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Prediction of minesite-drainage chemistry through closure using operational monitoring data

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Abstract

Post-mining drainage chemistry depends strongly on geochemical and hydrologic processes that occur during the operational years. Where routine operational monitoring data are abundant, the dominant processes can often be evaluated with no additional, special studies. Thus, post-mining drainage chemistry can be predicted with confidence based on the operational data. This is referred to here as 'empirical drainage-chemistry modelling' (EDCM).

This paper presents examples of EDCM using routine monitoring databases from several minesites, each containing thousands of analyses and spanning up to 30 years of mine operation and closure. Simple statistical interpretations in the EDCM can reveal annual cycles and trends that aqueous concentrations display during operation and into closure.

A new compilation of 12 EDCM equations for copper versus pH is presented to illustrate similar trends with pH among the sites. However, this compilation also shows that average-annual copper concentrations at a particular pH can vary by three orders of magnitude, reflecting site-specific factors. Also, a new case study comparing actual closure concentrations to those predicted with EDCM in 1991 demonstrates that predictive accuracy is within a factor of two.

Keywords: water chemistry; chemical equilibrium; metal leaching; mining; environment

1. Introduction

Concentrations in minesite-drainage waters are typically created by the dissolution of minerals into those waters. According to principles of geochemistry, there are two basic, endpoint controls on aqueous concentrations: kinetic and equilibrium processes (Table 1). Kinetic-controlled concentrations fluctuate significantly with time and are dependent on physical factors like flow rates and dilution. In contrast, equilibrium-controlled concentrations are often more stable and persistent through time.

The implication for minesite-drainage chemistry is that, if some type of equilibrium is the major control on aqueous concentrations, then concentrations during closure can be predicted more reliably. The predictions remain applicable, for example, if flow rates change due to placement of a soil cover over waste rock or tailings, or if pH changes due to oxygen depletion. However, such events would lessen the reliability of closure predictions under kinetic controls.

While equilibrium controls are relatively simple in concept, they are difficult to delineate at a minesite.

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Table 1
Idealized kinetic vs. equilibrium mineral reactions

Kinetic	Equilibrium
Aqueous concentrations (as mg/l) change with time	Aqueous concentrations (as mg/l) do not change with time
Aqueous concentrations (as mg/l) can depend on the ratio of water to mineral	Aqueous concentrations (as mg/l) are independent of the amount of water and mineral
If water remains in contact with minerals long enough (stagnant drainage), equilibrium will eventually be reached	If drainage moves into contact with other minerals, equilibrium will change, resulting in either new equilibrium or kinetic conditions

There are computer programs, like MINTEQA2 (Allison et al., 1990), that calculate equilibrium conditions based on solubility products from published literature. However, the solubilities of many minerals vary from literature values due to natural factors like solid solutions (e.g. Morin and Cherry, 1986) and crystallinity. For example, calcite ($CaCO_3$) with a small amount of substituted iron, which would be typical at metal minesites, could be in equilibrium at one order-of-magnitude below the literature value in a computer program like MINTEQA2. This 'apparent equilibrium' for calcite can vary from minesite to minesite depending on the amount of substituted iron.

A simple empirical technique has been developed, named the 'empirical drainage-chemistry model' or EDCM, to evaluate site-specific equilibrium controls based on existing routine monitoring data (Morin and Hutt, 1993, 1997; Morin et al., 1993; Morin et al., 1994a,b; Morin et al., 1995a). Equilibrium controls identified by an EDCM during mining are then used to make predictions of closure drainage chemistry. No additional studies or special monitoring are required.

The EDCM approach has been used with relatively large databases since early 1991, and was tested for strengths and weaknesses on small databases by the former Canadian MEND Program (Norecol et al., 1996; Morin and Hutt, 1997). For reasonably valid statistical information to be obtained, more than 100, and often more than 1000, datapoints spanning at least several years are needed for one minesite. While such databases are apparently uncommon, several do exist, extending up to nearly 30,000 analyses over 40 years. The exact time span, number of analyses, and sampling locations are intentionally ambiguous here, because each minesite is different. For example, 100 analyses may be sufficient to distinguish trends at one site (Morin and Hutt, 1997, bottom of p.74), but not another (Norecol et al., 1996).

It is important to understand that the EDCM approach does not adhere to standard statistical procedures (Norecol et al., 1996), because it is intended to delineate site-specific conditions. For example, it uses least-linear, rather than least-squares, fitting because one datapoint should not automatically be given more weighting than any other. Otherwise one season's data might be given more weighting and thus distort annual averages. Also, the approach uses standard deviations rather than standard errors, because an independent variable, like pH, does not often fluctuate significantly through a year at a particular location.

It is also important to understand that concentrations can be empirically predicted only within pH ranges already occurring in the site. For a minesite with drainage only at pH 8, but with predictions of future acidic drainage, this empirical approach will not work. However, as shown below, minesites with both acidic and near-neutral drainages often produce 'preferred' pH ranges that do not change over the years, allowing EDCM evaluations.

