

A Compilation of Empirical Drainage-Chemistry Models (EDCMs)

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Abstract: Compilations of large minesite-drainage databases from around the world have shown that cycles of concentrations can reappear on an annual basis, through operation and closure phases. These cycles are caused by various natural and artificial processes, like secondary-mineral equilibrium, temperature variations, organic and inorganic feedback, and analytical error. A method for identifying and defining the cycles is known as an “empirical drainage-chemistry model” (EDCM). The empirical nature of the EDCM arises from the realization that it is not practical or even realistically possible to identify all factors that affect concentrations. Nevertheless, the cumulative results of all factors can be quantified and used for (1) concisely defining past and current drainage chemistry and (2) predicting future drainage chemistry including seasonal variations after mine closure.

This is the first time that statistics from all EDCMs have been compiled and compared for copper, zinc, lead, and nickel. This shows that, for example, average aqueous-copper concentrations are quantitatively unique to each minesite, but follow similar qualitative patterns with pH. Depending on pH, average-annual copper concentrations among the sites differ by up to three orders of magnitude. For eight months each year, copper concentrations statistically remain within plus-and-minus one standard deviation of the annual average. This is a total span of one order of magnitude (a factor of 10) for the average site, but varies from 0.4 to 1.6 orders of magnitude among the sites. For four months every year, concentrations are outside (above and below) this span around the annual average. Similar observations are made for zinc, lead, and nickel.

Introduction

Some minesites have existed for decades and have accumulated thousands of water-quality analyses to address environmental concerns and regulatory conditions. These analyses are often interpreted and reported once, and then rarely used later. In reality, an accumulating database of drainage chemistry represents a valuable environmental asset for a minesite at no additional cost. Hidden in the data may be long-term trends or repeating cycles that can be used for longer-term predictions.

With this in mind, the authors began ten years ago compiling large databases and data warehouses of drainage-chemistry analyses, summarizing and interpreting them statistically, searching for trends and cycles, and then using the statistical information for short- and long-term predictions. As more minesites with large databases were located, the authors refined and clarified the approach, which was eventually given the simplistic name of “Empirical Drainage-Chemistry Model” or EDCM. There can be some debate on whether a set of statistical equations and values based on actual site data truly represents a “model” compared to, for example, a set of differential equations purportedly representing all important on-site processes after calibration to site data. However, this debate lies outside the scope of this paper.

The authors have published several papers on individual EDCMs, the procedure for creating them, and their use and success in predicting drainage chemistry at minesites (Morin and Hutt, 1997, 2001a, and in press; Morin et al., 1993, 1994, and 1995a and b). However, equations and statistics for all non-confidential EDCMs have not been previously compiled in one paper and compared. That is the objective of this paper.

Overview of the EDCM Approach

The most labour-intensive part of creating an EDCM is to compile all existing water-quality analyses, particularly if they exist only as paper copies. Once all data have been entered into any spreadsheet program, scatterplots of one parameter against another are created and checked for correlations. Typically, some correlation will be noted with parameters like aqueous pH or sulphate, which then become independent variables (or “master” parameters) for predicting concentrations of other elements and parameters.

Correlations may be seen within the entire database as a whole, or only with certain sampling locations, or only with certain time periods. This must be checked before proceeding to statistical calculations. Most of the existing EDCMs displayed correlations using all site data from all sampling locations spanning the entire monitoring period, but a few EDCMs required dividing the database into sampling areas or time periods (e.g., Table 1).

Once reasonable correlations are obtained with the master parameters, “best-fit” equations are determined, to allow the calculation of an average value of the dependent parameter from a value of the master parameter (e.g., left sides of Figures 1 and 2). If an entire database is used, this best-fit equation is often synonymous with the site-wide annual average. In other words, using the left side of Figure 1, the equation will provide the average-annual concentration of copper for any value of pH at this minesite.

On the left sides of Figures 1 and 2, it is not immediately apparent that there are many points close to the average-annual equation with the number decreasing vertically away from the lines. This is shown on the right sides of the figures, where all datapoints are plotted based on their vertical distance from the average-annual lines on the corresponding left side. Frequently a statistical distribution resembling lognormal is seen in such figures, and a standard deviation in logarithmic cycles can then be calculated. If the entire database is used, the standard deviation often reflects the seasonal variability around the average annual equation. Mathematically, this means that all variations in concentrations caused by the countless inorganic and organic processes operating at a minesite (Morin and Hutt, 2001b) are incorporated into the standard deviation. Again, it is important to note that some parameters do not correlate well with pH (e.g., Figure 3), but may correlate with others (e.g., Figure 4).

