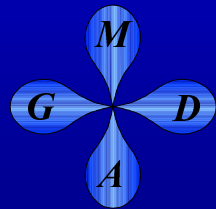


7th Annual BC Metal Leaching/ARD Workshop
Session: Use of Solubility Constraints in ML/ARD Prediction

Case Studies in Metal Solubility at Minesites

by



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Background

- M.Sc. In Geology with Minors in Mathematics & Engineering, 1979, University of North Dakota, under Dr. Lee Clayton
- Ph.D. in Contaminant Hydrogeology, 1984, University of Waterloo, under Dr. John Cherry
- First detailed field studies of minesite drainage in 1978 at lignite (coal) mines of North Dakota; to date, ~160 detailed studies of proposed, operating, and closed minesites
- First journal paper published in 1980; approximately 55 papers published to date; co-author with Nora Hutt of the textbook, *Environmental Geochemistry of Minesite Drainage*
- Research scientist, regulator, and consultant for mining companies, provincial and federal governments, First Nations, and other consulting companies

What Is “Solubility”?

- “The amount of a substance that will dissolve in a given amount of another substance.”
- For minesite drainage, the term often implies some constant (equilibrium) or maximum amount of dissolution.

What Is “Solubility”?

- At chemical equilibrium, solid-liquid interactions do not cease. Instead, they reach a balance.
- $K_{\text{equil}} = \frac{\text{rate of dissolution}}{\text{rate of precipitation}}$
- Anything that affects either rate will therefore affect the solubility and the resulting aqueous concentrations

What Can Affect Aqueous Concentrations and Solubility?

- Countless (thousands?) of physical, chemical, and biological processes acting on the air, water, and solids. For example,
 - *Flow*
 - *Infrared radiation*
 - *Enzymatic reactions*
 - *Ground-to-air electrostatic-potential difference*

How does the variability in aqueous concentrations depend on the variability in the contributing processes?

- Relative Error (RE) = [standard deviation/mean]; and assume concentrations display lognormal distribution
- $(\text{RE in aqueous concentration})^2 =$
 $(\text{RE in process \#1})^2 +$
 $(\text{RE in process \#2})^2 +$
 $(\text{RE in process \#3})^2 +$
 etc.

What Else Can Affect Aqueous Concentrations and Solubility?

- Nonidealities. e.g.,
 - *Mineral solid-solution series*

Nonideality: Solid-Solution Series of Carbonate

- Calcium carbonate is calcite (CaCO_3) and ferrous-iron carbonate is siderite (FeCO_3). However, iron and calcium (as well as magnesium and manganese) can form a continuum of minerals between the pure endpoints.
- Based on ideal, simplistic assumptions, a carbonate mineral with one-half calcium and one-half iron would produce aqueous concentrations indicating calcite is around a factor-of-two undersaturated and siderite is at equilibrium.
- Field data at minesites show the ideal assumptions are not applicable, and that supersaturation with siderite occurs.

Nonideality:
Simultaneous Precipitation of Related Minerals

- Schwertmannite (ideally $\text{Fe}_8\text{O}_8(\text{OH}_6\text{SO}_4)$) with α - FeOOH
- Ferrihydrite (nominally $\text{Fe}_5\text{HO}_8 \cdot 4\text{H}_2\text{O}$) with α - FeOOH

What Else Can Affect Aqueous Concentrations and Solubility?

- Nonidealities? These do not affect aqueous concentrations. They only reflect human limitations in understanding and predicting aqueous concentrations.

Open-Environment vs Closed-Laboratory Solubilities and Aqueous Concentrations?

- Is “solubility”, as defined by carefully controlled laboratory experiments, really applicable to open-environment systems, considering all the physical, chemical, and biological factors and all the human-created non-idealities?
- Is there a problem with semantics here?
- If on-site aqueous concentrations decrease as pH rises from acidic to neutral values, as solubility generally dictates for several metals, is this a solubility effect although concentrations still fluctuate at a particular pH?

How does the variability in aqueous concentrations depend on the variability in the contributing processes?

- Observed variability in aqueous concentrations ~
(variability in process #1) +
(variability in process #2) +
(variability in process #3) +
etc. + etc.

Is “solubility” the final result (the aqueous concentration) or one of the contributing processes?

- Observed variability in aqueous concentrations ~
(variability in process #1) +
(variability in process #2) +
(variability in process #3) +
etc. + etc.

What happens when a mechanistic explanation is not found for decreasing aqueous concentrations with pH?

- For more than the last two decades, it is often along the lines of “the metal is likely co-precipitating with, or being adsorbed to, another precipitating mineral like iron oxyhydroxide.”
- This has actually been demonstrated, in a way, by non-mineral-specific, empirical procedures like soil-extraction tests (acid-soluble, oxalate-soluble, etc.). But where are the carefully controlled mineralogical studies to explain and quantify the co-precipitation or adsorption?

Empirical Drainage-Chemistry Model (EDCM)

- Concise summary of past chemistry and predictive model of future chemistry.
- Simple statistical approach for any computer-based spreadsheet.
- Implicit incorporation of effects of natural and artificial processes, like site-specific solubilities and analytical error.

Empirical Drainage-Chemistry Model (EDCM)

- Large monitoring database (hundreds to thousands of analyses) required.
- No special or additional studies needed.
- Valuable for reducing:
 - frequency of monitoring
 - size of holding ponds
 - annual costs for water-treatment plants
 - acceptable seepage rates through clay/soil covers
 - etc.

What is a Predictive “Model”?

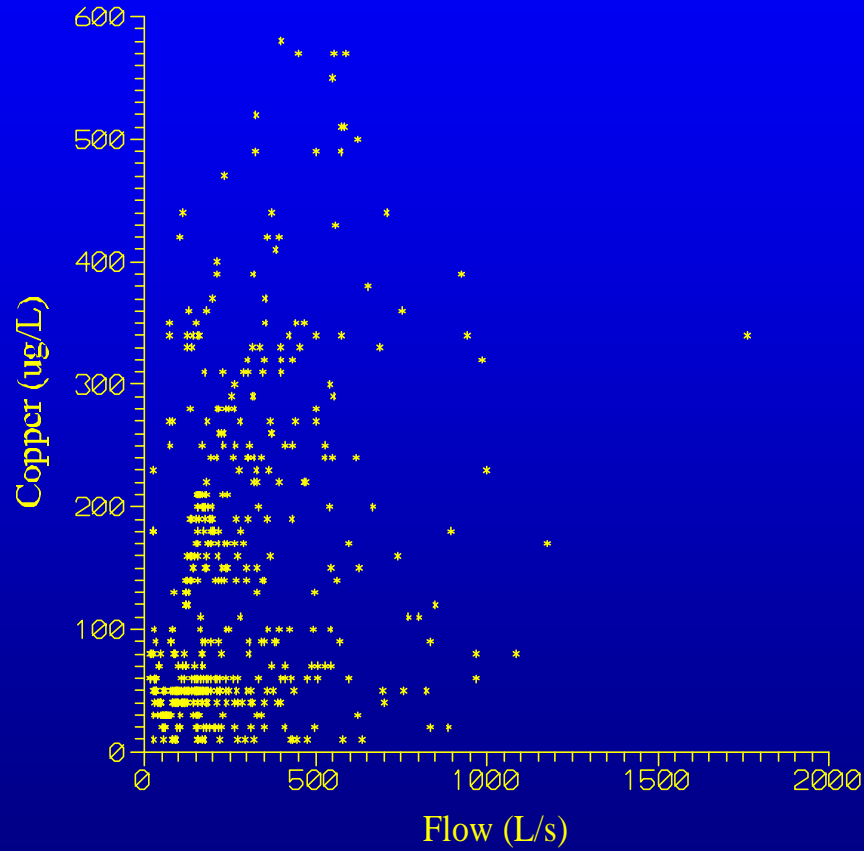
- A series of equations that approximately represent one or more processes, made to simulate a particular site by calibration of “fitting parameters” to existing data?
- A series of equations that describe the cumulative behaviour of a system over decades, which requires no explicit calibration since it is derived from the site-specific data?

How Does One Develop an EDCM?

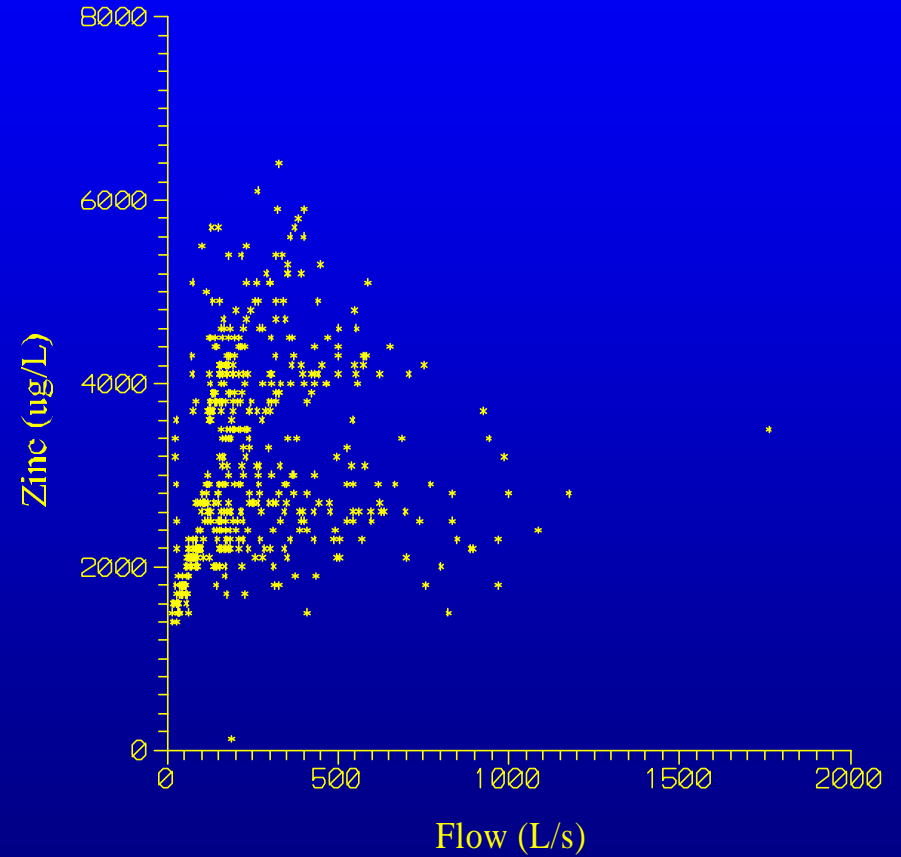
Search for Correlations

- Observed variability in aqueous concentrations ~
(variability in process #1) +
(variability in process #2) +
(variability in process #3) +
etc. + etc.