2. The EDCM approach

If the aqueous concentration of a metal is controlled primarily by equilibrium, then its concentration will remain relatively constant year after year, as long as the dominant 'independent' variables like pH remain relatively constant. This does not mean the concentration remains exactly the same and, in fact, seasonal variations around an annual mean should be expected due to changing seasonal conditions like temperature. The EDCM approach determines the annual mean and the shorter-term variations using simple scatterplots and simple statistical procedures available in any spreadsheet software. As such, it is not a rigorous research procedure, but a convenient, inexpensive, and relatively easily understood tool for summarizing and predicting aqueous concentrations at minesites.

The first step in the EDCM is to compile all available monitoring data for an entire minesite or one or more of its components. Concentrations from the compilation are then plotted against independent, or

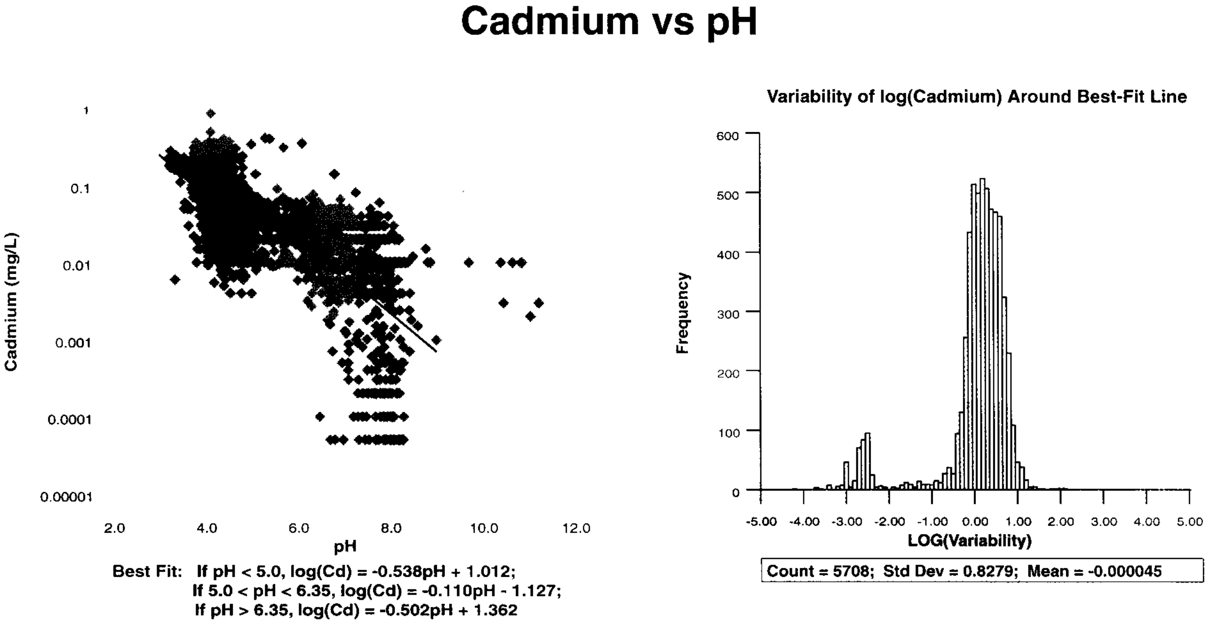

Fig. 1. Example of a best-fit line for cadmium and pH (left side), and variability around the best-fit line (right side), for 5708 analyses over 25 years from an entire minesite (more than a dozen monitoring locations).

'master', geochemical parameters which are typically pH and sulphate at sulphide-bearing minesites. If there are geochemical equilibrium controls, then there will be noticeable correlations (Figs. 1–4). A 'best-fit' line can then be drawn through the correlation using least-linear fitting (left sides of Figs. 1–4), and this line often represents the annual-average concentration at a particular value of the master parameter.

The standard deviation can be used to estimate short-term extreme (high-low) concentrations, even for time intervals shorter than the frequency of monitoring, like one-day high-lows. Based on a normal distribution of time over a one-year period (Table 2), the theoretical one-day high will be 3.00 log standard deviations above the annual-average concentration. The validity of this approach has been confirmed using monitoring data collected every four hours over several months (Morin and Hutt, 1997; Morin et al., 1994a). However, extrapolations beyond the actual frequency cannot detect any physical or non-equilibrium chemical limits to theoretical maximum concentrations.

The EDCM is created from the compilation of all best-fit equations and standard deviations for a minesite (e.g. Table 3). The EDCM serves a variety of functions, such as concisely summarizing drainage chemistry, providing annual mean concentrations at a particular value of the master variable, and predicting post-mining chemistry even if a master variable like pH changes after closure. The EDCM can also contribute to other tasks, like (1) estimating acceptable failure rates of control technologies like clay covers so that a specified downstream concentration is not exceeded, and (2) determining the optimum retention time and size for a holding pond to a water-treatment plant so that a very short-term concentration will be diluted in the pond and not exceeded in the plant feed.