After a database is searched for correlations and is statistically evaluated, the resulting equations and standard deviations are compiled into a table, which formally represents the EDCM for the minesite (Table 1). If average-annual and seasonal ranges of concentrations remain generally steady from year to year, then the EDCM will allow long-term predictions. The standard deviations, combined with statistical values (Table 2), allow predictions, for example, of seasonal variations, peak concentrations that may occur between sampling events, and sizing of collection ponds to smooth out peak concentrations to an acceptable level.

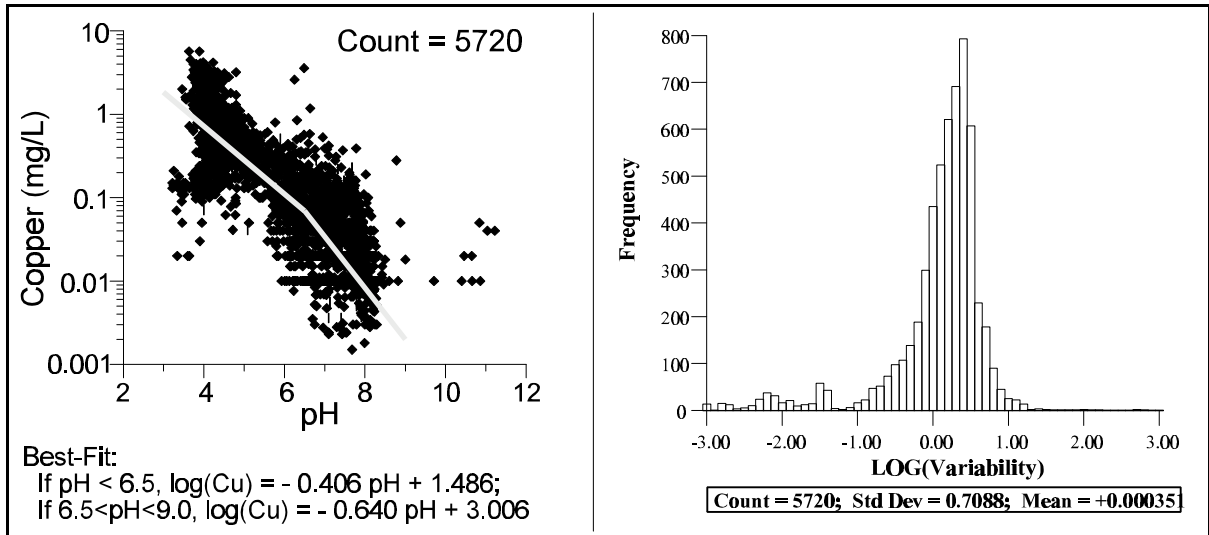


FIGURE 1. Correlation of Copper with pH in an EDCM; left side is best-fit correlation and right is vertical distribution around the best-fit equations (adapted from Morin et al., 1995a).