Copper vs Flow



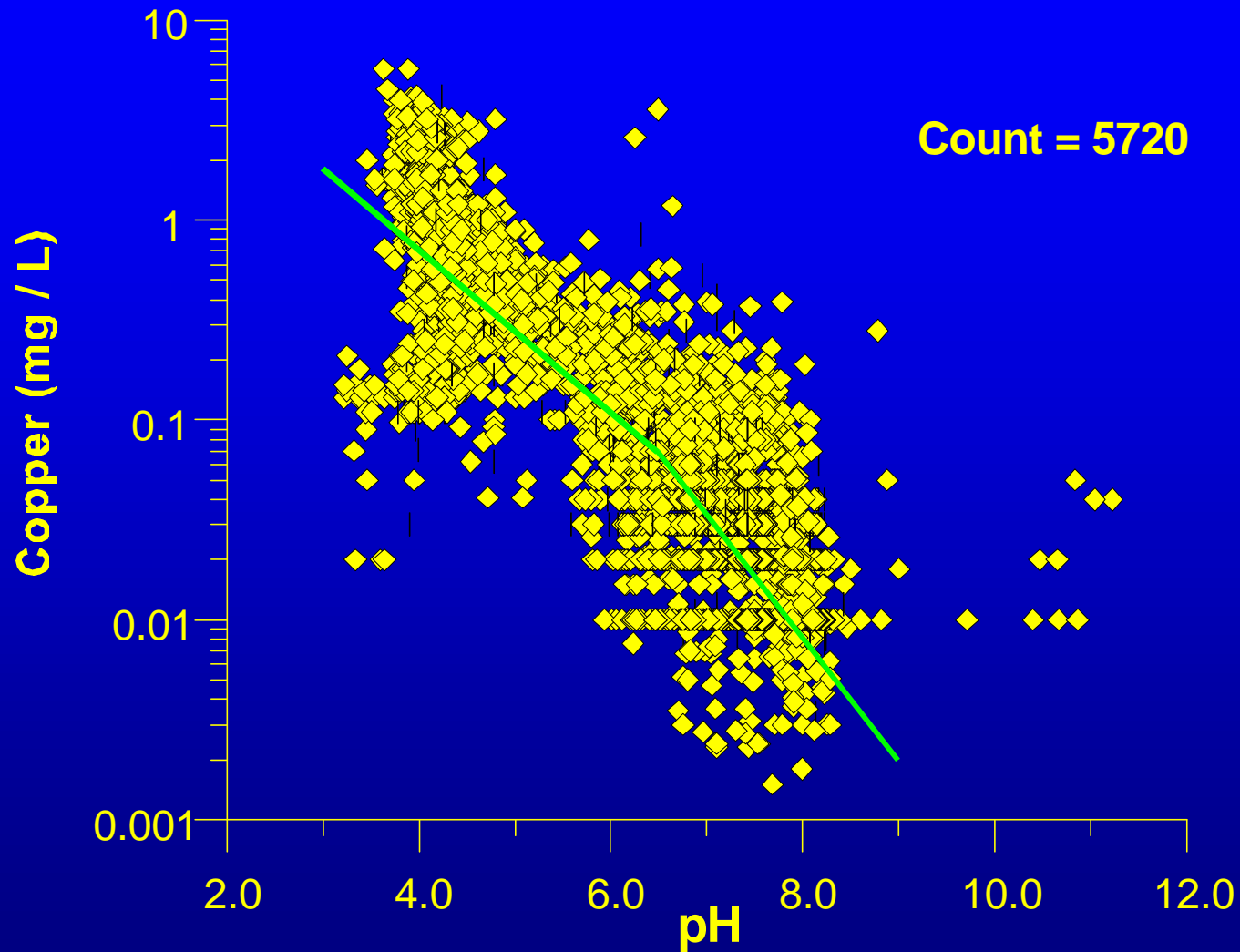
Zinc vs Flow



Annual Logarithmic Means and Standard Deviations for Station WME

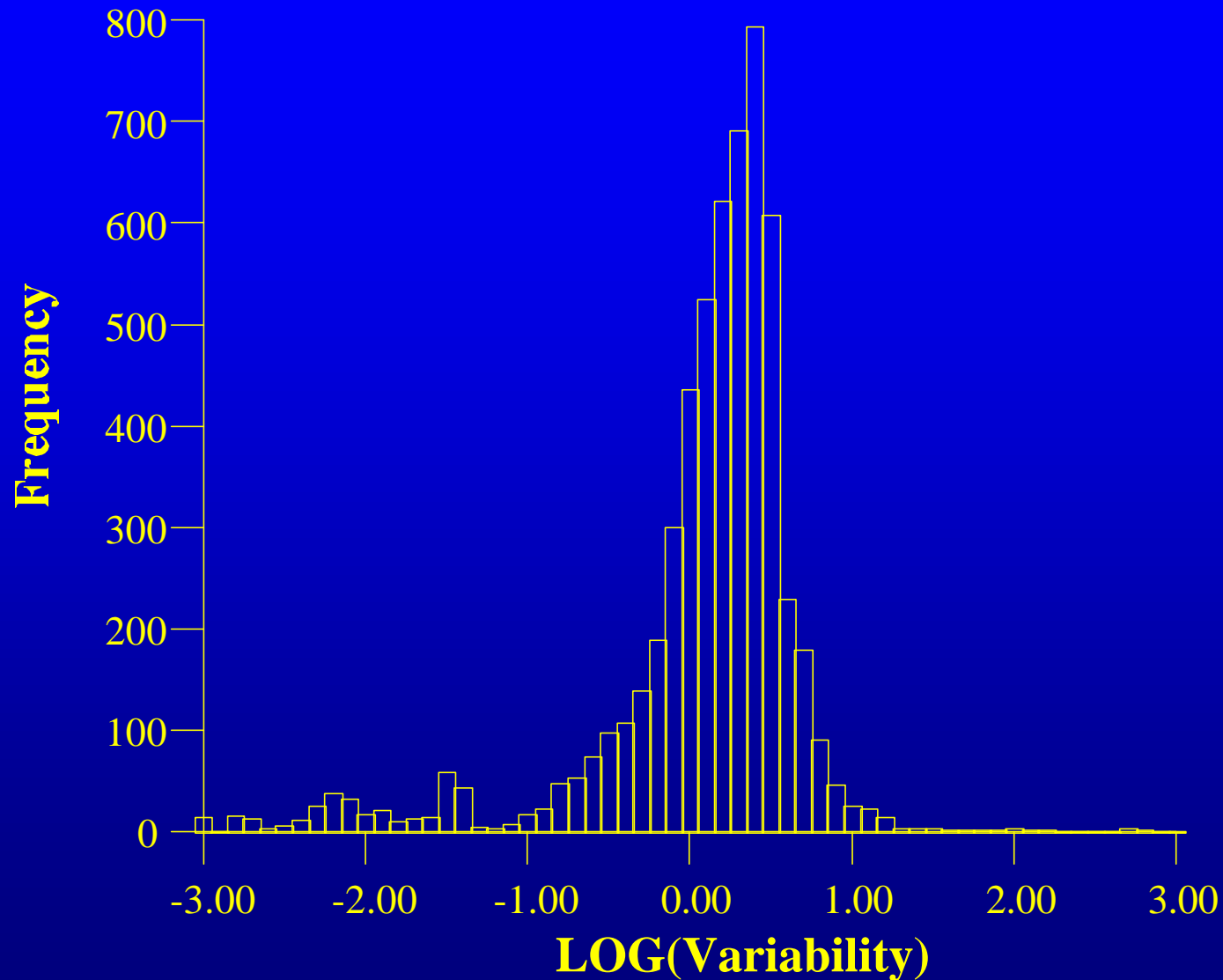
	LOG ₁₀ MEAN				LOG ₁₀ STD DEV			
	<u>90-91</u>	<u>91-92</u>	<u>92-93</u>	<u>93-94</u>	<u>90-91</u>	<u>91-92</u>	<u>92-93</u>	<u>93-94</u>
pH (arithmetic)	6.27	6.93	7.08	6.86	0.71	0.85	0.67	0.69
Conductivity	3.06	3.09	3.1	3.16	0.12	0.09	0.11	0.06
Alkal. (mg/L)	1.74	1.71	1.7	1.62	0.07	0.45	0.36	0.35
Acidity (mg/L)	1.32	1.33	1.51	1.6	0	0.33	0.24	0.05
Cu (mg/L)	-0.94	-1.23	-1.49	-1.43	0.41	0.46	0.42	0.46
Zn (mg/L)	0.41	0.22	0.25	0.41	0.38	0.44	0.4	0.34
Cd (mg/L)	-1.74	-1.82	-1.79	-1.72	0.17	0.22	0.23	0.21
Sulfate (mg/L)	2.89	2.9	2.91	2.93	0.06	0.09	0.08	0.08
Ca (mg/L)	2.37	2.39	2.43	2.44	0.04	0.09	0.06	0.07
Mg (mg/L)	1.46	1.51	1.59	1.6	0.04	0.16	0.07	0.07
Al (mg/L)	-0.78	-0.71	-0.56	-0.57	0.68	0.33	0.35	0.37