For example, a hypothetical water-treatment plant cannot treat aqueous zinc concentrations above 70 mg/l. The EDCM for this site indicates concentrations would not exceed 70 mg/l for more than one day each year (i.e. 70 mg/l is 3.00 log standard deviations above the average-annual concentration at the particular pH). Also, the highest average one-week concentration would be 50 mg/l (2.34 log standard deviations above average annual). Therefore, the

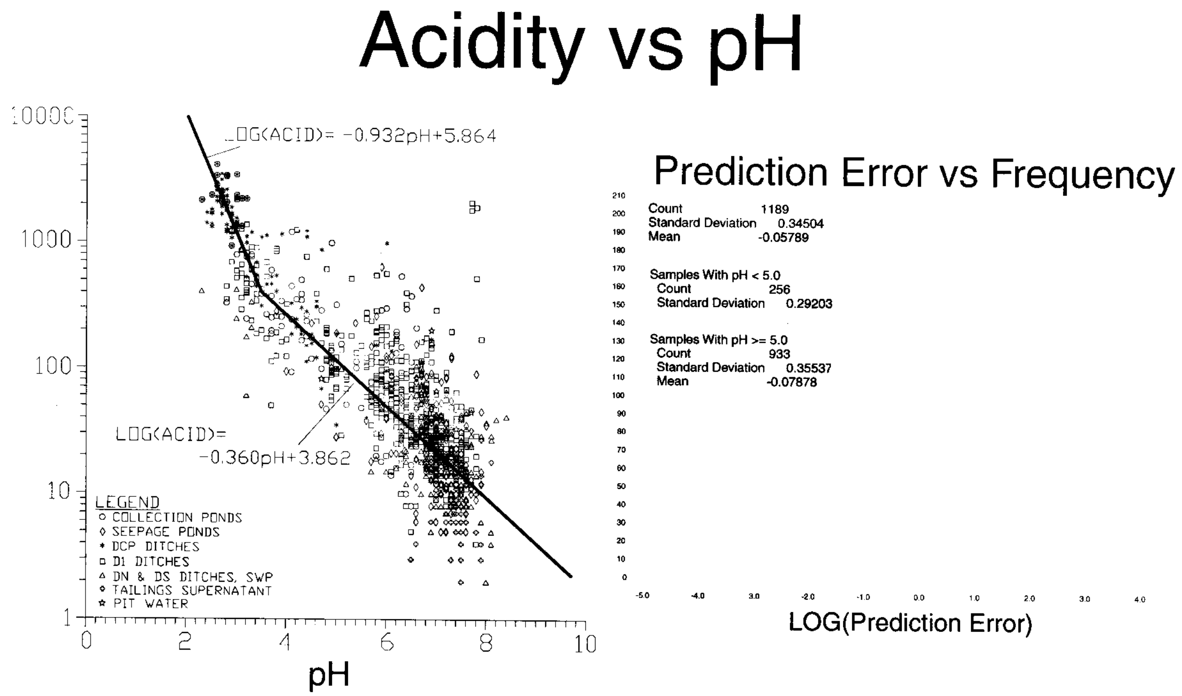

Fig. 2. Example of a best-fit line for titration acidity and pH (left side), and variability around the best-fit line (right side), for 1189 analyses over 12 years from an entire minesite (approximately 20 monitoring stations).

treatment plant should have a pre-treatment holding pond with more than one-day-retention time, and preferably about one-week retention.

EDCM has been applied to more than a dozen databases with more than 1000 analyses. Approximately 85% have resulted in notably strong trends and correlations with pH and/or sulphate. A new compilation of 12 best-fit (average-annual) equations for copper shows that all the minesites display similar, but not identical, trends (Fig. 5). Furthermore, at a particular pH, average-annual concentrations vary by as much as three orders of magnitude. This is consistent with the observation that equilibrium controls and solubilities are site specific and thus require site-by-site evaluation. Evaluations with MINTEQA2 rarely reveal any minerals close to equilibrium across a range of pH at any of these minesites, suggesting theoretical or experimental solubility and site-specific equilibrium controls is rarely applicable.

Approximately 15% of the EDCMs have displayed erratic trends or poor correlation with master geochemical parameters like pH. These sites are apparently subject to kinetic controls (Table 1) or other processes, and thus their drainage chemistries are affected significantly by many factors like flow rates in addition to pH. Predictions of post-mining water chemistry for these 'kinetic sites' will have a higher degree of uncertainty unless all the significant physical, chemical, and biological factors are characterized.

An important issue at this point is whether the master parameters on which EDCMs are based can vary outside the range measured during operation. For example, could pH become much more acidic during closure? This has not been observed in our databases spanning several decades. Instead, as acidic conditions appear around a minesite, the databases show preferred ranges of acidic and near-neutral pH (e.g. pH 3.5–4.5 and