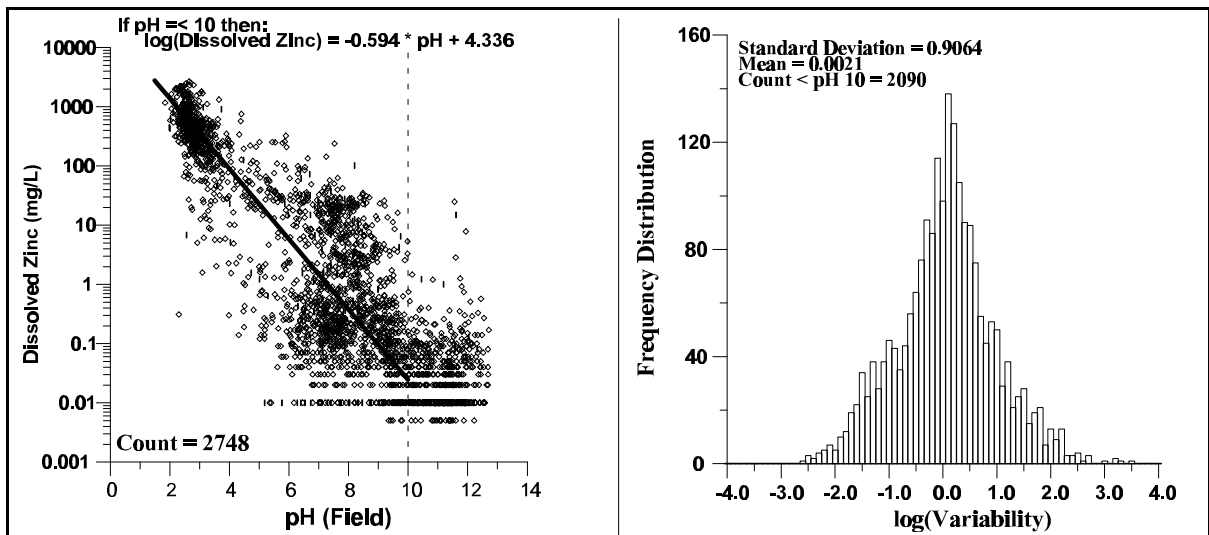


FIGURE 2. Correlation of Zinc with pH in an EDCM.

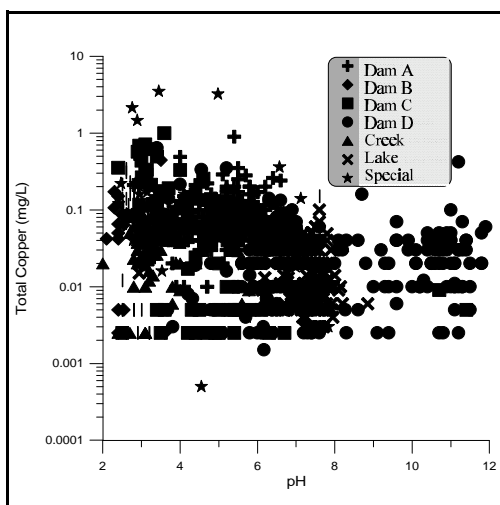


FIGURE 3. Example of Poor Correlation with pH.

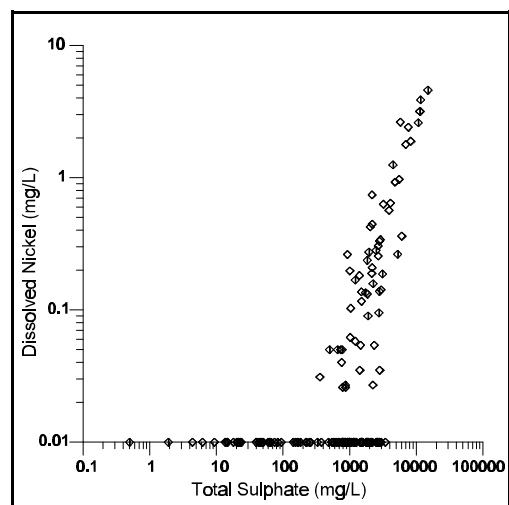


FIGURE 4. Example of Good Correlation with Sulphate.

TABLE 1
Abridged Example of an EDCM from a Minesite with a Large Pit, Several Waste-Rock Dumps, and Several Tailings Impoundments

