4.7	2.8	11.8
6/23/04	Ebbing	1.3	0.8	2.5	1.9	3.1
				Mean	2.9	6.9
* Concentration: $\mu\text{g/L}$				Median	2.3	4.5
				n	11	11

Cyanide Incident



Cyanide Stations going away from the Plant



Cyanide Attenuation Study

Watershed Investigations

and

Laboratory Staff

Watershed Protection Group

Environmental Services Department

City of San Jose

September 1, 2004

Report available at:

http://www.sanjoseca.gov/esd/pub_res.htm