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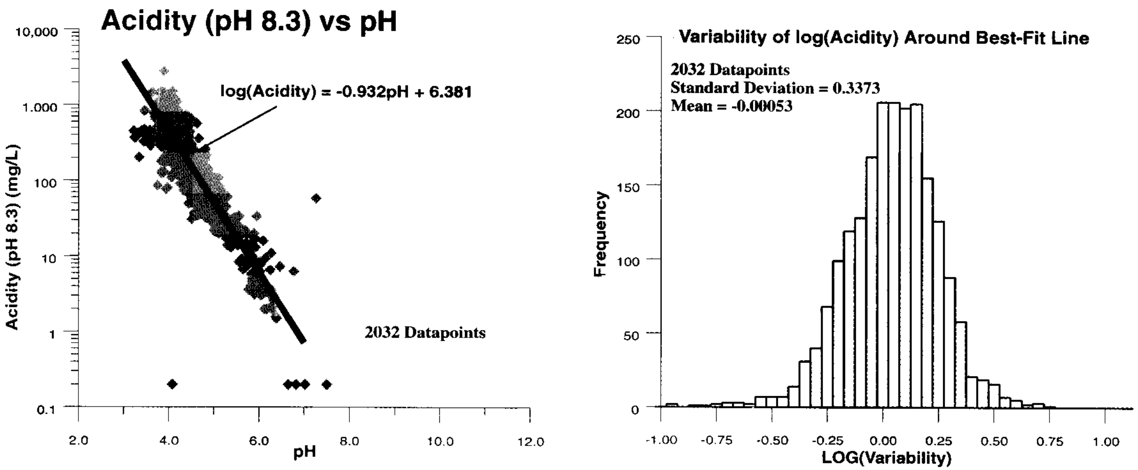
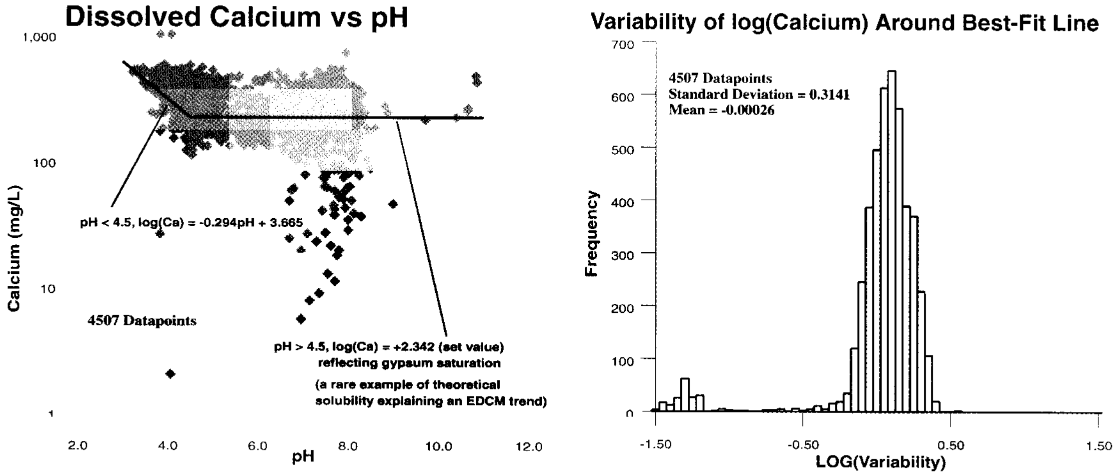
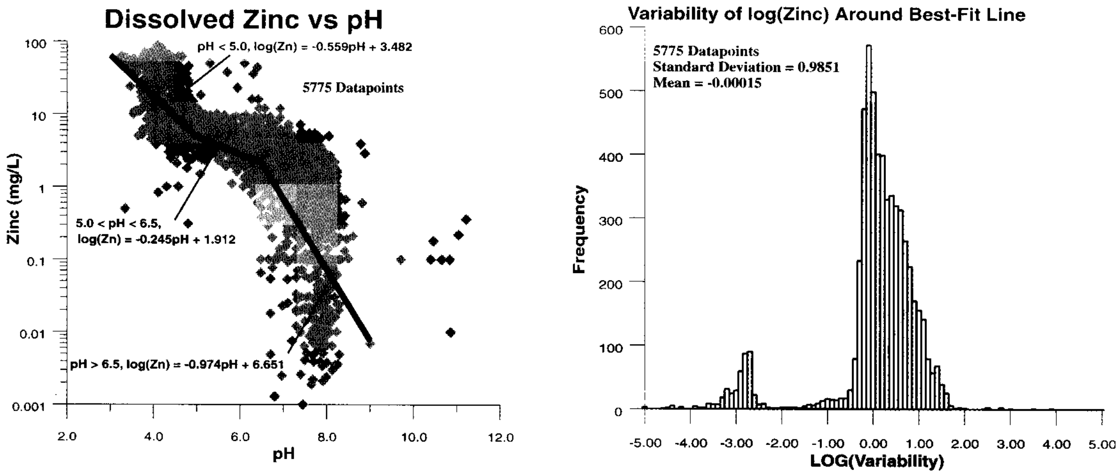
Fig. 3. Empirical Drainage-Chemistry Model (EDCM) Correlations of Several Parameters with pH from One Minesite (from Morin and Hutt, 1997).