<u>Parameter</u>	<u>Condition¹</u>	<u>Best-Fit Correlation to Predict Concentration (in mg/L)²</u>	<u>Std Dev³</u>
Total Sulphate	All sites except #1 after 1993	$\log(\text{Total Sulphate}) = -0.061\text{pH} + 3.599$	0.213
	#1 after 1993	$\log(\text{Total Sulphate}) = -0.395\text{pH} + 5.219$	0.239
Acidity	All sites except #1 with pH > 3.0	$\log(\text{Acidity}) = -0.312\text{pH} + 3.510$	0.382
	All sites except #1 with pH < 3.0	$\log(\text{Acidity}) = -2.100\text{pH} + 8.858$	0.462
	#1	$\log(\text{Acidity}) = -0.615\text{pH} + 5.382$	0.368
Carbonate Alkalinity	All sites with pH > 4.5	$\log(\text{Carb Alkalinity}) = 0.584\text{pH} - 2.160$	0.418
	All sites with pH < 4.5	$\log(\text{Carb Alkalinity}) = \text{NA}$	NA
Total Hardness	All locations	Total Hardness = 1030	0.301
Specific Conduct.	All locations	$\log(\text{Sp Cond}) = -0.103\text{pH} + 4.019$	0.441
Total Organic Carbon	All locations	$\log(\text{TOC}) = 0.454\text{pH} - 1.952$	0.412
Dissolved Al	#1	$\log(\text{D-Al}) = -1.007\text{pH} + 5.889$	0.466
	All sites except #1	$\log(\text{D-Al}) = -0.648\text{pH} + 3.690$	0.354
Total Al	All sites	T-Ag \approx D-Ag for D-Al > 2.0 mg/L	
Dissolved As	North Dump with pH < 4.5	$\log(\text{D-As}) = -1.206\text{pH} + 4.056$	0.542
	North Dump with pH > 4.5	D-As < 0.2	NA
	All locations with pH < 4.0 except North Dump	$\log(\text{D-As}) = -0.300\text{pH} + 0.179$	0.448
	All locations with pH > 4.0 except North Dump	D-As < 0.2	NA
Total As	All locations	T-As \approx D-As for all data	
Diss Be	All locations	$\log(\text{D-Be}) = -0.205\text{pH} - 1.231$	0.273
Total Be	All locations	T-Be \approx D-Be for D-Be > 0.02 mg/L	
Diss Cd	All sites	$\log(\text{D-Cd}) = -0.200\text{pH} - 1.016$	0.323
Total Cd	All sites	T-Cd \geq D-Cd for all data	
Dissolved Co	#1	$\log(\text{D-Co}) = -0.741\text{pH} + 3.080$	0.468
	All sites except #1	$\log(\text{D-Co}) = -0.430\text{pH} + 1.128$	0.39
Total Co	All sites	T-Co \approx D-Co for D-Co > 0.01 mg/L	
Dissolved Cu	#1	$\log(\text{D-Cu}) = -1.030\text{pH} + 5.299$	0.479
	All sites except #1	$\log(\text{D-Cu}) = -0.461\text{pH} + 2.136$	0.798

Parameter	Condition ¹	Best-Fit Correlation to Predict Concentration (in mg/L) ²	Std Dev ³
Total Cu	All sites	T-Cu ≈ D-Cu for D-Cu > 10 mg/L	
Diss Cr	All locations	$\log(D-Cr) = -0.278pH - 0.273$	0.413
Total Cr	All locations	T-Cr ≈ D-Cr for all data	
Dissolved Fe	All sites with pH < 3.8	$\log(D-Fe) = -1.850pH + 7.471$	0.547
	All sites with pH > 3.8	$\log(D-Fe) = -0.535pH + 2.472$	0.707
Total Fe	All sites	T-Fe ≈ D-Fe for D-Fe > 7 mg/L	
Diss Mn	All locations	$\log(D-Mn) = -0.308pH + 2.075$	0.756
Total Mn	All locations	T-Mn ≈ D-Mn for D-Mn > 2 mg/L	
Diss Mo	All sites	No correlation	NA
Total Mo	All sites	T-Mo ≈ D-Mo for D-Mo > 0.02 mg/L	
Dissolved Ni	#1	$\log(D-Ni) = -0.499pH + 1.924$	0.339
	All sites except #1	$\log(D-Ni) = -0.307pH + 0.492$	0.442
Total Ni	All sites	T-Ni ≈ D-Ni for D-Na > 0.01 mg/L	
Diss Pb	All locations	$\log(D-Pb) = -0.304pH + 0.364$	0.468
Total Pb	All locations	T-Pb ≈ D-Pb (Based on only 2 values)	
Dissolved Zn	#1	$\log(D-Zn) = -0.790pH + 3.565$	0.532
	All sites with pH < 3.8 except #1	$\log(D-Zn) = -0.616pH + 1.890$	0.34
	All sites with ≥ pH 3.8 except #1	$\log(D-Zn) = -0.272pH + 0.571$	0.78
Total Zn	All sites	T-Zn ≈ D-Zn for D-Zn > 0.3 mg/L	

¹ “#1” is Waste-Rock Dump #1.

² To use pH correlations, aqueous sulphate must be greater than 300 mg/L.