Copper vs pH



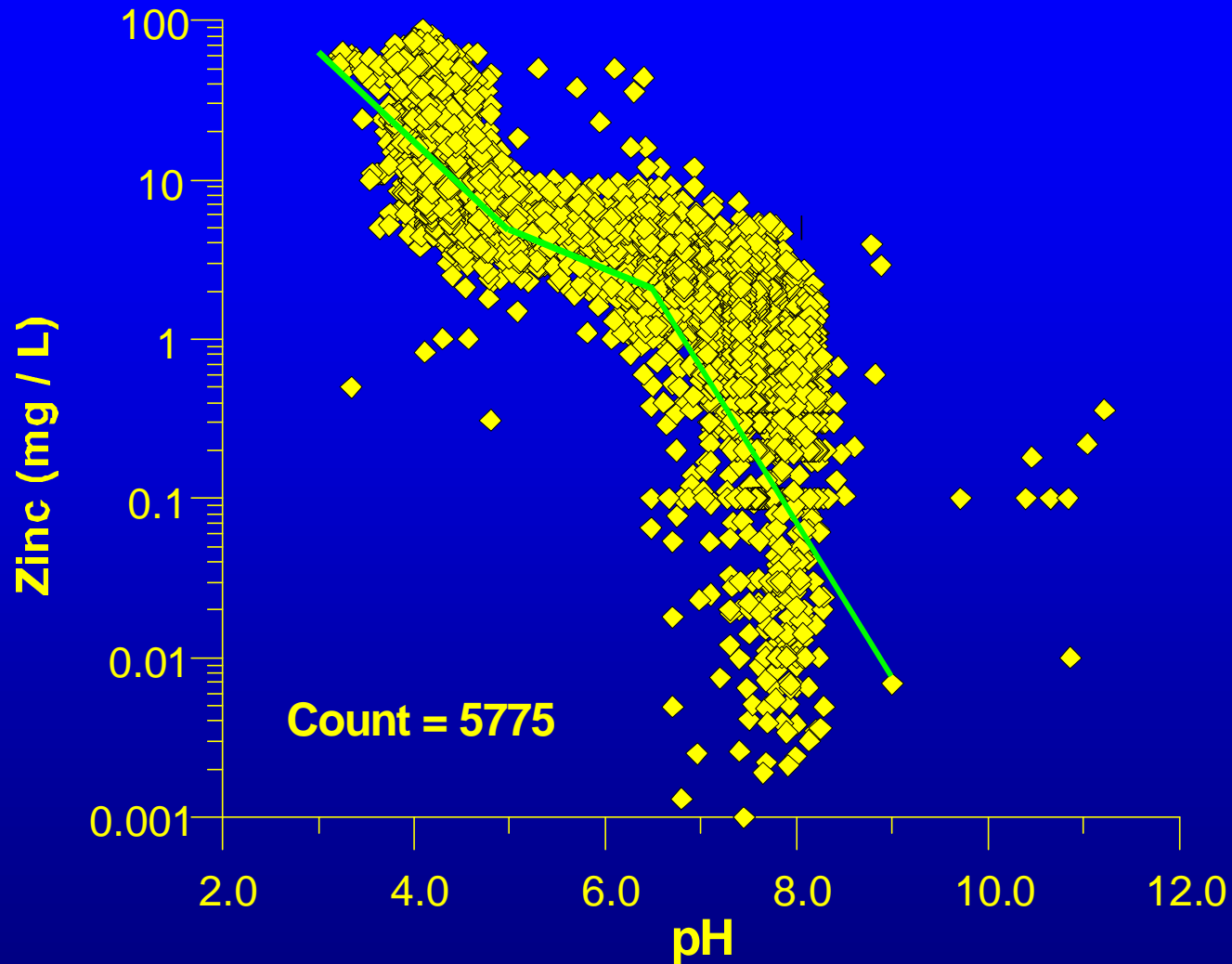
Best Fit: If $\text{pH} < 6.5$, $\log(\text{Cu}) = -0.406\text{pH} + 1.486$;
If $\text{pH} > 6.5$, $\log(\text{Cu}) = -0.640\text{pH} + 3.006$

Variability of log(Copper) Around Best-Fit Line



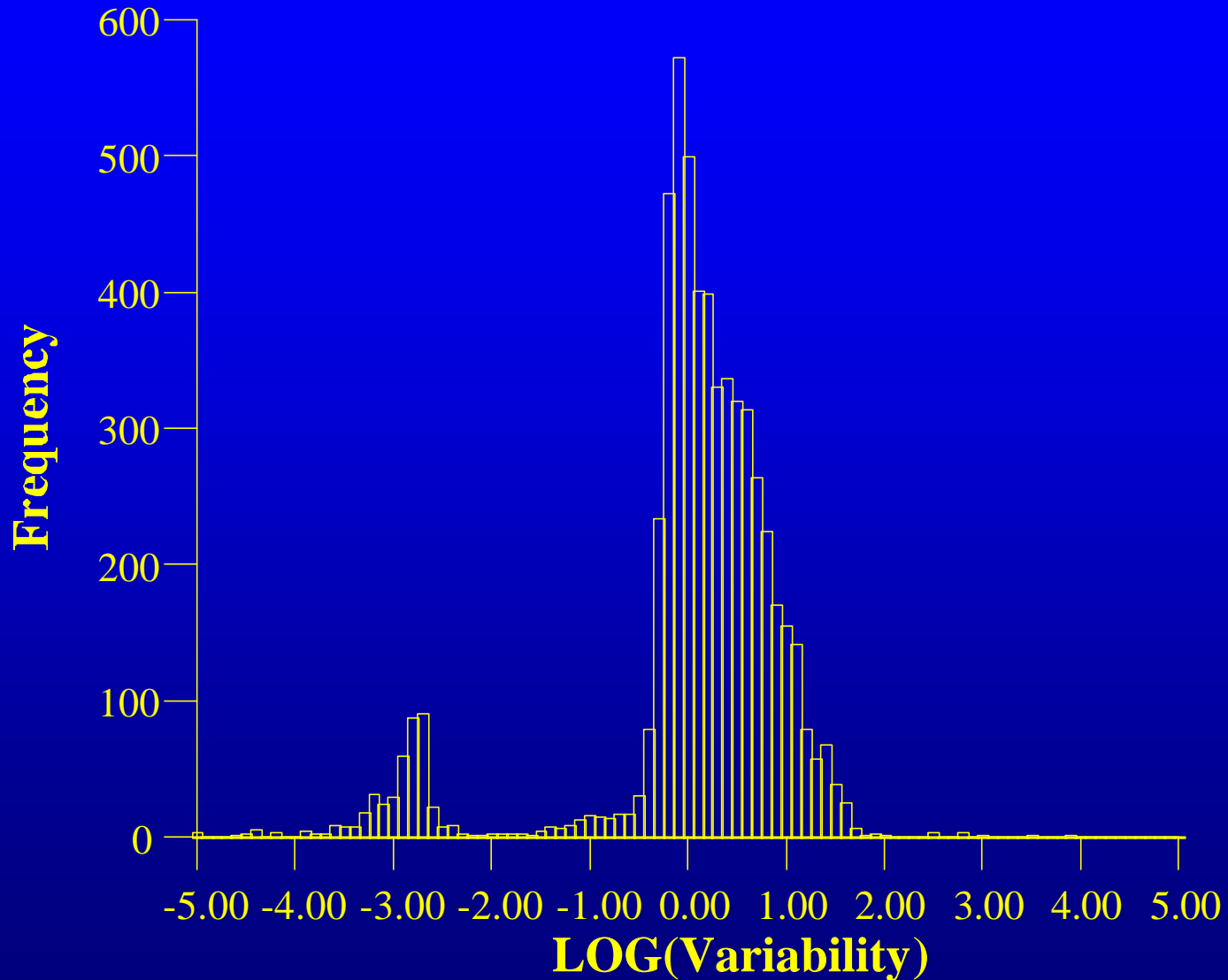
Count = 5720; Std Dev = 0.7088; Mean = +0.000351

Zinc vs pH



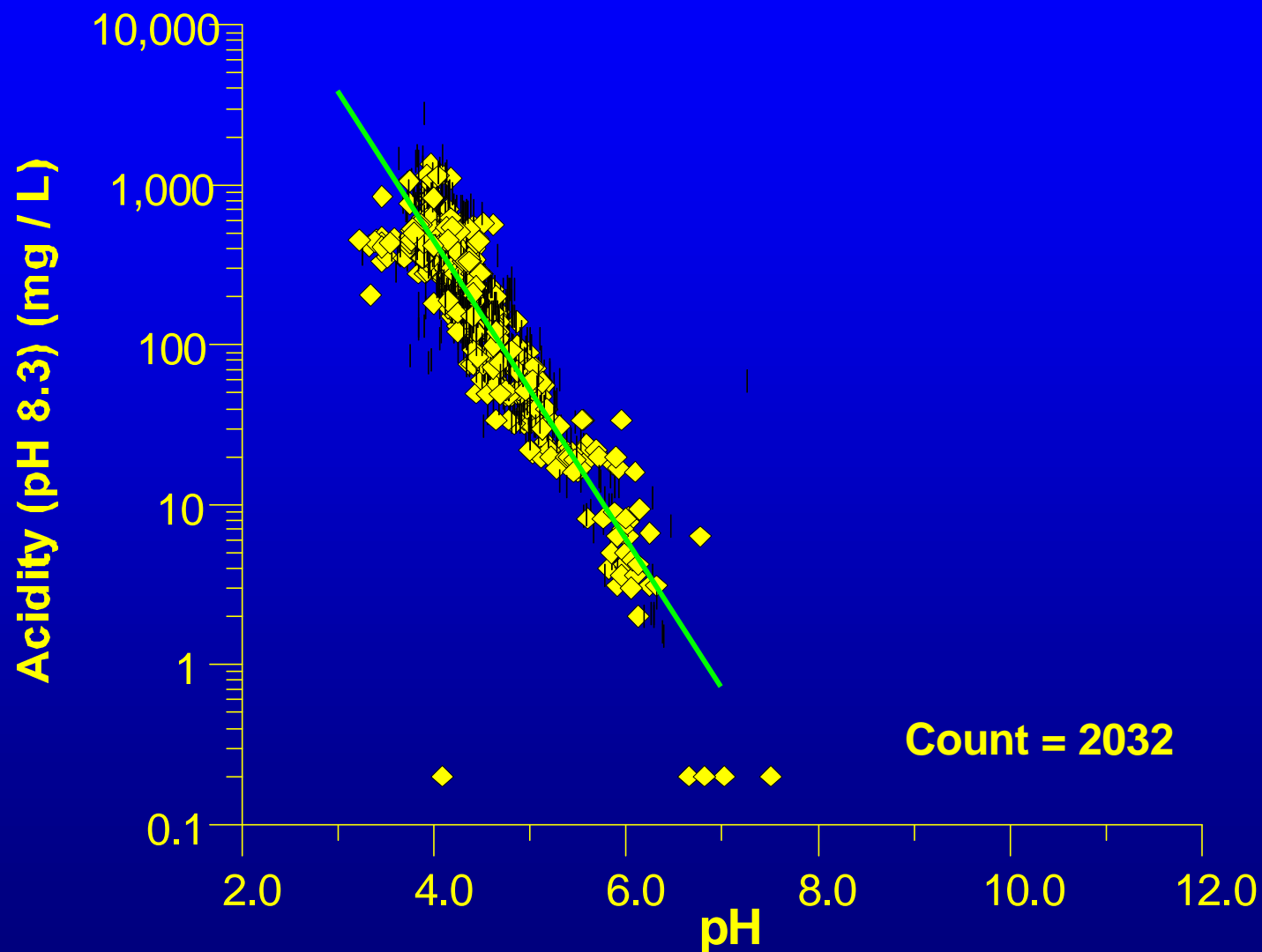
Best Fit: If $\text{pH} < 5.0$, $\log(\text{Zn}) = -0.559\text{pH} + 3.482$;
If $5.0 < \text{pH} < 6.5$, $\log(\text{Zn}) = -0.245\text{pH} + 1.912$;
If $\text{pH} > 6.5$, $\log(\text{Zn}) = -0.974\text{pH} + 6.650$