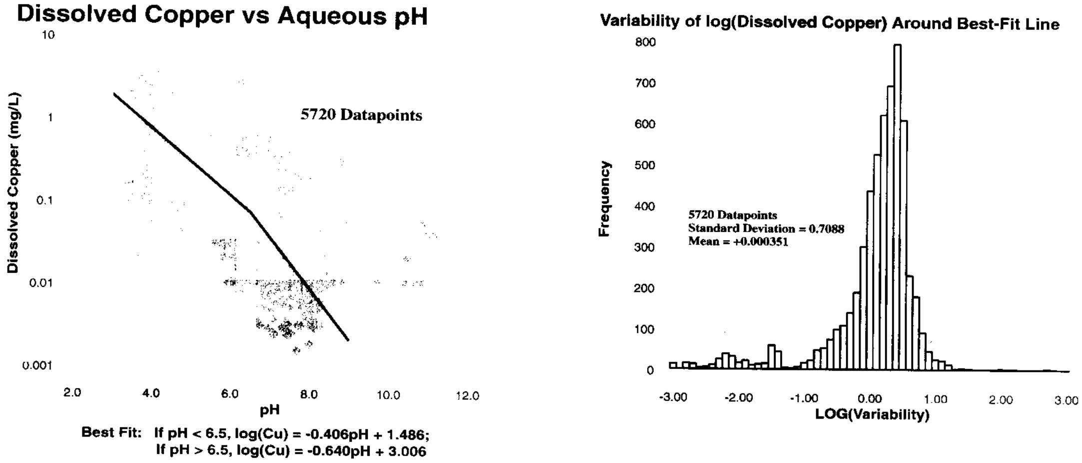
a) an empirical relationship of acidity to pH



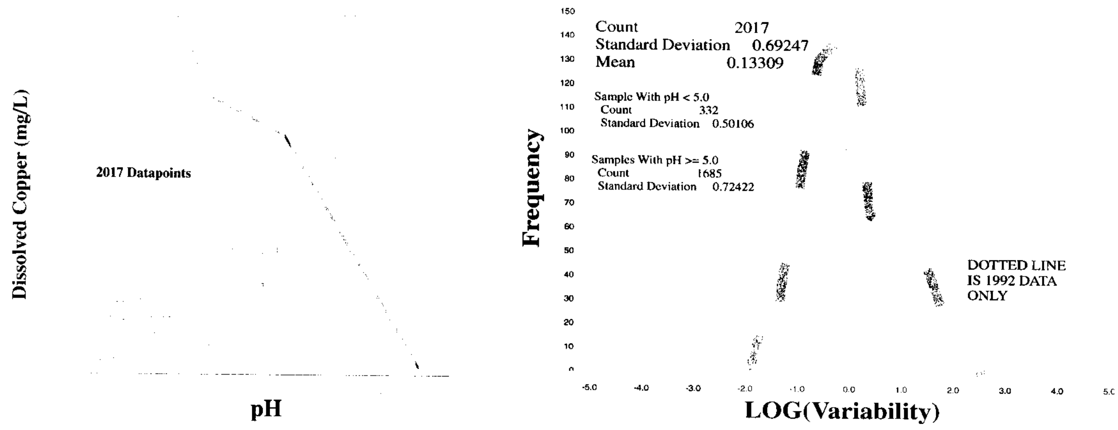
b) an empirical relationship of calcium to pH



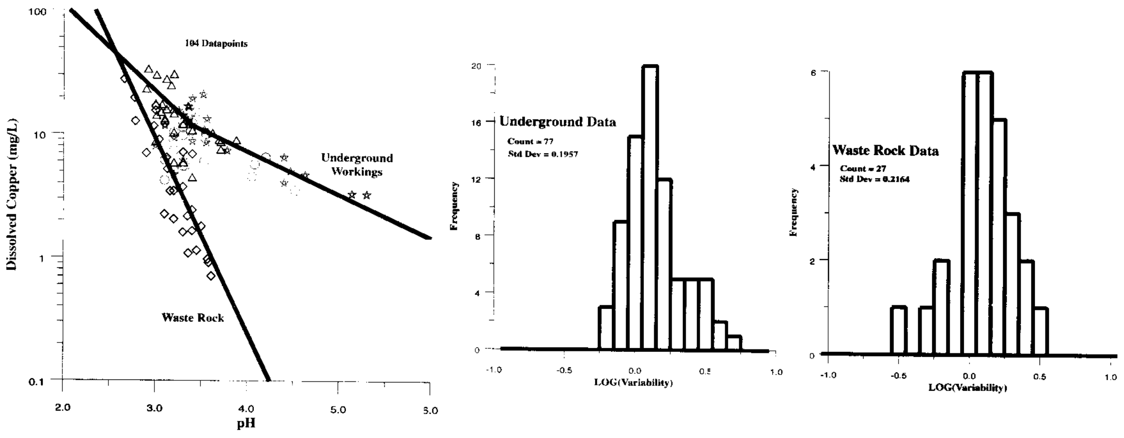
c) an empirical relationship of zinc to pH



a) empirical relationship of copper and pH at Island Copper Mine



b) empirical relationship of copper and pH at Bell Mine



c) empirical relationship of copper and pH at Mine C

Fig. 4. EDCM copper correlations with pH at three minesites (from Morin and Hutt, 1997).

Table 2
Number of standard deviations above/below the average-annual concentration for high–low concentrations during intervals shorter than one year

	Highest/lowest average concentration over etc.				
Time interval	1 Year	1 Month	1 Week	1 Day	1 h
No. of standard deviations above/below annual average[a]	0	± 1.73	± 2.34	± 3.00	± 3.85

[a] Based on normal-distribution tables (e.g. Pollard, 1977), assuming average concentrations represent higher-than-average values half the time and lower-than-average values for the other half.