³ Log standard deviation in logarithmic cycles

TABLE 2					
Number of Standard Deviations above/below the Average-Annual Concentration for High-Low Concentrations during Intervals Shorter Than One Year					
Time interval →	Highest/Lowest Average Concentration Spanning . . .				
	1 Year	1 Month	1 Week	1 Day	1 Hour
Number of standard deviations above/below annual average ^a	0	± 1.73	± 2.34	± 3.00	± 3.85

^a Based on normal-distribution tables where concentrations are higher than average values half the time and lower than average values for the other half, which has been observed for most of the EDCMs.

Compilation of EDCMs

The authors have created a number of EDCMs, but only a few have been published in the aforementioned references. This paper provides the opportunity to compile and examine many more. EDCMs often include at least a dozen parameters, but the space limitation of this paper allows the discussion of only copper, zinc, lead, and nickel.

Best-fit equations for copper are available from 15 minesites (Table 3). For three of these sites (Sites 1, 11, and 14), their entire databases had to be divided into separate areas because of the different correlations between the areas. For example, the correlation of copper with pH at Site 1 was different at a waste-rock dump than at the remainder of the site. For Site 14, the correlation in the mine water was different from that in the waste rock. For Site 9, there was no good correlation of copper with pH, but a correlation with sulphate instead.

When the best-fit lines for copper are compiled (Figure 5), concentrations are seen to vary among the minesites by two to three orders of magnitude at any particular pH. Concentrations are typically above 10 mg/L at pH 2.5 (including extrapolations of equations for those sites with no measured pH below 3) and below 0.1 mg/L at pH 8. Area B at Site 11 has the highest concentrations across much of the pH range, and falls below 1 mg/L only above pH 7.

To illustrate the standard deviations for each site, an arbitrary pH of 3.5 was selected and used to create Figure 6. The three-order-of-magnitude difference in mean values is again apparent among the minesites. Also, within each site, the plus-minus one logarithmic standard deviation (vertical line for each site or area) is seen to span 0.4 to 1.6 orders of magnitude, or a factor of 2.5 to 40, with an average of 0.94 orders of magnitude. Based on statistics used to develop Table 2, concentrations at pH 3.5 at each site will be within the vertical lines shown in Figure 6 for eight months on average each year, and thus above and below the vertical lines for the other four months.

The compilation of best-fit lines for zinc generally shows differences among the sites at a particular pH, as with copper, around 2-3 orders of magnitude (Figure 7). Unlike Site 11 (Area B) for copper, Site 7 in this case produces the highest zinc concentrations at acidic pH, but not at near-neutral values. At pH 3.5 (Figure 8), the vertical lines representing plus-minus one log standard deviation typically span an average of 1.4 orders of magnitude, compared to 0.94 orders for copper. Thus zinc concentrations at these minesites are seasonally more variable than copper. However, the site with the highest concentration for copper (Figure 6) does not have the highest zinc concentration (Figure 8), and sites with relatively high standard deviations for copper do not necessarily have relatively high values for zinc. This highlights the need for assessing and predicting each metal of concern separately.

Lead (Figures 9 and 10) and nickel (Figures 11 and 12) concentrations among the minesites generally span about two orders of magnitude, which tends to be less than copper and zinc. This is perhaps due to the fewer number of sites with abundant lead and nickel analyses. The spans of plus-minus one standard deviation for lead and nickel are 1.1 and 0.99 orders of magnitude, respectively, which is close to the copper value of 0.94 but less than the zinc value of 1.4.