Variability of log(Zinc) Around Best-Fit Line



Count = 5775; Std Dev = 0.9851; Mean = -0.00015

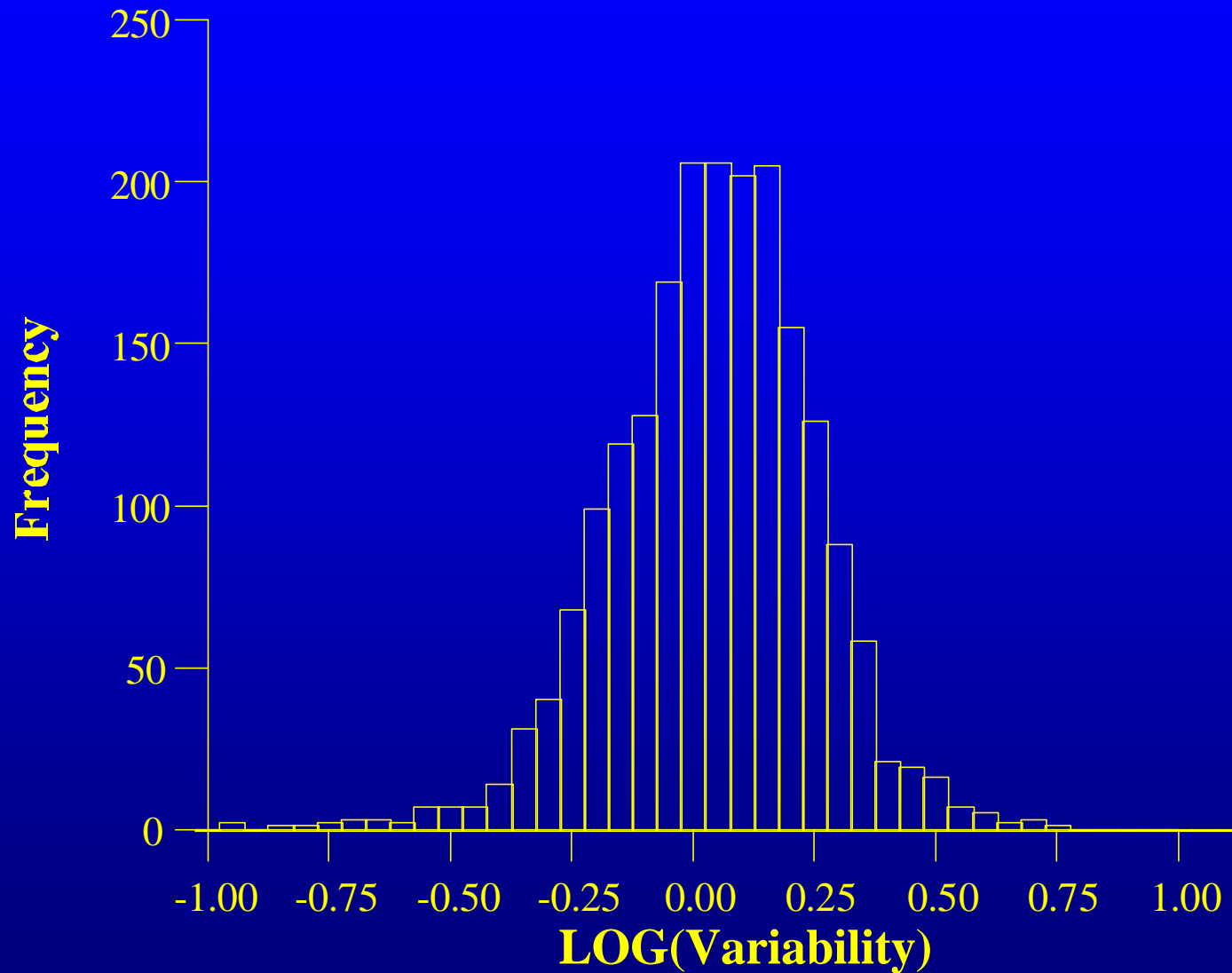
Acidity (pH 8.3) vs pH



Count = 2032

Best Fit: $\log(\text{Acidity}) = -0.932\text{pH} + 6.381$

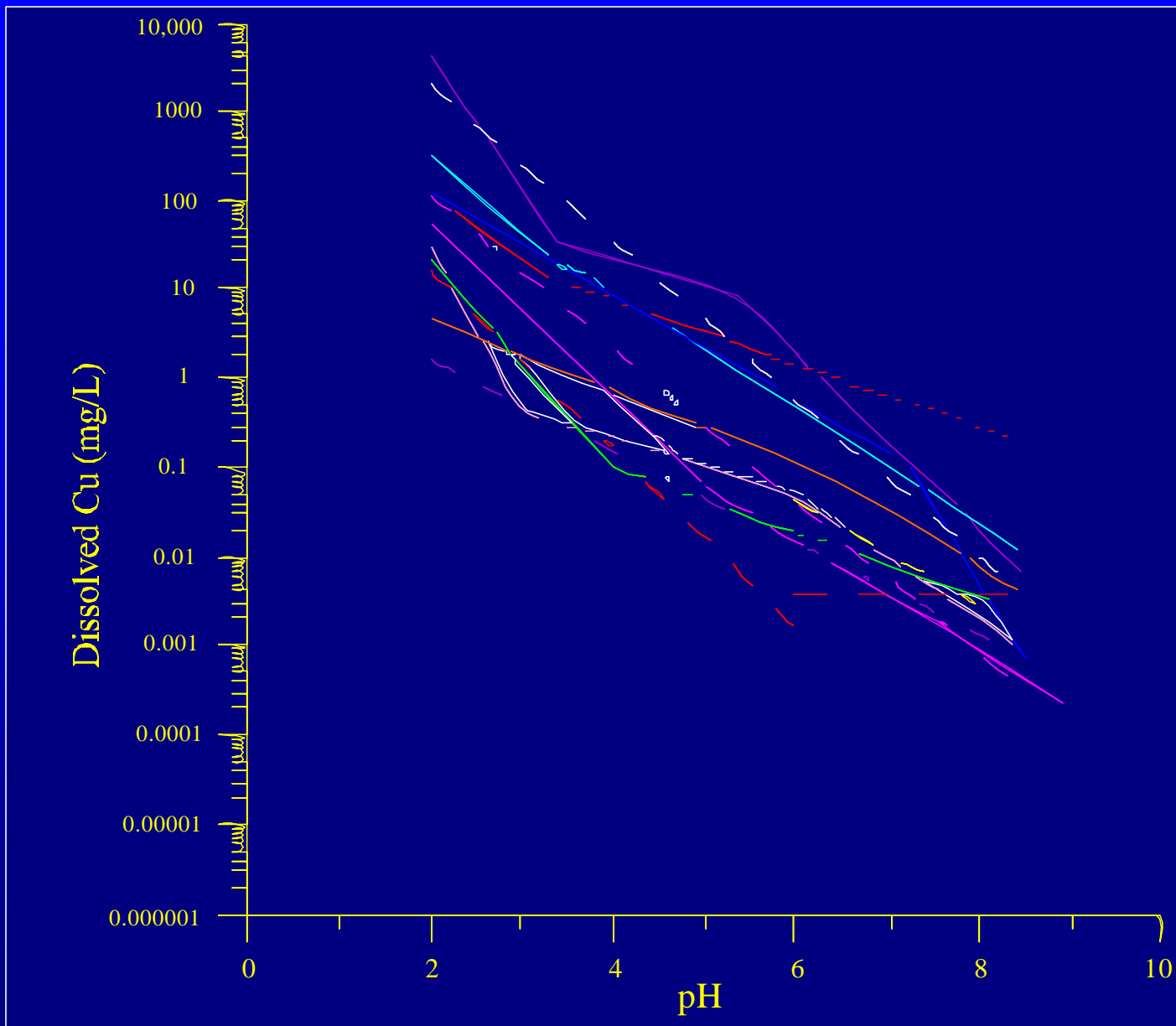
Variability of $\log(\text{Acidity})$ Around Best-Fit Line