7.0–8.0 in Fig. 1), connected by 'transient-pH' samples whose pH is changing with time. While occasional pH values below the preferred acidic range are occasionally found, such as in small, concentrated seepages, the preferred ranges do persist for at least decades and into closure (Morin and Hutt, 2000). Therefore, the authors have found no minesites with pre-existing acidic drainage where pH decreased significantly decades later, and thus master geochemical parameters like pH are not expected to change significantly from preceding values

3. Conclusions

Confidence that EDCMs with well-defined trends will predict future concentrations comes partially from year-by-year similarities of mean values and standard deviations at operating minesites. These data are too voluminous to reproduce here, but see Table 4.2.5-1 of Morin and Hutt, 1997.

Also, a new study (Morin and Hutt, 2000) compared eight years of closure data to an EDCM created in 1991

Table 3
Example of an empirical drainage-chemistry model (EDCM) for a minesite that includes an open pit, several waste-rock dumps, and a tailings impoundment (adapted from Morin et al., 1995b)

Aqueous parameter (mg/l)[a]	Applicable pH range	Best-fit (average-annual) equation	Logarithmic Standard deviation
Acidity	$pH < 3.5$	$\log(Acid) = -0.932pH + 5.864$	0.345
	$pH > 3.5$	$\log(Acid) = -0.360pH + 3.862$	
Alkalinity	$pH > 4.5$	$\log(Alk) = +0.698pH - 3.141$	0.654
Dissolved aluminum	$pH < 6.0$	$\log(Al) = -0.925pH + 4.851$	0.429
	$pH > 6.0$	$Al < 0.2$ mg/l	
Dissolved arsenic	All	< 0.2 mg/l	0
Dissolved cadmium	$pH < 3.0$	$Cd < 0.07$ mg/l	0
	$pH > 3.0$	$Cd < 0.015$ mg/l	
Dissolved calcium	All	$\log(Ca) = +0.619 \log(SO_4) + 0.524$	0.375
Dissolved copper	$pH < 3.4$	$\log(Cu) = -1.485pH + 6.605$	0.692
	$3.4 < pH < 5.4$	$\log(Cu) = -0.327pH + 2.666$	
	$pH > 5.4$	$\log(Cu) = -1.001pH + 6.307$	
Total copper	All	$\log(CuT) = +0.962 \log(CuD) + 0.180$	0.23
Dissolved iron	$pH < 4.4$	$\log(Fe) = -1.429pH + 6.286$	0.807
	$pH > 4.4$	$\log(Fe) = -0.455pH + 2.000$	
Total iron	All	If diss $Fe > 1.0$, total $Fe =$ diss Fe	0
Dissolved lead	All	$Pb < 0.05$ mg/l	0
Dissolved nickel	All	$\log(Ni) = -0.317pH + 0.853$	0.607
Total nickel	All	Total $Ni =$ diss Ni	0.613
Dissolved selenium	All	$Se < 0.2$ mg/l	0
Dissolved silver	All	$Ag < 0.015$ mg/l	0
Dissolved zinc	All	$\log(Zn) = -0.441pH + 1.838$	0.667
Total zinc	All	Total $Zn =$ diss Zn	0.144

[a] 'Total' refers to unfiltered aqueous concentrations; 'Dissolved' refers to dissolved aqueous concentrations from 0.45 μm filtration.

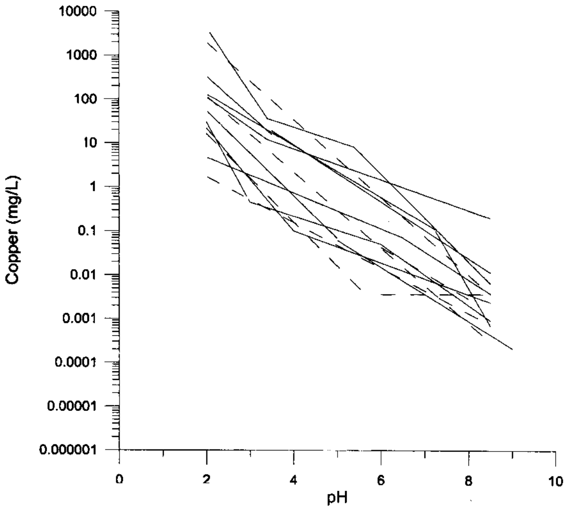


Fig. 5. Compiled EDCM copper correlations for 12 minesites.

based on operational data (Table 3). Most parameters required no adjustment to the best-fit equation and standard deviation, and the largest adjustment was a factor of two. However, no temporal trend of increasing or decreasing concentrations was evident, so the changes to the equations apparently represent artefacts of the numbers and locations of samples from operation to closure. Nevertheless, at this time, it would be prudent to assume up to factor-of-two uncertainties in closure concentrations that are based solely on operational data.

In summary, EDCM provides a relatively simple and inexpensive approach for summarizing existing aqueous concentrations and predicting future concentrations at minesites with a wide range of pH. This does not require any additional studies or special sampling. Based on databases to date, well-defined trends against master parameters like pH repeat yearly during operation and continue into closure, providing an empirical indication of reliability for predictions.