TABLE 3
Compilation of EDCM Equations for Dissolved Copper

<u>Minesite¹</u>	<u>Condition</u>	<u>Best-Fit Equation to Predict Cu in mg/L</u>	<u>Log Std Dev</u>
Site 1 - Dump #1		$\log(\text{Cu}) = -1.030\text{pH} + 5.299$	0.479
Site 1 - All Other		$\log(\text{Cu}) = -0.461\text{pH} + 2.136$	0.798
Site 2	pH < 3.4	$\log(\text{Cu}) = -1.485\text{pH} + 6.605$	0.692
	3.4 < pH < 5.4	$\log(\text{Cu}) = -0.327\text{pH} + 2.666$	
	pH > 5.4	$\log(\text{Cu}) = -1.001\text{pH} + 6.307$	
Site 3	pH ≤ 6.5	$\log(\text{Cu}) = -0.406\text{pH} + 1.486$	0.709
	pH > 6.5	$\log(\text{Cu}) = -0.640\text{pH} + 3.006$	
Site 4	2.00 ≤ pH ≤ 3.00	$\log(\text{Cu}) = -1.828\text{pH} + 5.133$	0.581
	3.00 ≤ pH ≤ 6.00	$\log(\text{Cu}) = -0.317\text{pH} + 0.601$	
	6.00 ≤ pH ≤ 8.50	$\log(\text{Cu}) = -0.819\text{pH} + 3.613$	
Site 7	pH < 5.00	$\log(\text{Cu}) = -0.739 \text{pH} + 3.045$	0.369
Site 8		$\log(\text{Cu}) = -0.943\text{pH} + 4.264$	0.794
Site 9	all SO ₄	$\log(\text{Cu}) = +0.959\log(\text{SO}_4) - 3.382$	
Site 10	pH < 3.5	$\log(\text{Cu}) = -0.889\text{pH} + 4.302$	0.586
	3.5 ≤ pH ≤ 8.0	$\log(\text{Cu}) = -0.646\text{pH} + 3.54$	
Site 11 Area A	pH ≤ 5.25	$\log(\text{Cu}) = -0.334\text{pH} + 2.369$	0.633
	pH > 5.25	$\log(\text{Cu}) = -1.169\text{pH} + 6.754$	
Site 11 Area B	pH ≤ 3.90	$\log(\text{Cu}) = -0.181\text{pH} + 3.252$	0.568
	pH > 3.90	$\log(\text{Cu}) = -0.726\text{pH} + 5.378$	
Site 11 Both Areas	SO ₄ ≥ 50 mg/L	$\log(\text{Cu}) = +2.000\log(\text{SO}_4) - 3.986$	0.727
Site 12	pH < 5.0	$\log(\text{Cu}) = -0.976\text{pH} + 3.67$	0.705
	5.0 ≤ pH ≤ 9.0	$\log(\text{Cu}) = -0.618\text{pH} + 1.88$	
Site 13	pH < 7.25	$\log(\text{Cu}) = -0.588\text{pH} + 3.294$	0.603
	pH > 7.25	$\log(\text{Cu}) = -1.739\text{pH} + 11.609$	
Site 14 - Mine	pH < 3.40	$\log(\text{Cu}) = -0.6934\text{pH} + 3.4284$	0.196
	pH ≥ 3.40	$\log(\text{Cu}) = -0.3494\text{pH} + 2.2589$	
Site 14 - Waste Rock		$\log(\text{Cu}) = -1.5707\text{pH} + 5.6754$	0.216
Site 15	pH < 4.0	$\log(\text{Cu}) = -1.170\text{pH} + 3.680$	0.390
	pH ≥ 4.0	$\log(\text{Cu}) = -0.364\text{pH} + 0.456$	

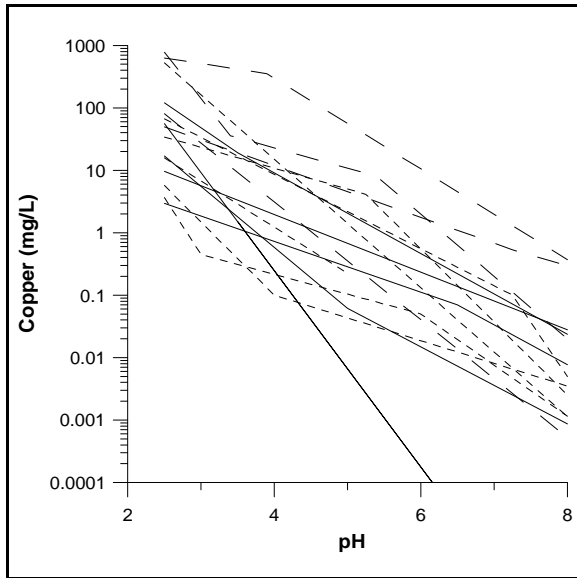


FIGURE 5. Compilation of Copper Best-Fit Lines Among the Minesites.