Count = 2032; Std Dev = 0.3373; Mean = -0.00053

**EMPIRICAL DRAINAGE-CHEMISTRY MODEL
FOR ISLAND COPPER MINE**

Parameter (mg/L)	Valid pH Range	Predictive Equation for Mean	Standard Deviation from Mean
Acidity (to pH 8.3, N=2032)	pH < 8.0	= -0.932 pH + 6.381	0.3373
Copper (N=5720)	pH ≤ 6.5	= -0.406 pH + 1.486	0.7088
	pH > 6.5	= -0.640 pH + 3.006	
Zinc (N=5775)	pH ≤ 5.0	= -0.559 pH + 3.482	0.9851
	5.0 < pH < 6.5	= -0.245 pH + 1.912	
	pH ≥ 6.5	= -0.974 pH + 6.650	
Aluminum (N=4186)	pH ≤ 5.65	= -1.341 pH + 6.908	1.3156
	pH > 5.65	= -0.068 pH - 0.285	



Solubilities and Models Like MINTEQA2 Cannot Explain Most of These Trends

Number of Standard Deviations above/below the Average-Annual Value for High/Low Concentrations Over Selected Intervals

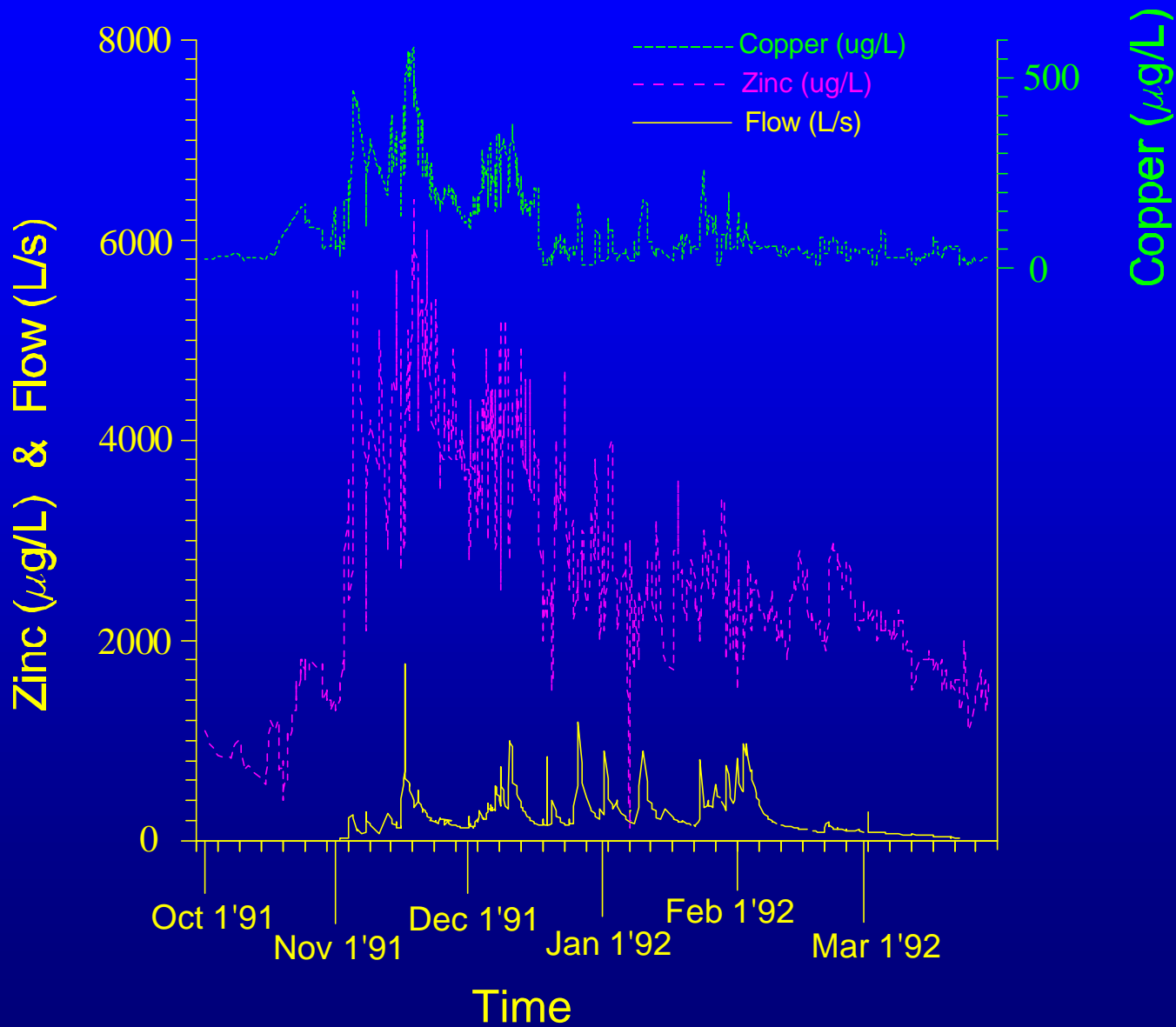
Time Interval	1 YEAR	1 MONTH	1 WEEK	1 DAY	1 HOUR
Number of Standard Deviations above/below average-annual value	+0.00	+1.73	+2.34	+3.00	+3.85

Can an EDCM Actually Predict Short-Term Concentrations?

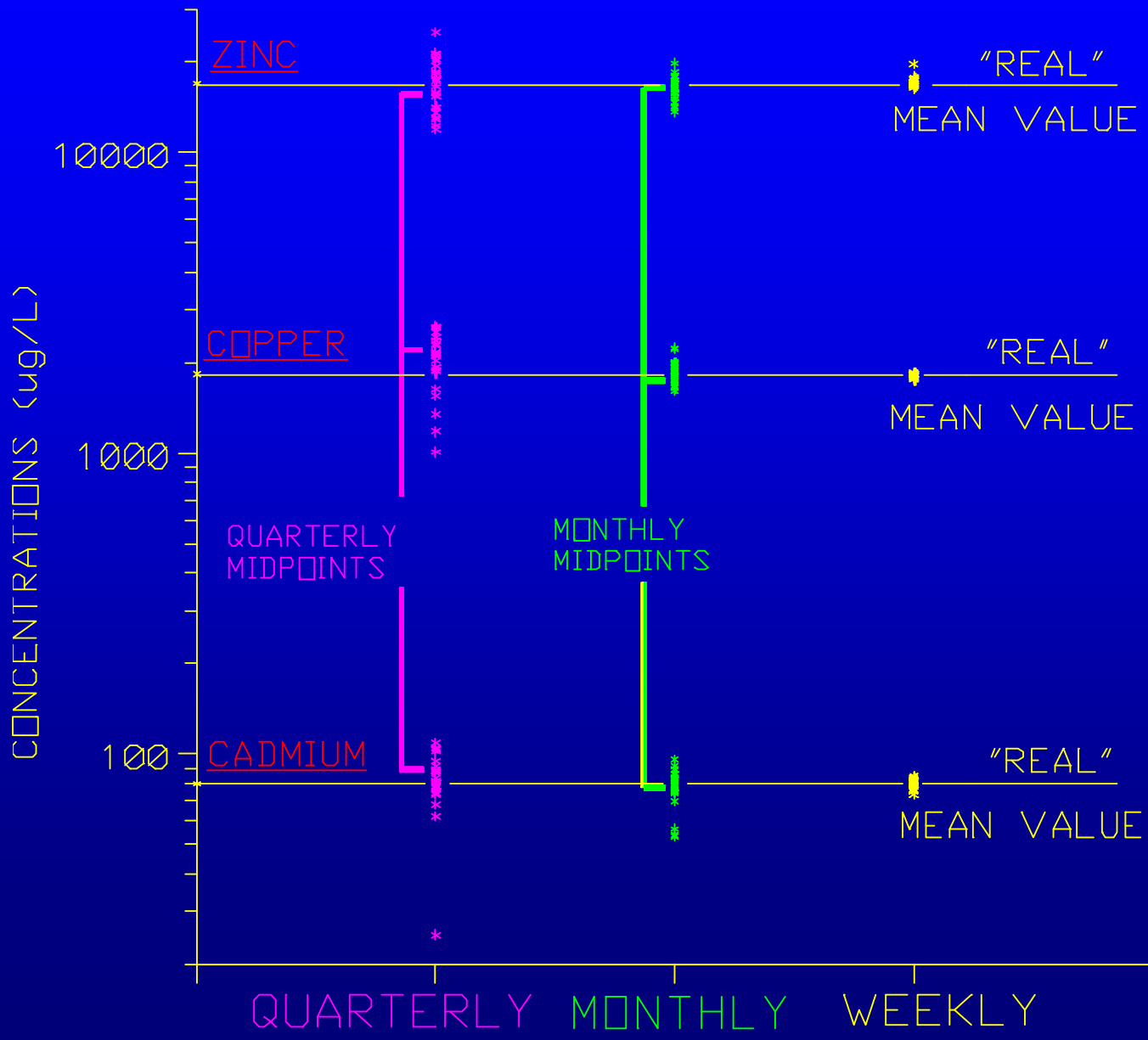
High-Frequency Sampling at Island Copper

- Eight stations around the minesite
- Flow measured as frequently as every 15 minutes
- Water sample collected for analysis as frequently as every four hours
- Water analyzed for: pH, conductivity, alkalinity, acidity, sulfate, copper, zinc, cadmium, calcium, magnesium, and aluminum