Acknowledgements

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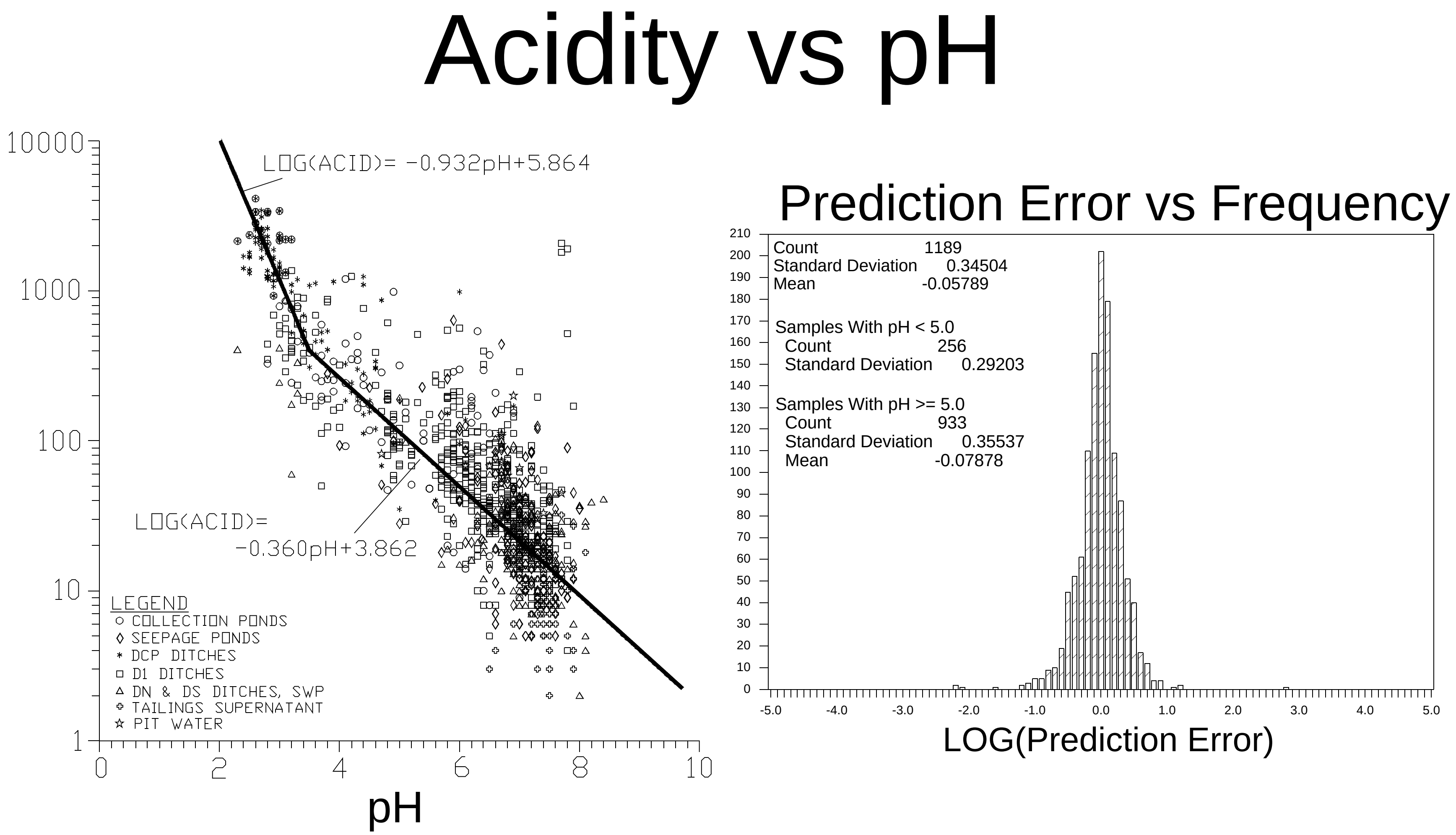