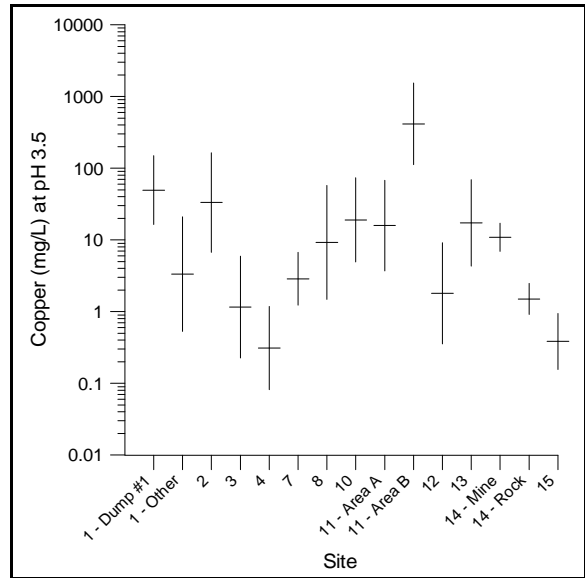


FIGURE 6. Copper Concentrations at pH 3.5 Among the Sites (Mean at Lateral Line \pm 1 Log Std Deviation).

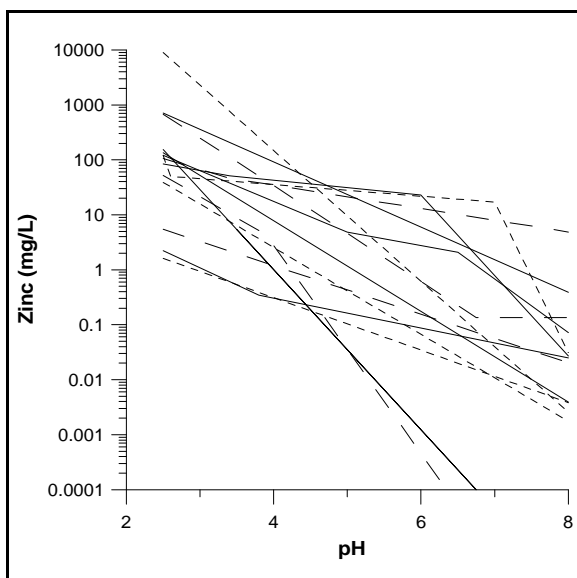


FIGURE 7. Compilation of Zinc Best-Fit Lines Among the Minesites.

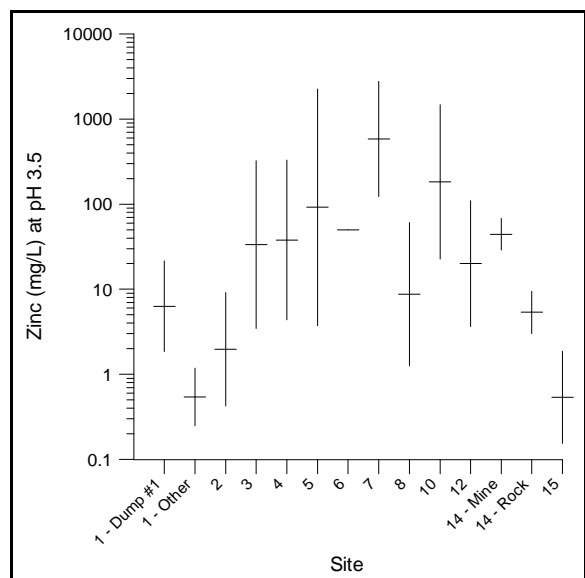


FIGURE 8. Zinc Concentrations at pH 3.5 Among the Sites (Mean at Lateral Line \pm 1 Log Standard Deviation).

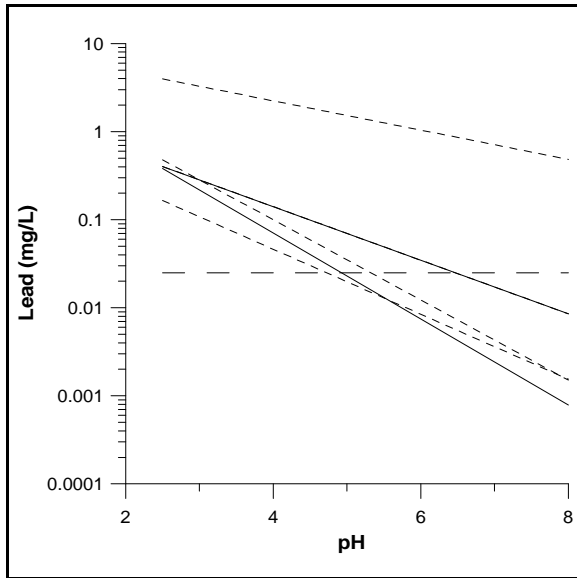


FIGURE 9. Compilation of Lead Best-Fit Lines Among the Minesites.