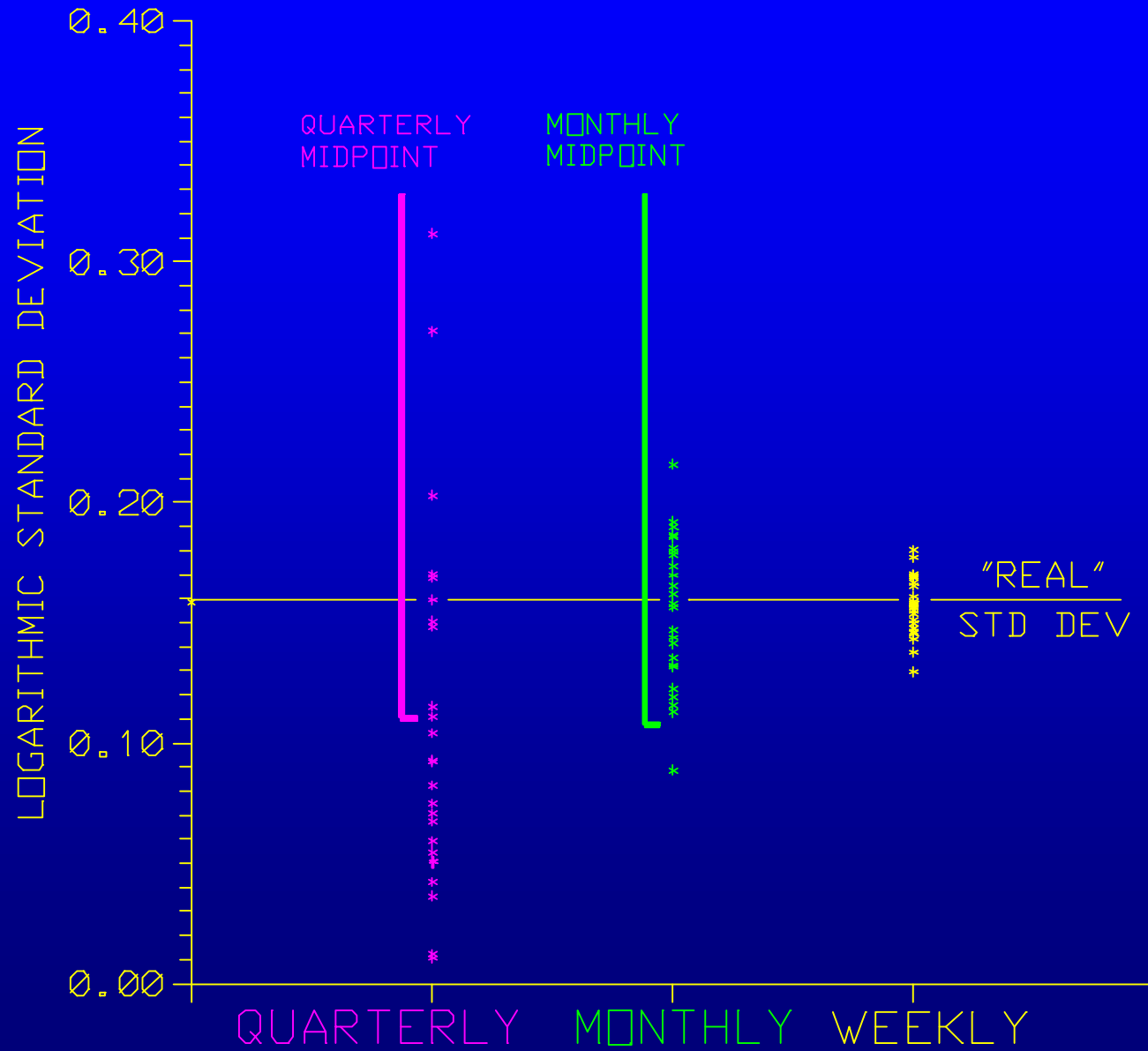
Zinc, Flow & Copper vs Time



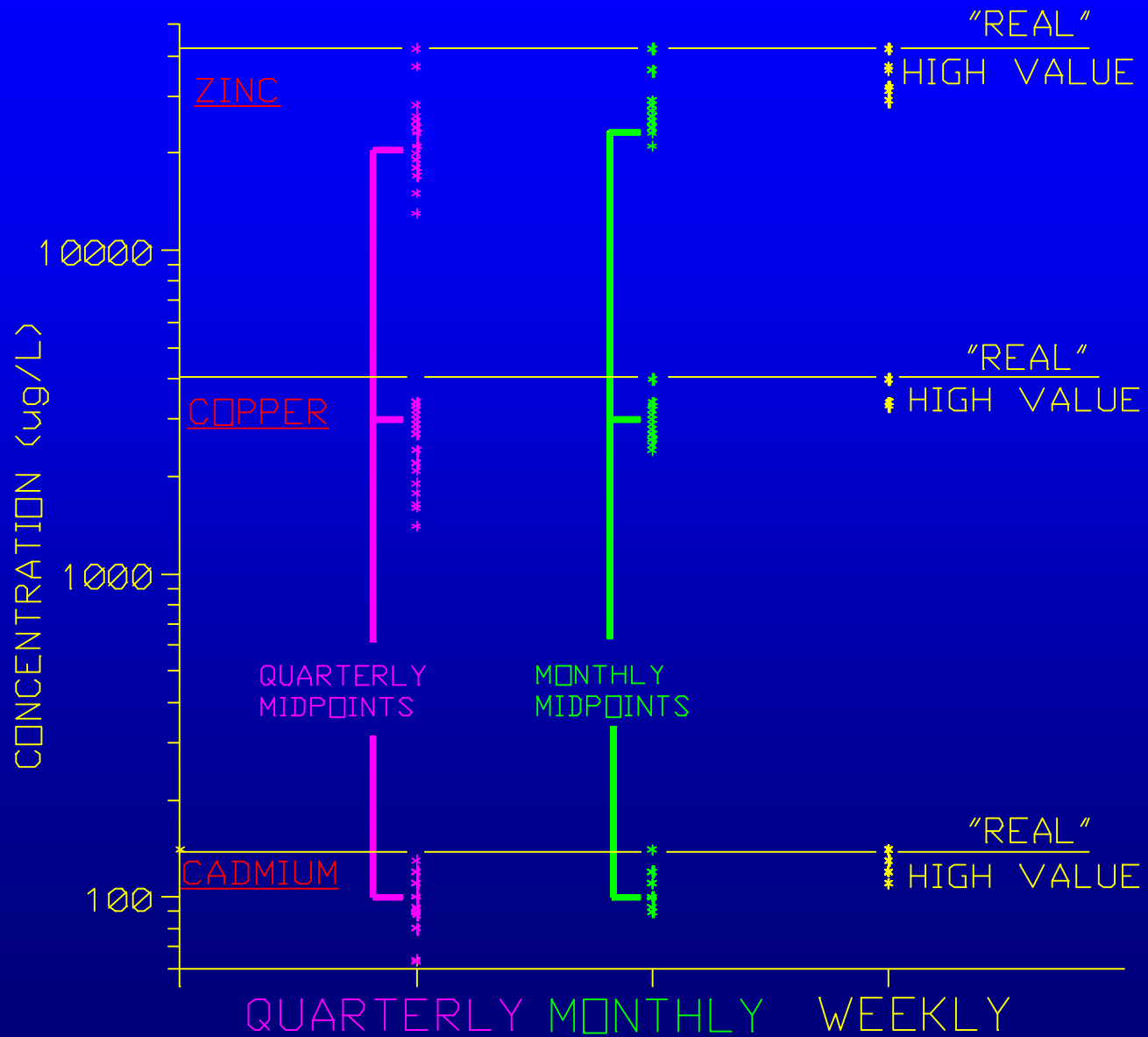
EMO - MEAN VALUES



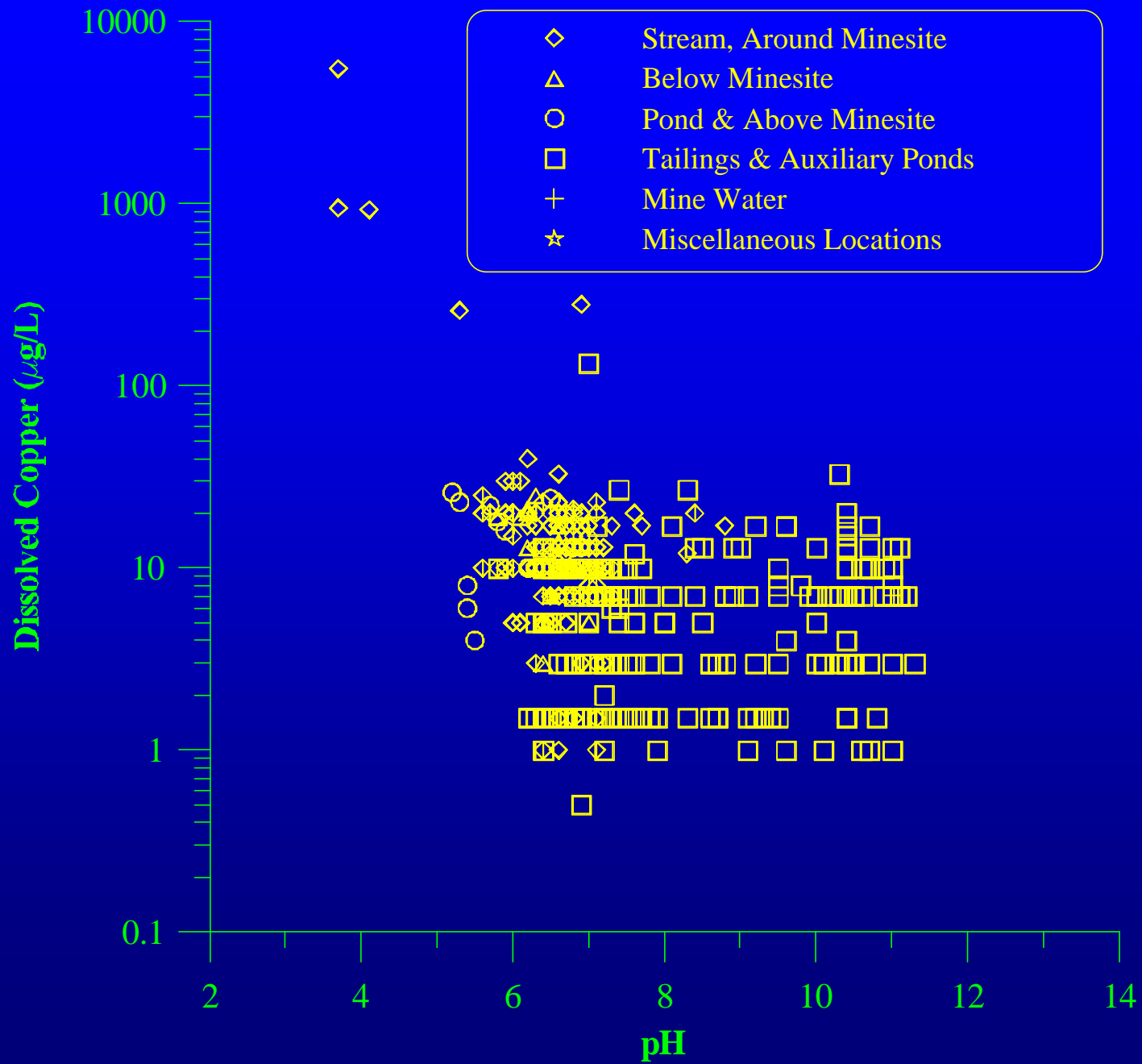
EMO - ZINC STANDARD DEVIATION

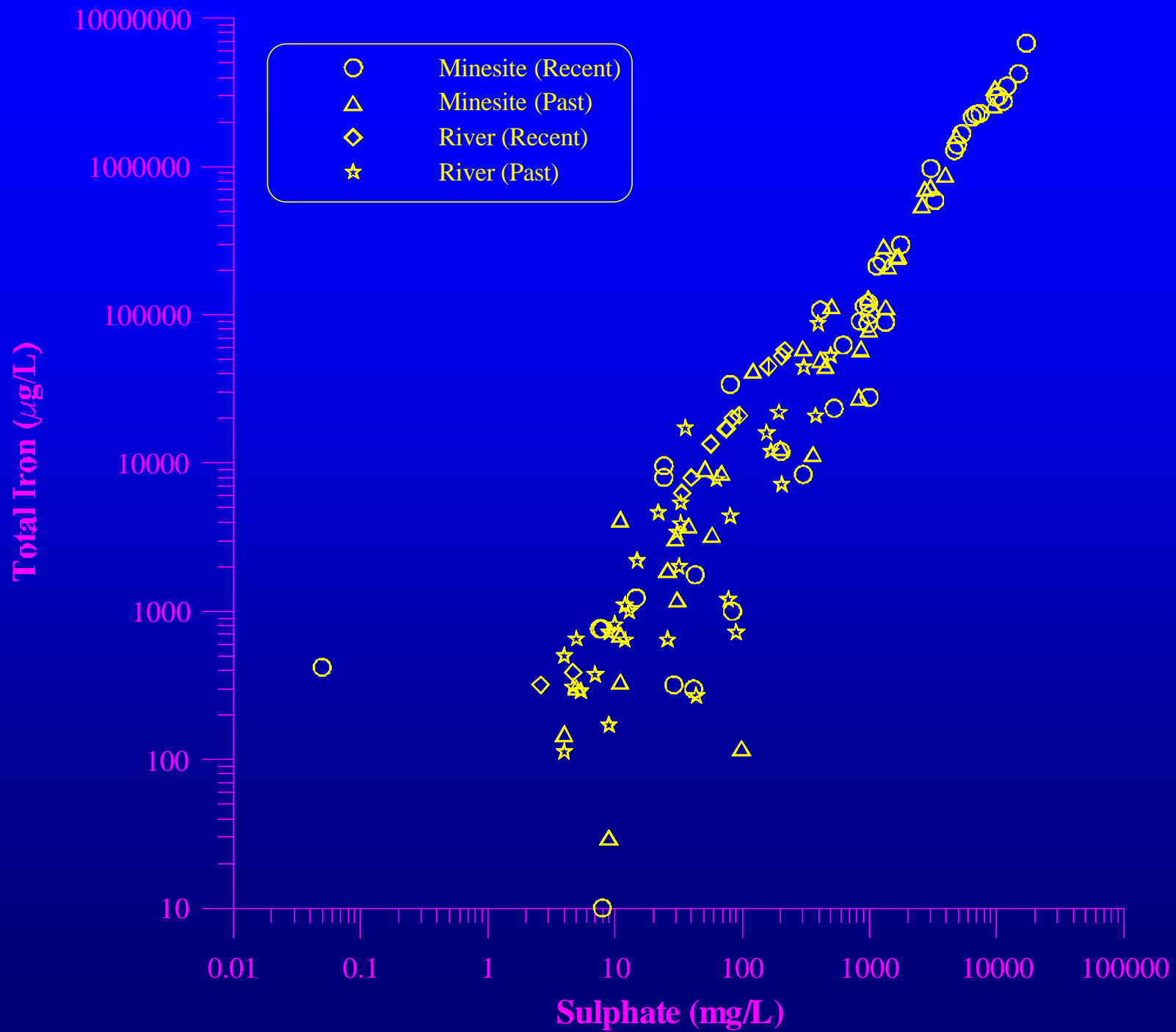


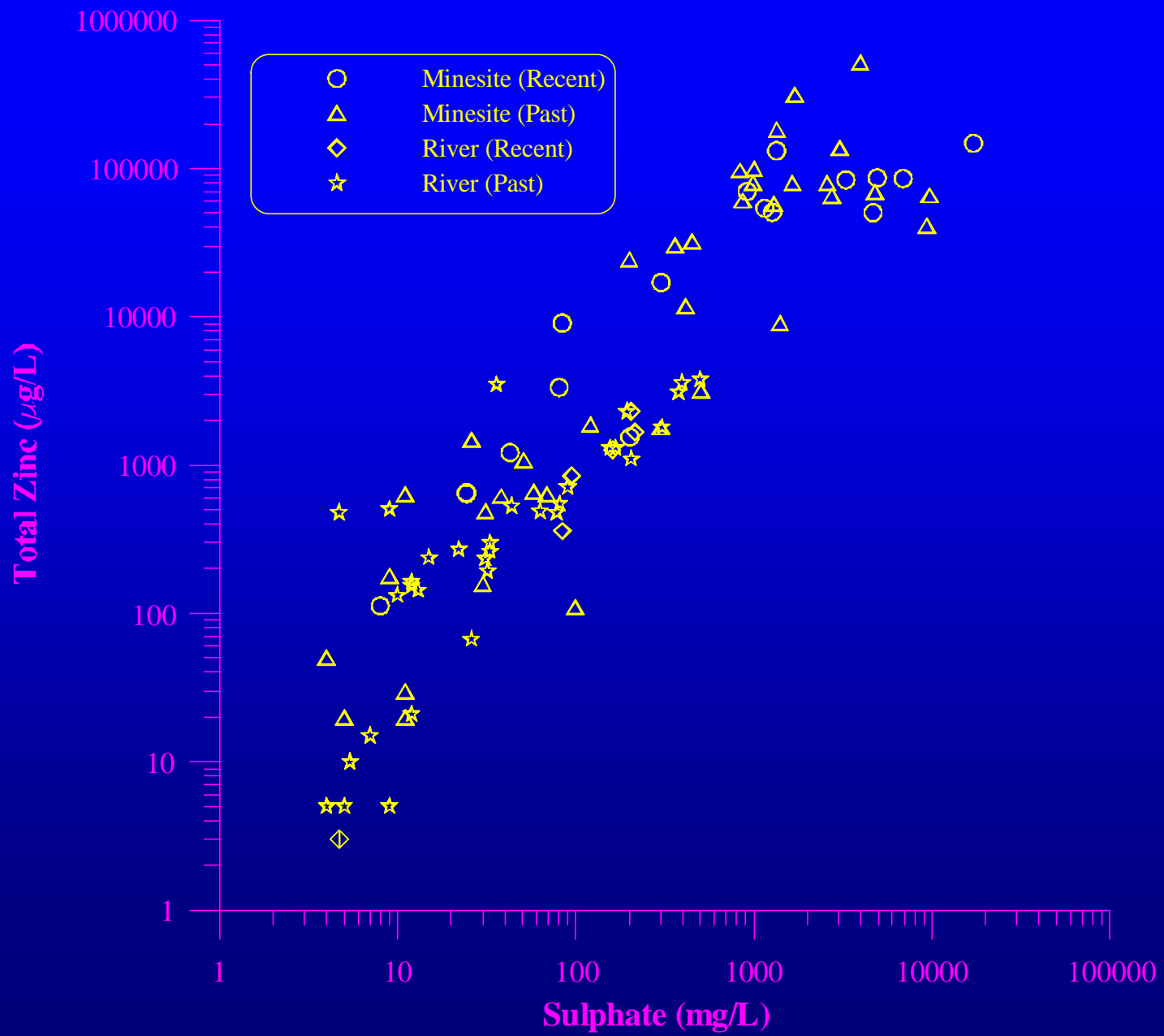
EMO - HIGHEST MEASURED VALUE



Do Concentrations Always Correlate
Well with pH?







How Well Do EDCMs Predict Future Concentrations?

- Since many EDCMs that we have done span a few decades, the simpler question is: Can concentrations in a later year be predicted from earlier decades of data? Yes.
- Some want a specific answer to how well an EDCM based on operational data predicts closure concentrations.

How Well Do EDCMs Predict Future Concentrations?

- Bell Mine in British Columbia had an EDCM created in 1991 based on about a decade of monitoring data at more than two dozen locations. The 1991 concentrations were predicted well from the earlier data. The mine closed in 1992. In 2000, we compared the closure concentrations (mid-1992 to 2000) to the earlier EDCM.

Bell Drainage-Chemistry Update

- As predicted, aqueous concentrations of parameters still regularly measured at Bell Mine have remained around the same seasonal range and annual average.
- Where adjustments were made to the best-fit equations for predicting concentrations, the adjustments were within a factor of two, which is a common resolution in this type of geochemical work.
- The adjustments were perhaps related to the new frequency and cumulative number of samples, or to changes in real processes.