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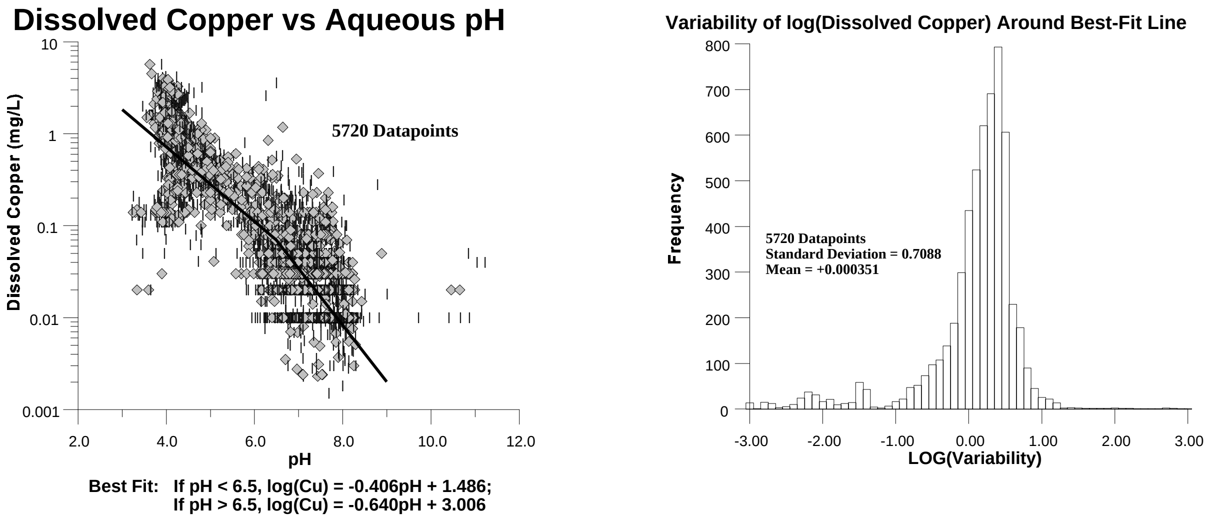
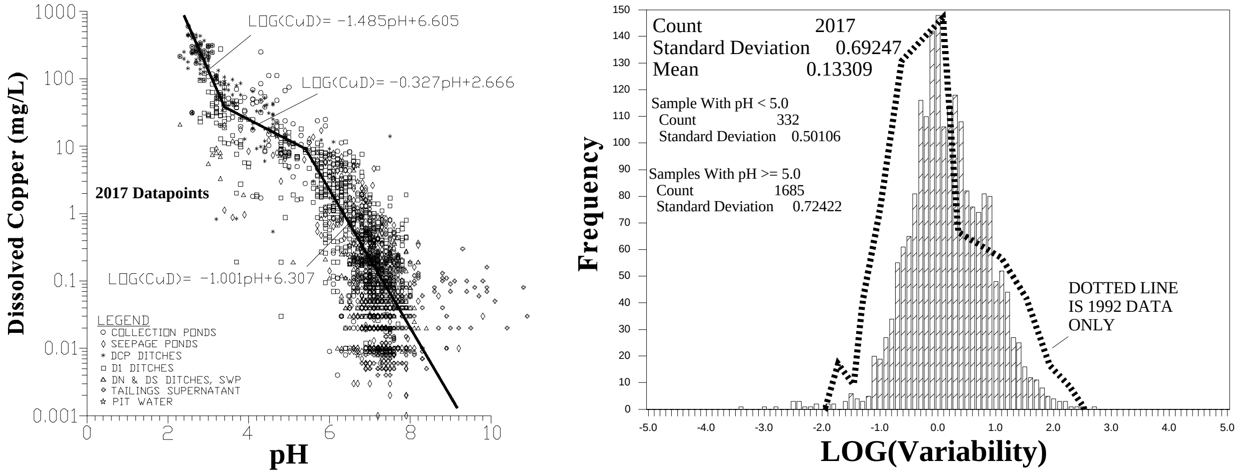
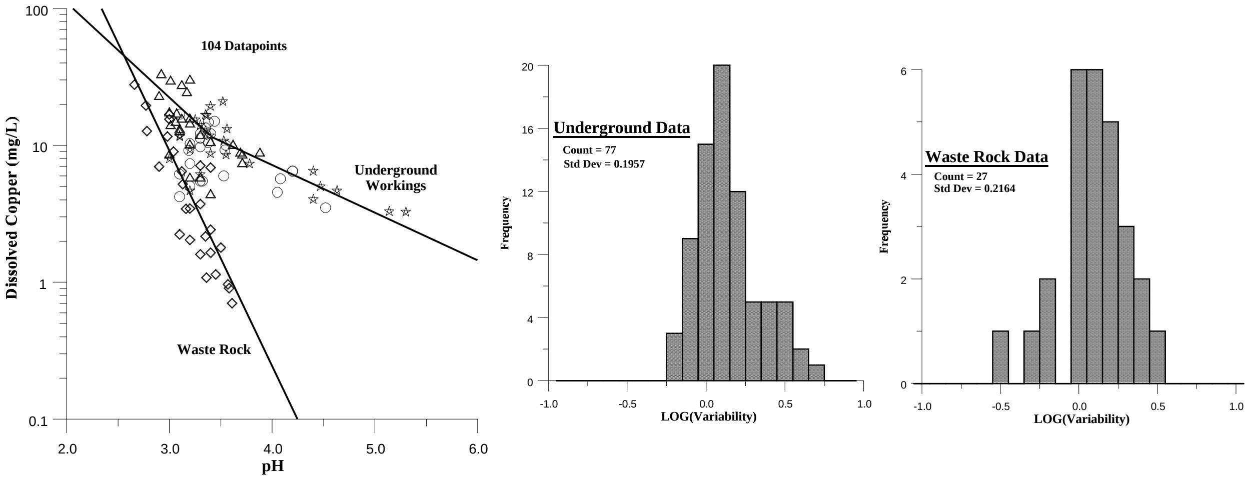


a) empirical relationship of copper and pH at Island Copper Mine



b) empirical relationship of copper and pH at Bell Mine



c) empirical relationship of copper and pH at Mine C

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