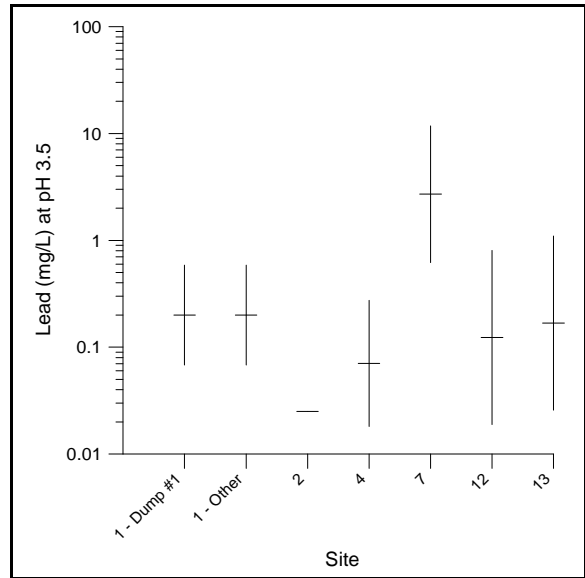


FIGURE 10. Lead Concentrations at pH 3.5 Among the Sites (Mean at Lateral Line \pm 1 Log Standard Deviation).

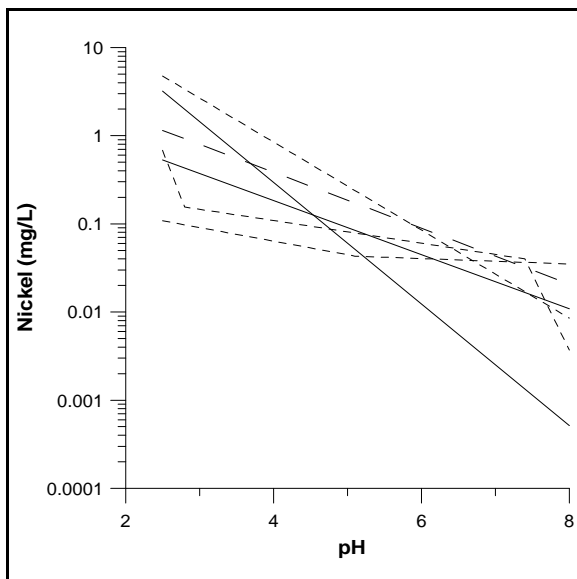


FIGURE 11. Compilation of Nickel Best-Fit Lines Among the Minesites.

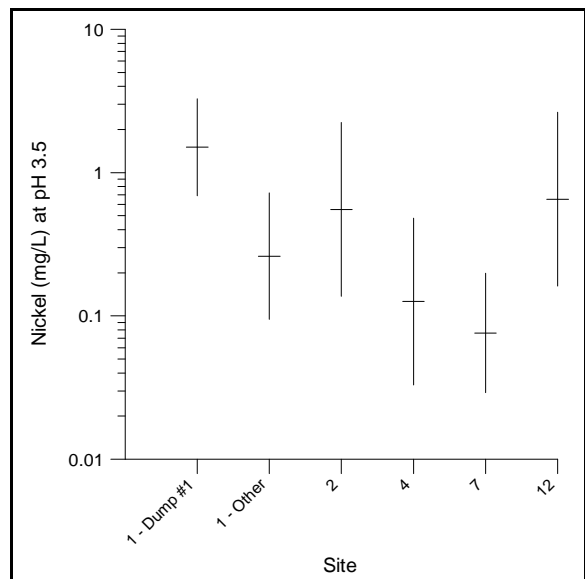


FIGURE 12. Nickel Concentrations at pH 3.5 Among the Sites (Mean at Lateral Line \pm 1 Log Standard Deviation).

Conclusion

This paper has been the first compilation of best-fit equations and standard deviations from EDCMs for 15 minesites. This compilation has focussed on copper, zinc, lead, and nickel. Among minesites, concentrations of these metals typically span two to three orders of magnitude at a particular pH. Standard deviations, reflecting seasonal variability in concentrations, were variable among the sites, but averaged roughly 0.5-0.7 orders of magnitude for each metal. As a result, a plus-minus one standard deviation span, reflecting the range of concentrations statistically encountered through eight months each year, was around 1.0 to 1.4 orders of magnitude.

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