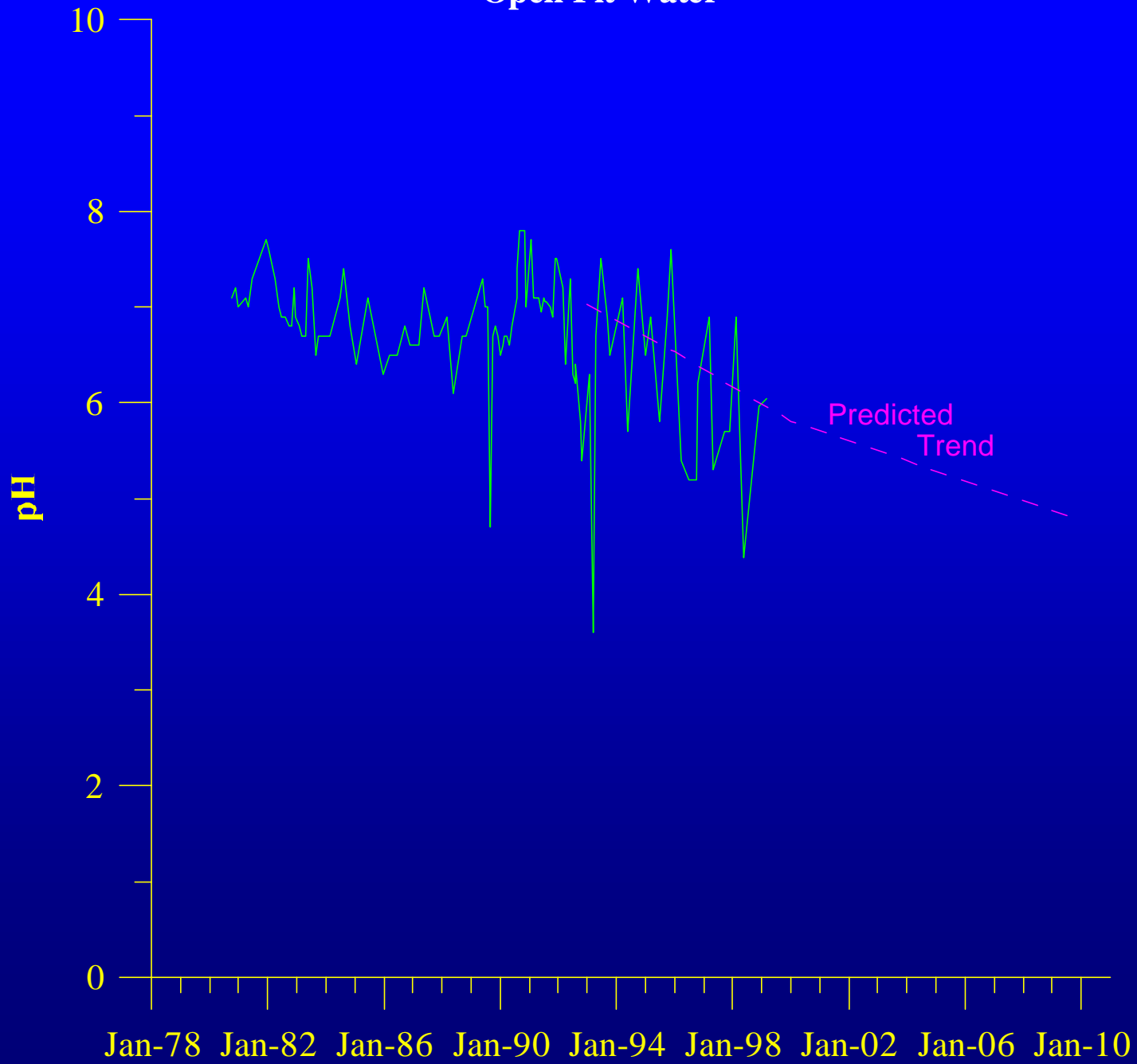
Bell Drainage-Chemistry Update

- For example, dissolved copper around the minesite during closure has generally been about one-half that observed during operation.
- However, dissolved copper does not show a pattern of decreasing concentrations from year to year.
- Therefore, either copper concentrations experienced a single significant shift, or the fewer number of samples during closure lead to different statistical values.

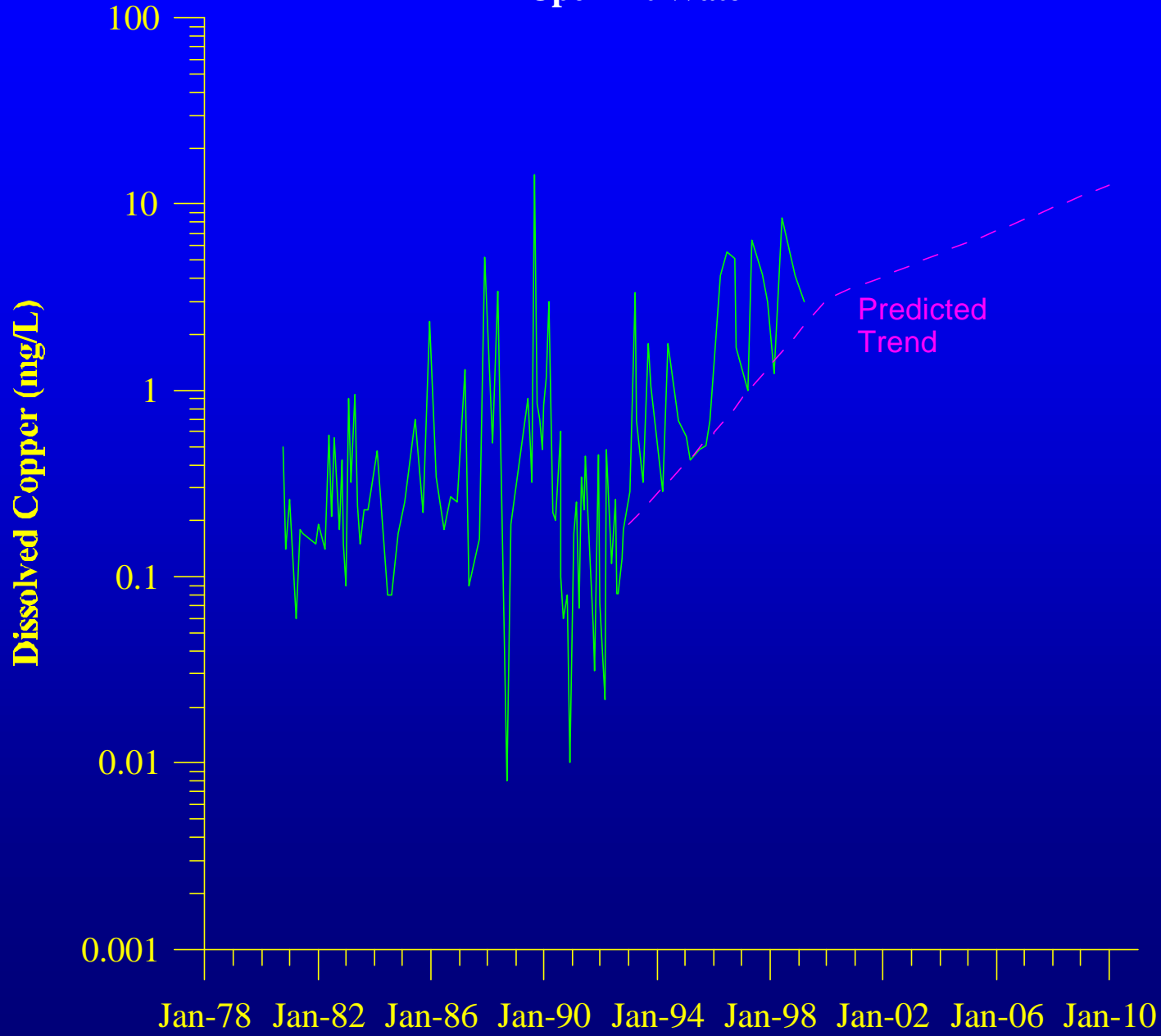
Bell Drainage-Chemistry Update

- The pit receives all drainage from around the minesite that is not acceptable for discharge, and detailed predictions were made for its cumulative chemistry through time in the Closure Plan.
- Samples are collected seasonally from the surface of the pit, but this surficial water may not always be representative of the entire pit-water column.
- In any case, the observed good agreement with predicted trends and concentrations, indicate the original predictions remain generally valid and that the pit water is evolving towards acidic conditions as predicted. No adjustments to the original predictions for the pit are needed at this time.

Open Pit Water



Open Pit Water



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 - frequency of monitoring
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 - annual costs for water-treatment plants
 - acceptable seepage rates through clay/soil covers
 - etc.

Do Theoretical Solubilities and
Programs Like MINTEQA2 Always Fail
Us?

Copper Leaching at Mount Polley

- There is no ARD at Mount Polley, aqueous pH values are around neutral, and the rate of sulphide oxidation is low.
- Sobek-type humidity cells, 24-hour shake flasks, and on-site monitoring data all show that the theoretical solubility of tenorite (CuO) frequently explains observed copper concentrations.

Copper Leaching at Mount Polley

- The presence of tenorite in Mount Polley rock has been confirmed by mineralogy.
- Therefore, programs like MINTEQA2 can be used to simulate and predict copper concentrations at Mount Polley.

Conclusion

Next Time You Are Presenting Your Predictions to a Local Community, First Nations, etc.

- **SCIENTIFIC APPROACH:** Tell the audience that there are only a number of important processes that control aqueous concentrations and that humans understand them all reasonably well. As a result, a series of equations can be assembled into a model that provides accurate predictions.

Next Time You Are Presenting Your Predictions to a Local Community, First Nations, etc.

- **EMPIRICAL APPROACH:** Tell the audience that aqueous concentrations, like the weather, are difficult to predict. However, decades of monitoring have revealed patterns and cycles that have repeated over and over again. This repetition should continue to happen for many more years.

Next Time You Are Presenting Your Predictions to a Local Community, First Nations, etc.

- **EMPIRICAL WITH SOME SCIENCE:** Use the empirical approach, but back it up with mechanistic explanations and justifications when these are apparent in the data.
- **OUR OBSERVATION:** In much of our work, the mechanistic explanations are frequently not apparent. But then they have not been critical for explaining the predictions or for having people accept them.

THE END